



**CATALYST DEVELOPMENT FOR OXIDATIVE DEHYDROGENATION
OF ALKANES**

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ALKANES
(Ph.D. Thesis)

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ABSTRACT

In this study, the aim was to synthesize chromium-based catalysts with high activity, selectivity, and hydrothermal stability for the oxidative dehydrogenation (ODH) of isobutane. To enhance the hydrothermal stability of the MCM-41 support, a modification with titanium was performed. Hydrothermal tests showed that the addition of 2.5 wt.% titanium increased the hydrothermal stability of the MCM-41 structure by forming strong Ti-O-Si and Ti-OH bonds. Ti-MCM-41 supported catalysts were then synthesized using both hydrothermal and impregnation methods, with chromium loadings of 3 wt.%, 6 wt.%, and 10 wt.%. In studies conducted to determine the appropriate $i\text{-C}_4\text{H}_{10}/\text{CO}_2$ molar ratio for the reaction, the optimal feed ratio was found to be 1/5. Among the Cr-based catalysts prepared, the one containing 10 wt.% chromium, synthesized using the hydrothermal method, exhibited the highest isobutane conversion (92%) and isobutene selectivity (98%). Catalytic tests were also conducted with a titanium-unmodified catalyst (10Cr/MCM-41) to determine the effect of titanium modification on catalytic activity. It was shown that, in addition to the increased hydrothermal stability provided by the titanium, the enhanced hydrophilic properties also contributed to high conversion and selectivity. Catalytic tests conducted at different reactor temperatures (500°C and 600°C) showed that the endothermic reverse water-gas shift reaction did not occur at lower temperatures, resulting in lower isobutane conversion and isobutene selectivity values. At higher WHSV (weight hourly space velocity), which correspond to shorter contact times, lower isobutene selectivity values were observed, due to the difficulty of reactant adsorption on the catalyst surface. It was also noted that at shorter contact times, the reverse water gas shift reaction did not take place initially, and the presence of excess CO_2 increased surface acidity, which negatively impacted reaction activity. A rate expression for the isobutane ODH reaction on the 10Cr/Ti-MCM-41 catalyst was developed using the power-law method. The experimentally determined reaction orders were found to be 0.82 for isobutane and 0.03 for CO_2 . The activation energy for the reaction was calculated as 27.9 kJ/mol. In reactor modeling studies, the discrepancy between the experimental and model results was attributed to side reactions occurring in the reactor. The reaction model, developed based on the Mars–van Krevelen mechanism, and the experimental results showed consistency. It was confirmed that there were no heat or mass transfer limitations within the reactor system.

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ALKANLARIN OKSİDATİF DEHİDROJENASYONU İÇİN KATALİZÖR GELİŞTİRİLMESİ

(Doktora Tezi)

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ÖZET

Yürütülen çalışmada, izobütanın oksidatif dehidrojenasyonunda (ODH) kullanılmak üzere yüksek aktivite ve yüksek seçicilik yanında hidrotermal kararlılığa sahip krom temelli katalizörlerin hazırlanması amaçlanmıştır. Katalizör hazırlama çalışmalarında MCM-41 desteğin hidrotermal kararlılığını artırmak üzere titanyum ile modifikasyon işlemi gerçekleştirilmiştir. Hidrotermal testler, yapıya kütlece %2,5 oranında eklenen titanyumun güçlü Ti-O-Si ve Ti-OH bağları oluşturarak MCM-41 yapısının hidrotermal kararlılığını artırdığını göstermiştir. Ti-MCM-41 destekli katalizörler, yapılarında kütlece %3, %6 ve %10 krom içerek şekilde hidrotermal sentez ve emdirme yöntemleriyle hazırlanmıştır. Reaksiyon için uygun $i\text{-C}_4\text{H}_{10}/\text{CO}_2$ molar oranını belirlemek amacıyla yürütülen çalışmalarda en iyi besleme oranı 1/5 olarak tespit edilmiştir. Hazırlanan Cr temelli katalizörler içinde en yüksek izobütan dönüşümü (%92) ve izobüten seçicilik değeri (%98) yapısında kütlece %10 krom bulunan hidrotermal sentez yöntemiyle hazırlanan katalizörde tespit edilmiştir. Titanyum ile yapılan modifikasyon işleminin katalizörün katalitik aktivitesine etkisini belirlemek amacıyla yapısında titanyum bulunmayan katalizör (10Cr/MCM-41) ile de katalitik testler yürütülmüştür. Yapıya eklenen titanyum ile artan hidrotermal kararlılık yanında artan hidrofiliklik özelliğinin yüksek dönüşüm ve seçicilik sağladığı gösterilmiştir. Farklı reaktör sıcaklıklarında (500°C ve 600°C) yürütülen katalitik test çalışmaları, düşük sıcaklıkta endotermik ters su gazı reaksiyonunun gerçekleşmediğini ve bunun sonucu olarak da düşük izobütan dönüşümü ve izobüten seçicilik değerlerinin gözlemlendiğini göstermiştir. Düşük temas süresine karşılık gelen yüksek kütsel akış hızı (WHSV) değerinde çalışıldığında reaktantların katalizör yüzeyine adsorplanmasının güçleşmesine bağlı olarak daha düşük izobüten seçicilik değerleri gözlenmiştir. Düşük temas sürelerinde reaksiyonun başlangıcında ters su gazı reaksiyonunun gerçekleşmediği, ortamda fazla bulunan CO_2 'in yüzey asitliğini artırarak reaksiyon aktivitesini olumsuz etkilediği de gösterilmiştir. 10Cr/Ti-MCM-41 katalizörü üzerinde izobütan ODH reaksiyonu için üst kuralı yöntemiyle hız ifadesi geliştirilmiştir. Deneysel olarak belirlenen reaksiyon mertebesi izobütana göre 0,82 ve CO_2 'e göre 0,03 olarak bulunmuştur. Reaksiyon aktivasyon enerjisi 27,9 kJ/mol olarak hesaplanmıştır. Reaktör modelleme çalışmalarında deneysel ve model sonuçları arasındaki farklılık, reaktörde gerçekleşen yan reaksiyonlar ile açıklanmıştır. Mars-van Krevelen mekanizmasına göre geliştirilen reaksiyon modelinin deneysel çalışma sonuçları ile uyumlu görülmüştür. Reaktör sisteminde ısı ve kütle transfer sınırlamalarının olmadığı gösterilmiştir.

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SYMBOLS AND ABBREVIATIONS

The symbols and abbreviations used in this study are presented below, along with their explanations.

Symbols	Explanation
$-R_A^*$	Observed rate of reaction of species A (mol A/g _{cat} .s)
C_p	Specific heat capacity at temperature T (kJ/kmol.K)
X_{Ae}	Equilibrium conversion species A (%)
$C_{A,centre}$	Concentration of A at the center of catalyst (mol/m ³)
C_A	Exit concentration of A (mol/m ³)
C_{Ab}	Bulk concentration of gas A
C_{As}	Concentration of A at the surface of catalyst (mol/m ³)
C_{WP}	Weisz prater parameter
C_m	Mears parameter
K_{eff}	Effective thermal conductivity of catalyst
K_f	Thermal conductivity of fluid
K_s	Thermal conductivity of solid
N_A	Mass flux of A (kg/m ² .s)
S_{BET}	BET (Brunauer, Emmett, and Teller) specific surface areas (m ² /g)
S_a	Surface area of catalyst (m ² /g)
a_o	Lattice parameter
k_1''	Rate constant per unit surface area of catalyst
q_r	Heat flux (W/m ²)
v_0	Volumetric flow rate (m ³ /s)
ρ_b	Catalyst Bulk density (g/cm ³)
ρ_c	Catalyst density (g/cm ³)
$-\Delta H_r$	Heat of the reaction
D	Distance between layers
D_{AB}	Knudsen diffusivity of A in B (m ² /s)
D_e	Effective diffusivity (m ² /s)
E_A	Activation energy (kJ/mol)
K_c	Mass transfer coefficient (m ³ /m ² .s)

Symbols	Explanation
K_e	Equilibrium constant (dimensionless)
L	Crystallite size
P_i	Partial pressure of species i (Paskal)
R	Ideal gas constant ($\text{m}^3 \cdot \text{atm} / \text{k} \cdot \text{mol}$)
R	Radius of catalyst particle (μm)
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number
ΔH_T	Enthalpy at temperature T (kJ/mol)
ρ	Density of gas (g/cm^3)
η	Effectiveness factor
θ	Reflected angle (deg)
k_0	Pre-exponential factor ($\frac{\text{mol}}{\text{Pa}^{(0.82+0.03)} \text{g}_{\text{cat}} \cdot \text{s}}$)
λ	Wavelength of the beam used $\text{\AA}$
ϵ	Porosity of catalytic bed
Φ	Thiele modulus
k	Specific reaction rate (constant) ($\frac{\text{mol}}{\text{Pa}^{(0.82+0.03)} \text{g}_{\text{cat}} \cdot \text{s}}$)
δ	Pore wall thickness ($\text{\AA}$)
α	Reaction order of species A
β	Reaction order of species B
τ	Tortuosity

Abbreviations	Explanations
FWHM	Full Width at Half Maximum of Peaks (degree)
ODH	Oxidative dehydrogenation
WHSV	Weigh Hourly Space Velocity (h^{-1})

1. INTRODUCTION

Light olefins are the fundamental components of petrochemicals, and they are considered to be the main chemical intermediates since they may be catalytically changed into basic substances such as oligomerized alkenes, alcohols, ketones, aldehydes, carboxylic acids, and amines.

Catalytic dehydrogenation of isobutane holds significant industrial importance, primarily due to the growing demand for isobutene. Isobutene serves as a key raw material in the synthesis of various chemical components, including methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), and 1,3-butadiene (1,3-BD). Additionally, it functions as a gasoline additive to enhance the octane number and substitute lead. Furthermore, it is also used in the production of synthetic rubber and various plastics, either as a monomer or in copolymerization processes.

Isobutene is predominantly produced through the catalytic dehydrogenation of isobutane, along with methods like steam cracking or fluidized catalytic cracking (FCC) of naphtha and heavier oil fractions. There are two primary methods for isobutane dehydrogenation: direct dehydrogenation (DH) and oxidative dehydrogenation (ODH). The direct dehydrogenation (DH) process has already been commercialized. Industrial applications commonly utilize supported CrOx and Pt-based catalysts. There are several processes utilize catalysts such as Pt-Sn/Al₂O₃ or CrOx/Al₂O₃. Current research efforts in both industry and academia are focused on the development of innovative catalysts for dehydrogenating isobutane.

Since direct isobutane dehydrogenation (DH) is thermodynamically limited, a relatively higher reaction temperature is needed for this endothermic process to produce a commercially desirable isobutene yield. As a result, coke formation and quick catalyst deactivation are unavoidable. Industrial processes prevent catalyst deactivation by applying alternating reaction steps and complex regeneration steps. However, thermodynamic equilibrium still limits the amount of isobutene that can be produced.

The oxidative dehydrogenation (ODH) process for light alkanes demonstrated significant potential. Various oxidants, including oxygen, nitrogen dioxide, and carbon dioxide, have been used as co-feeds in these reactions. From a thermodynamic perspective, oxidative

dehydrogenation (ODH) is preferred over direct hydrogenation (DH) for the conversion of alkane to alkene. O_2 enables the oxidative dehydrogenation of light alkanes to occur at low temperatures, which results in significant cost reductions. However, due to the deep oxidation of light alkanes to CO_2 and tar, also its low selectivity towards the required product is not favorable to us. Therefore, identifying appropriate oxidants is crucial for the dehydrogenation of light alkanes.

It is important to note that CO_2 can affect the reaction process by reacting with H atoms that are released from alkanes, which can lead to the production of water (H_2O). Additionally, CO_2 can modify catalysts and impact their redox, adsorption, and electronic properties. This ultimately affecting the activity and selectivity for alkane dehydrogenation. Apart from dehydrogenating alkanes to olefins and H_2 , catalysts can also break down CO_2 into carbon monoxide (CO) and surface-bound oxygen species (O^*). which can then react with the released H_2 to regenerate active surface sites for subsequent reactions. Over the past few decades, several catalytic systems related to CO_2 -ODH have been developed.

The utilization of CO_2 in the oxidative dehydrogenation (ODH) of light alkanes to produce light olefins is a highly promising reaction with significant industrial applications. This process employs heterogeneous catalysis, utilizing carbon dioxide (CO_2) instead of using O_2 as an oxidant heterogeneous catalysis in the presence of. This approach is more sustainable and environmentally friendly as CO_2 is a softer and controllable option for converting light alkanes into olefins. This catalytic process not only transforms light alkanes into their corresponding olefins but also enables the utilization of CO_2 as a feedstock for the production of high-value chemical compounds.

The extensive research on catalysts made from various metals and their oxides has led to the discovery of Cr-based catalysts as being highly effective. This is due to the multi-oxidation state of the chromium, which allow for the establishment of redox cycles between its high and low chemical valences. As a result, these catalysts demonstrate improved yield and selectivity. Consequently, Cr-based catalysts have garnered significant attention and are proven to exhibit exceptional performance in the oxidative dehydrogenation of alkanes using carbon dioxide (CO_2).

The catalyst life is short in industrial procedures that produce isobutene, such as CATOFIN, Oleflex, and STAR. Therefore, catalyst development studies are being conducted for isobutane dehydrogenation. These commercial processes are carried out with problems that cannot be overcome, such as carbon accumulation on the catalyst, causing short catalyst life and equilibrium limitations. Therefore, all industrial processes must include a catalyst regeneration step.

Heterogeneous catalysis is essential in industrial manufacturing, the chemical and energy sectors, and environmental protection. Over the past several decades, one of the most significant developments in science and technology has been the development of catalyst synthesis techniques that produce catalysts with enhanced activity and selectivity. Catalytic supports with high surface area and specifically designed porous structure are important for the generation of a large number of desired active sites. Looking to the future, the oxidative dehydrogenation of light alkanes in the presence of CO₂ using heterogeneous catalysis presents a promising sustainable approach.

Heterogeneous catalysts are widely utilized in the chemical industry. These catalysts are synthesized as materials with active phases, which are often placed on a support, as well as pure components. The active phases are usually metallic forms, metal oxides, or sulfide compounds. In catalyst preparation, it is desirable for the active phase to have small particles/crystals. However, these small particles are not thermodynamically stable due to their high surface energy. At high temperatures, these particles tend to sinter into larger clusters. The role of the support material is to provide a large surface area and prevent the sintering process from occurring. Many support materials are used in current applications, with the most commonly used being alumina, silica, zirconium oxide, and titanium oxide. Additionally, carbon and zeolite supports are used. Withal diffusion problems are frequently observed in the micropores of zeolites.

In materials science and engineering, the discovery of ordered mesoporous silica from the M41S family in 1992 was a groundbreaking advancement. Significant research efforts have been dedicated to control the characteristics of mesoporous silica particularly focusing on pore size and morphology. However, the low thermal, hydrothermal, and mechanical stability of mesoporous silica is a significant drawback. Developing techniques to improve mesoporous silica's stability has thus been the next challenge. Fortunately, techniques for

synthesizing ordered mesoporous materials with thicker silica walls, like MCM-41 and SBA-15, have partially overcome the mechanical stability problem.

MCM-41 is an excellent support for catalysts with high surface area, narrow pore diameter distribution, and pore size, allowing different molecules to pass through the channels. It is possible to use MCM-41 material as a catalyst support by adding metal/metal oxides such as Al, V, Fe, Mn, B, Ga, Ti, Zr, Cs, etc. into the mesoporous structure of MCM-41. The main disadvantage of using MCM-41 material as support is its low resistance to water vapor due to low hydrothermal stability. Despite this drawback, the MCM-41 is a very good model material used as a catalyst support.

In the synthesis of MCM-41, basically, two solutions are used. These solutions contain a silica source and surfactant. The most commonly used surfactant is long-alkyl chain quaternary ammonium ions. In an aqueous solution, surfactant ions combine to minimize the reverse interaction with polar water molecules. The structure formed as a result of this union is called "micellular". When the solution in which the silica source is found is added to the medium where the micelles are located, the micelles begin to be coated with silica in a single layer due to electrostatic attraction, and as a result, the repulsions between the micelles are reduced. Silica-coated micelles combine with condensation. The calcination process eliminates organic templates by burning them in an oxygen or air atmosphere (CO_2 , NO_x , and water vapor). This results in a completely mesoporous material.

Within the scope of this doctoral thesis, the objective is to synthesize chromium-based catalysts with high activity and selectivity for oxidative dehydrogenation of isobutane using CO_2 as a soft oxidant. To achieve this, mesopores MCM-41 catalyst support was synthesized using N-cetyl-N, N, N-trimethyl ammonium bromide ($\text{C}_{19}\text{H}_{42}\text{BrN}$) as a surfactant and sodium silicate solution as silica source. In the oxidative dehydrogenation reactions, oxygen source is used for the removal of H_2 that why water is expected as a side product. However, MCM-41 is known for its low hydrothermal stability. Therefore, the MCM-41 material was modified with titanium. After that a hydrothermal stability test was carried out to investigate the effect of titanium modification on the hydrothermal stability of the MCM-41 materials. Then, a series of chromium-based catalysts supported on titanium-modified MCM-41 were synthesized. Cr-based catalysts were synthesized using hydrothermal synthesis and wet impregnation synthesis methods. Synthesized catalysts and supports were characterized

using N₂ adsorption/desorption, XRD, FTIR, and SEM/EDS. Equilibrium calculations were carried out for the reaction. Variation of isobutane equilibrium conversion with temperatures at different i-C₄H₁₀/CO₂ molar ratios were calculated using GASEQ program. Catalytic activity tests were conducted using fixed-bed reactors at 873K temperature and atmospheric pressure. The optimum i-C₄H₁₀/CO₂ molar ratio was determined experimentally. Then the effect of different Cr loading on the catalytic activity was investigated, as well as the effect of temperature and WHSV change on the catalytic activity. The results of the catalytic activity test led to the development of a reaction rate expression for oxidative dehydrogenation of isobutane over the selected catalyst. Also, kinetics studies of oxidative dehydrogenation over Cr-based catalysts were carried out using the Mars-Van-Krevelen (MVK) mechanistic model. After that, reactor modeling studies were carried out using the reaction rate expression developed from kinetic modeling studies. Model and experiment results were evaluated together. In the final part of the study, studies were conducted to investigate heat and mass transfer limitations in oxidative dehydrogenation of isobutane using Cr-based catalysts.

2. SCOPE OF THE STUDY

In the present doctorate study, the isobutane dehydrogenation was investigated over chromium-based catalysts supported on titanium-modified MCM-41. It is aimed to synthesis catalyst with large surface area, homogeneous pore size distribution, mesoporous size, regular pore structure, large pore volume, excellent hydrothermal stability, high anti-coking resistance, high catalytic activity, and selectivity

This section provides information about MCM-41 materials, which are used as support in the synthesis of Cr-based catalysts. Then, the catalyst synthesis techniques and isobutane dehydrogenation reaction are mentioned, respectively.

2.1. M41S Family

According to the IUPAC definition, porous materials are classified into three groups. Those with a pore diameter below 20 Å are called microporous, those with a pore diameter between 20-500Å are called mesoporous, and those with a pore diameter greater than 500 Å are called macroporous materials (Pineda et al., 2018). They can also be classified based on organic/inorganic, open/closed porous, and natural/synthetic properties. Porous materials like ceramics, glass, and clay are used in industry as catalysts, or adsorbents in gas separation systems, electronic systems, and insulation.

In 1992, researchers at the Mobil Research and Development Corporation developed a group of mesoporous materials called M41S. These materials are characterized by their controlled pore size and distribution, and a high surface area of over 1000 m²/g. The M41S family includes MCM-41, MCM-48, and MCM-50. MCM-41 features a one-dimensional hexagonal structure, MCM-48 has a three-dimensional regular cubic structure, and MCM-50 has an unstable laminate structure. The names are based on the synthesis number given during the synthesis studies and do not have any physical meaning. These materials differ from zeolites in that their pore walls are amorphous and their pore sizes are larger than zeolites.

In the synthesis of M41S materials, four main substances are used: surfactant, silica source, solvent, and a pH adjuster such as an acid or base. The mobile research group used alkyl

trimethyl ammonium halides as surfactants, and substances such as sodium silicate, tetraethyl ortho silicate (TEOS), "fumed silica" and Ludox as silica sources. To the synthesis solution, they added a base such as sodium hydroxide or tetraethyl ammonium hydroxide. The resulting solution was then left to stand for a period of 24 to 144 hours, at a temperature range of 100-150°C. Finally, the obtained solids were calcined at a temperature of about 540°C under nitrogen or dry air conditions to obtain porous material (Ciesla and Schüth, 1999). Some of the structural properties and synthesis conditions of these materials are summarized in Table 2.1.

Table 2.1. Some structural properties and synthesis conditions of MCM-41, MCM-48 and MCM-50 (Laha and Glaser, 2007)

Material Name	Pore Size (nm)	Pore Structure	Synthesis Condition	Synthesis Temperature	Surfactant Used in Synthesis	Silica Source Used in Synthesis
MCM-41	1.5-10	One-dimensional hexagonal	Basic	Room Temperature	-Cetyltrimethyl ammonium bromide -Cetyltrimethyl ammonium hydroxide	-Sodium silicate -Tetraethyl Orthosilicate
MCM-48	1.5-10	Three-dimensional hexagonal	Basic	Room Temperature	-Cetyltrimethyl ammonium bromide -Cetyltrimethyl ammonium hydroxide	-Sodium silicate -Tetraethyl Orthosilicate
MCM-50	4*	Irregular layered	Acidic/ Basic	Room Temperature	-Di-alkyl dimethyl ammonium bromide	-Sodium silicate -Tetraethyl Orthosilicate

MCM structures vary depending on pH, silica source, and surfactant/silica molar ratio. MCM-41 and MCM-48 are synthesized similarly, with the main difference being their surfactant/silica ratio. MCM-41 uses a ratio of less than 1, while MCM-48 uses a ratio between 1 and 1.1. MCM-50, on the other hand, uses surfactants with very long alkyl rings, resulting in a surfactant/silica ratio that exceeds that of MCM-48 (Karge and Weitkamp, 1999; Sing et al., 2002; Zhou et al., 2022). Figure 2.1 shows the structures belonging to the M41S family.

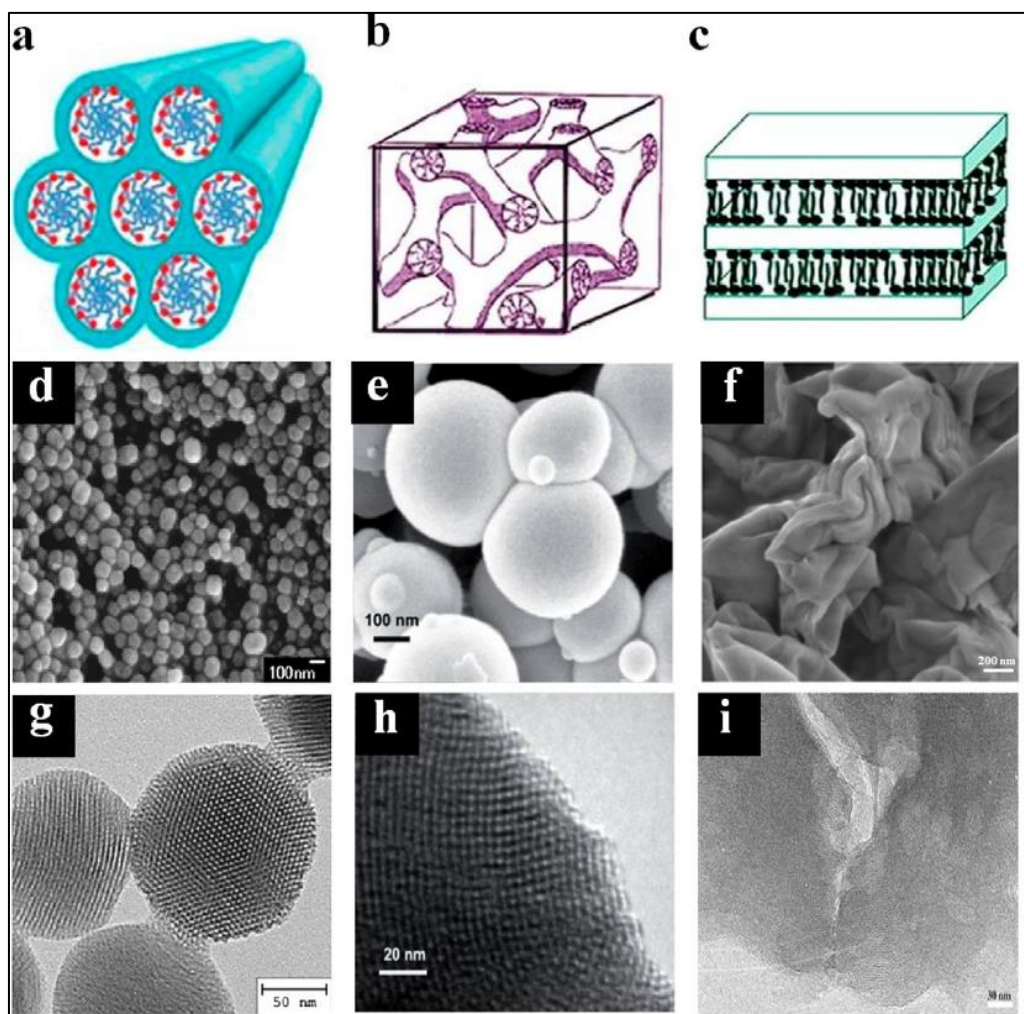


Figure 2.1. The SEM (d,e,f) and TEM (g,h, i) images of the M41S family members are as follows: (a, d, g) MCM-41, (b, e, h) MCM-48, and (c, f, i) MCM-50 (Zhou et al., 2022)

Although MCM-41 exhibits a uniform mesoporous hexagonal structure, it is composed of amorphous silica. Due to the presence of mesopores, MCM-41 has a large pore volume and a significantly high specific surface area. MCM-41 has advantages such as a high surface area, narrow pore size distribution, and pore size that allows the entry of different molecules into the channels. The pore diameter of MCM-41 silica is approximately 3-4 nm, and the pore volume is approximately 0.8 cm³/g (Asghari et al., 2016). These properties make MCM-41 an attractive catalyst support. In recent years, researchers have concentrated on using MCM-41 as a catalyst support for long-chain alkane hydroisomerization and alkylation, as well as for hydrodesulfurization of heavy petroleum (Kumar et al., 2017). The pore walls of MCM-41 provide organic functional groups for the support through the presence of free silanol groups (Si-OH) (Wang et al., 2022).

MCM-41 material has disadvantages like weak acidity and redox properties, which can make it unfavorable for catalytic processes. Also, MCM-41 materials exhibit limited stability due to their thin and amorphous pore walls. These pore walls are reactive towards certain agents and can combine with them, compromising the stability. Additionally, silica-supported materials are unstable to steam. Silica undergoes evaporation under the influence of steam. Considering the prevalence of steam usage in many processes, MCM-41 materials become unfavorable for industrial processes (Ha et al., 2019). MCM-41 is also unstable in the presence of mineralizing agents such as fluoride ions and hydroxide. Because silica is soluble in these agents. The instability of MCM-41 in aqueous solutions is limited to $\text{pH} \leq 7$.

However, the catalytic properties of MCM-41 can be improved by incorporating metal cations into the silica matrix (Zhao et al., 2013). Many studies have highlighted the high sensitivity of MCM materials to synthetic conditions (Kumar et al., 2017). Various methods were developed to enhance the hydrothermal stability of MCM-41 type materials. These methods include aluminum grafting on a pure silica matrix, removal of silanol groups, preparation of materials with thicker pore walls, enhancement of silanol group condensation with the addition of salt or a hydrothermal structure-directing agent (Ghasemi and Sanaeishoar, 2019; Wang et al., 2018).

MCM-41 can be synthesized using various methods. The presence of a surfactant and a silica source is common to all synthesis methods. The surfactant is typically a simple molecule or ion, around which the framework formation occurs. The most commonly used surfactants are alkyl chain-containing quaternary ammonium ions. The interaction between surfactant ions, with their apolar hydrophobic alkyl chains, and polar water molecules leads to the formation of clusters to minimize energy.

These clusters, formed by surfactant ions, are called micelles. Micelles consist of a hydrophobic core containing a large alkyl chain and a hydrophilic surface. Due to the ionic nature of the head groups in the ammonium ions, the most energetically favored configuration for micelles is spherical, as this shape effectively minimizes surface energy.

As the amount of surfactant in water increases, different micelle geometries begin to form. Initially, spherical micelles gradually transition into elongated rod-like micelles. With a

further increase in surfactant concentration, these rod-like micelles cluster together to form the hexagonal liquid crystal structure of MCM-41 (Figure 2.2).

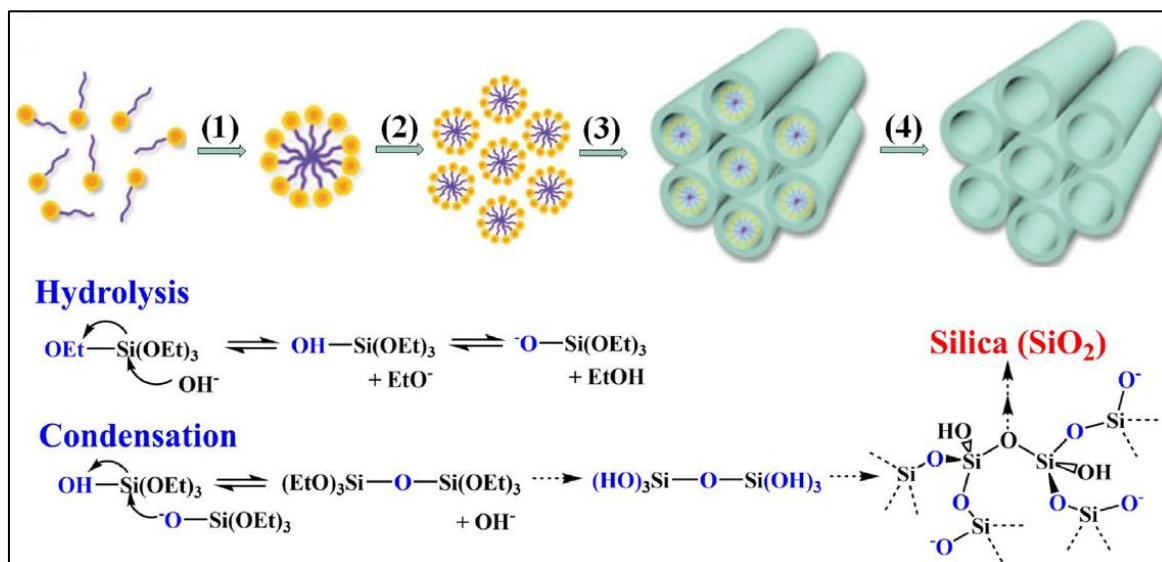


Figure 2.2. Formation steps of MCM-41: (1) Micelle formation, (2) Hexagonal packing of micelles, (3) Alignment and condensation, (4) Template removal (Zhou et al., 2022)

A wide range of silica sources are used in the synthesis of MCM-41. Examples include sodium silicate, amorphous silica, and kanemite (a silica structure composed of anodic silica sheets). Organic silicon alkoxides are also used as silica sources. Silica sources dissolve in mineralizing agents such as sodium hydroxide or concentrated ammonium solutions. This dissolution results in the production of small silicon oxy-anions. Within the rod-like template micelles, silica ions diffuse towards the surfaces of the micelles due to electrostatic interactions. Consequently, the concentration of silica ions on the surface of the micelles rapidly increases. To reduce these interactions, silica ions begin to condense with each other, leading to the formation of an amorphous silica monolayer around the micelles. The charge balance of the headgroup ions of the template is provided by the deprotonated silanol groups of the silica layer. At this stage, clustering begins with condensation reactions occurring between the silica layers of the individually coated micelles, resulting in the formation of the MCM-41 framework. The pore walls structure of the synthesized MCM-41 is amorphous and approximately 2-3 μm thick. This synthesis process occurs under broad synthesis conditions where parameters such as gel composition, pH, time, temperature, and pressure may vary. Once MCM-41 is formed, it is fully loaded with the surfactant, which must be removed to obtain a completely mesoporous support material. Two methods are suggested

for surfactant removal. The first method involves washing the synthesis product with a mixture of water and an organic solvent to extract the surfactant. The resulting solution contains the surfactant, which can be recovered after the evaporation process. If the synthesis conditions are moderate, the surfactant will not degrade and can be reused for another synthesis. Another method for surfactant removal is calcination. During the calcination process, the surfactant decomposes into carbon dioxide (CO_2), some nitrogen oxides (NO_x), and steam. Although MCM-41 is generally unstable to steam, the amount of released steam during this process is minimal and does not cause any damage to the MCM-41 framework structure.

Modifications can be made to the synthesis procedure of MCM-41. For example, hetero elements can be added to the pore walls of MCM-41 structure. The most commonly used hetero elements are aluminum and titanium. The presence of aluminum within the pore walls generates a significant amount of negative framework charge. When this charge combines with protons, the resulting material exhibits weak Bronsted acidity. The addition of titanium affects the oxidation properties. The modification of the pore size of MCM-41 is also possible. The most frequently used surfactant in MCM-41 synthesis is hexadecyltrimethylammonium bromide. The use of surfactants with longer or shorter alkyl chains can impact the pore size. In the modification of MCM-41 pore size, a limited number of alkali ammonium ions can be used. These ions must be apolar, insoluble in water, and capable of being absorbed into the hydrophobic core of the micelles.

In studies conducted on MCM-41 materials, various analytical techniques are used to determine their structural properties. The most commonly used ones include X-ray diffraction (XRD) for analyzing diffraction patterns, nitrogen adsorption-desorption isotherms for studying the adsorption behavior, and transmission electron microscopy (TEM) for examining the material's microstructure. Beside these techniques, TGA-DTA, SEM/EDS, XPS, TPR/TDR analysis are also used.

According to the results obtained from X-ray diffraction (XRD) studies on these materials (support structures), peaks are observed only in the region where 2θ is less than 10° , while at higher angle values (2θ above 10°), only a broad peak corresponding to the amorphous silica walls is detected. In the XRD graph of MCM-41, typically 3 or 5 peaks are identified

in the range where the Bragg angle is $2\theta=2^\circ$ and 5° (Figure 2.3). This observation is attributed to the amorphous nature of the pore walls.

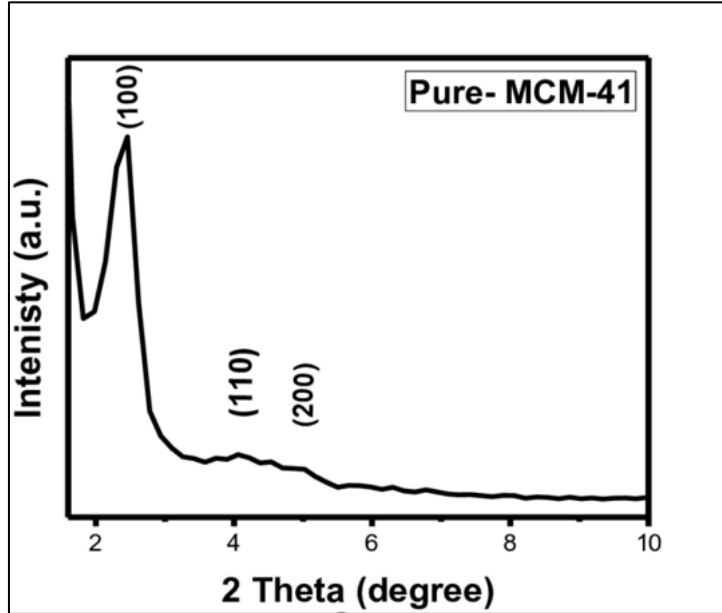


Figure 2.3. X-ray diffraction pattern of pure MCM-41 (Kılıçarslan et al., 2013)

The peaks in Figure 2.3 are based on the regular pore arrangement in the hexagonal structure. Taking the hexagonal unit cell into consideration, the XRD peaks obtained for MCM-41 mainly occur on the 100, 110, and 200 planes, as shown in Figure 2.3 (Kılıçarslan et al., 2013). XRD studies on MCM-48 and MCM-50, which belong to the same group as MCM-41, were reviewed in the literature, and the information obtained is summarized in Table 2.2.

Table 2.2. Peaks observed in the 2θ range of $1-10^\circ$ for materials in the MCM group (Szczesniak et al., 2020)

MCM Group	Angle range of observed peaks	Crystallographic planes of observed peaks	Source
MCM-41	$2-6^\circ$	2θ (100) $\sim 2.0^\circ$ 2θ (110) $\sim 3.2^\circ$ 2θ (200) $\sim 3.8^\circ$	(Ciesla and Schüth, 1999)
		2θ (100) $\sim 2.2^\circ$ 2θ (110) $\sim 4.0^\circ$ 2θ (200) $\sim 5.5^\circ$	(Karge ve Weitkamp, 1998)
MCM-48	$2-4^\circ$	2θ (221) $\sim 2.2^\circ$ 2θ (220) $\sim 4.0^\circ$ 2θ (321) $\sim 5.5^\circ$	(Karge ve Weitkamp, 1998)
MCM-50	$1-5^\circ$	2θ (100) $\sim 1.5^\circ$ 2θ (110) $\sim 5.0^\circ$	(Karge ve Weitkamp, 1998)

Physical adsorption is one of the characterization methods used to determine the pore size distribution, surface area, and pore volume of materials. Figure 2.4 shows the N_2 adsorption/desorption isotherms of MCM-41 samples. These isotherms conform to the IV Type isotherm according to the IUPAC classification. The prominent feature of the material is the narrow hysteresis between the adsorption and desorption regions. This type of hysteresis is classified as Type I hysteresis according to the IUPAC classification, indicating the presence of cylindrical pores in the structure.

To determine the pore size distribution of cylindrical pores, there are several well-known methods that take into account geometries, thermodynamics, and statistical thermodynamic approaches. The most commonly used method for determining the pore size distribution within a mesoporous structure is the Barrett-Joyner-Halenda (BJH) method. This method is thermodynamically based and relies on the Kelvin equation. However, it is not suitable for use with N_2 physical adsorption at P/P_0 values below 0.35 at 77 K (Karge and Weitkamp, 1999).

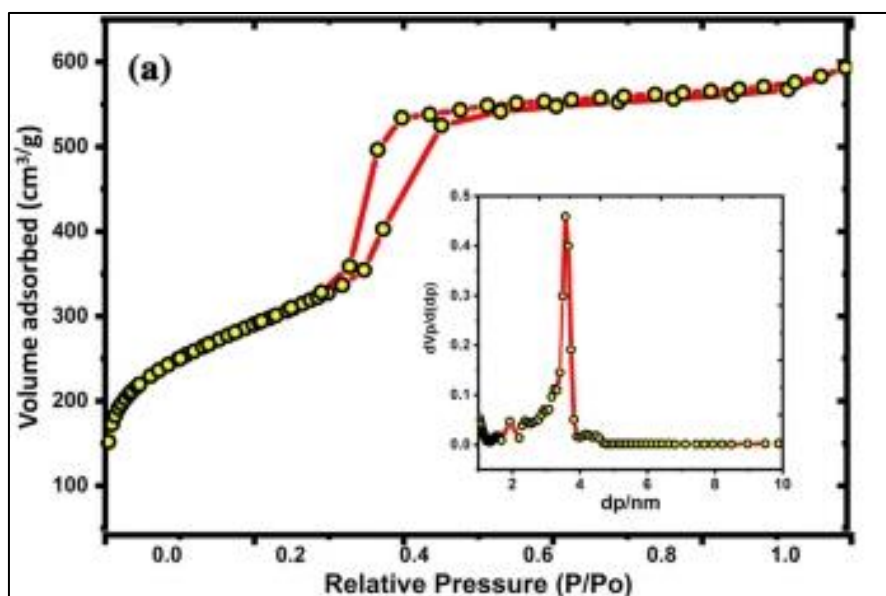


Figure 2.4. N_2 adsorption/desorption isotherm and pore size distribution curve of MCM-41 (Khaled et al., 2022)

Silica-based mesoporous materials are primarily used as catalyst supports, so it is important to know their thermal stability at the desired reaction temperatures. Thermal characterization methods such as thermogravimetric analysis (TGA), differential thermal analysis (DTA), etc., are used to determine the material's thermal stability. Through these analyses, it is

possible to identify the temperature at which the material's thermal stability is compromised and, furthermore, to determine the oxidation state of any metals present in the structure at specific temperature ranges.

The presence of Lewis acid sites, which are physical adsorption centers, and Bronsted acid sites, which are chemical adsorption centers, in mesoporous materials synthesized using different methods and with varying metal sources, is a crucial parameter that significantly impacts catalytic performance. The determination of catalytically active sites in the structure often relies on techniques such as the adsorption of pyridine or ammonia (Ramazani (Ramazani et al., 2019; Vutolkina et al., 2019). Studies in the literature have revealed that pure MCM-41 materials exhibit minimal surface acidity. To enhance the acidity, different metal sources are incorporated into the structure using diverse synthesis techniques, depending on the desired catalytic reaction for the material.

After synthesis, only a fraction of the metal source added to the initial synthesis solution can be incorporated into the structure of the resulting metal-loaded catalysts. Therefore, it is important to determine the quantity of metal source incorporated into the structure. Various analysis methods are employed for this purpose, with imaging techniques (SEM/EDS and TEM) being the most commonly used. SEM images is used to analyze the morphology of the materials. Chemical analysis conducted through SEM is referred to as EDS, which provides information about the bulk chemical composition of the material. Chemical analysis obtained through TEM is called EFTEM, which allows for the determination of the chemical composition of a smaller region (point analysis) within the structure. In addition to these techniques, mapping techniques are employed to determine the distribution of the metal within the support material.

The utilization of XPS (X-ray Photoelectron Spectroscopy) technique enables the determination of the chemical composition of the catalyst, similar to EDS technique. However, XPS technique specifically focuses on analyzing the chemical composition on the surface of the catalyst. By conducting depth analysis, it becomes possible to determine the quantity of metal source located at specific depths beneath the surface. Furthermore, this analysis technique also allows for the determination of the oxidation state of the metal source within the catalyst's structure.

Temperature Programmed Reduction (TPR) is a technique used to study the reduction behavior of metal oxides as a function of temperature. It provides valuable insights into the state and reducibility of the metal species present in catalyst materials. By subjecting the catalyst to a programmed temperature ramp in a reducing atmosphere, the extent of reduction can be determined. TPR analysis allows the identification of reduction temperatures at which specific metal species are transformed into their reduced forms. This information is crucial for understanding the catalytic activity and selectivity of the material. On the other hand, Temperature Programmed Desorption (TPD) is employed to investigate the desorption processes and bond strengths on the catalyst surface. By gradually increasing the temperature under controlled conditions, previously adsorbed gases or molecules are released from the catalyst surface. This enables the determination of desorption temperatures and provides insights into the strength of chemical bonds between the adsorbate and the catalyst. TPD analysis helps to characterize the surface properties of catalysts, such as the active sites and the stability of adsorbed species. Both TPR and TPD techniques are valuable tools in catalyst characterization, providing valuable information about the reduction behavior, active species, and surface properties of catalyst materials (Wang et al., 2018; Vutolkina et al., 2019).

2.2. Catalyst Preparation Methods

The materials used as catalyst supports often do not possess sufficient catalytic activity. However, the catalytic activity can be enhanced by modifying the structure with different elements. In this process, the element that will improve the catalytic properties of the material is incorporated into the structure using a selected synthesis method. There are several methods available for structure modification, but the most commonly used ones are hydrothermal and impregnation methods (Gambo et al., 2021). These methods, along with other frequently employed techniques, are briefly described below.

In the direct hydrothermal synthesis method, different metal sources are directly added to the synthesis mixture in the desired ratio during the synthesis process. The formation mechanism of mesoporous materials is based on the electrostatic interaction between the positively charged surfactant and the negatively charged silicate species. According to the liquid-crystal templating mechanism developed by Beck et al. (Figure 2.5), the first step of the synthesis involves the hydrophilic groups of the surfactant interacting with water

molecules to form micelles. In the second step, the added silica source coats these micelles, forming micellar rods. Finally, these micellar rods come together to form the hexagonal pore structure. The direct hydrothermal synthesis method allows for the controlled incorporation of different metal sources into the material structure, which can influence the catalytic properties of the resulting material. The formation mechanism described based on the liquid-crystal templating concept provides insights into the self-assembly process that leads to the formation of the desired mesoporous structure.

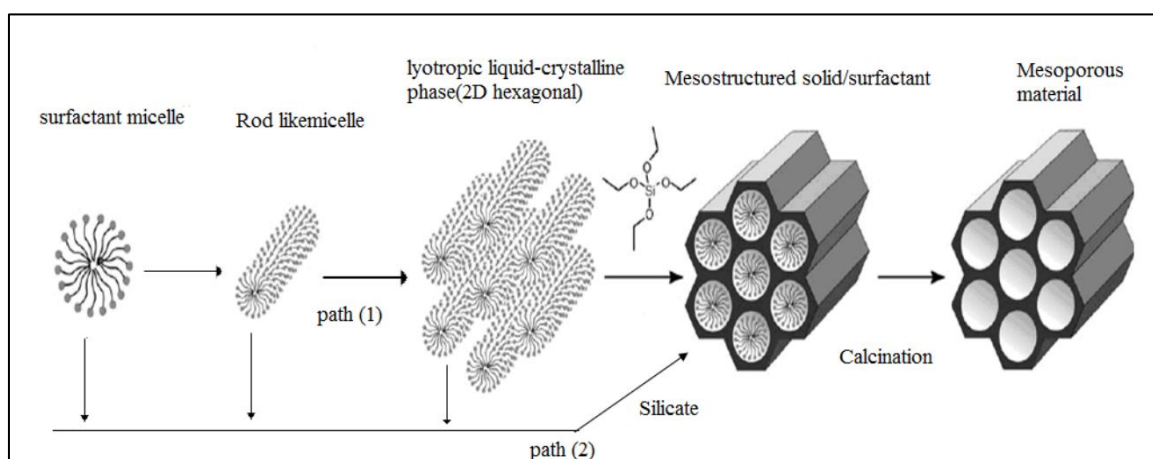


Figure 2.5. Schematic representation of the liquid-crystal templating mechanism (Kumar et al., 2017)

In the final step, the template material in the obtained product's structure is removed by subjecting it to a calcination process at high temperatures, resulting in the formation of pores in the material. If a metal-modified mesoporous material is desired, the metal source to be incorporated into the structure is added to the formed micelle structure in the second step, allowing the metal to attach to the outer parts of the micelles. Subsequently, the added silica source is introduced into the synthesis mixture, coating the micelles with silica, thus enabling the incorporation of the added metal into the silica walls. Similarly to the pure material, in the final step, the template structure is removed by the calcination process, resulting in the formation of pores in the material (Kumar et al., 2017).

In the impregnation method, the first step involves the synthesis of the support material, followed by the addition of the metal source to the structure in the desired ratio. The main difference between the impregnation method and the hydrothermal synthesis method is that in hydrothermal synthesis, the metal source directly incorporates into the silica inner walls,

while in the impregnation method, the metal source coats the catalyst surface or pore channels. As a result, it can lead to blockages in these regions. In the impregnation method, two techniques are used for the incorporation of the metal source into the structure: dry impregnation and wet impregnation. In dry impregnation, a small amount of solution containing the desired metal source is used. In this method, the mixture containing the metal source and mesoporous material is heated and stirred on a magnetic stirrer for a certain period to remove the water content, and the resulting solid is dried in an oven and then calcined. Wet impregnation involves a larger quantity of solution. The mesoporous material is immersed in the solution containing the metal source and stirred for a short period. Subsequently, the mixture is heated without stirring for a while and finally placed in an evaporator to evaporate the water content. The resulting solid is then calcined (Khalameida et al., 2016).

Other commonly used methods include homogeneous deposition-precipitation, co-precipitation, sol-gel, and ion exchange. These methods offer different approaches to introduce modifying elements into the catalyst structure and improve its catalytic performance.

The precipitation method, known as HDP (Homogeneous Deposition Precipitation), is based on the precipitation process achieved by mixing two or more solutions. Subsequently, the desired catalysts are synthesized through filtration, washing, drying, and calcination processes. In this method, an aqueous solution of metal salt is reacted with an aqueous alkali, resulting in the precipitation of metal hydroxide or carbonate. If the precipitate consists of a large number of crystals, their sizes can influence the particle size of supported metal catalysts. The formation of fine crystals in the process enables high surface area of the metal catalysts. However, extremely fine crystals can complicate the filtration process and prolong the required time for this stage. Centrifugation can be utilized to collect the crystals. Additionally, crystal sizes are affected by temperature and stirring. One of the significant advantages of this method is the even distribution of active centers in the catalyst. Moreover, it is a favorable method for controlling pore size and distribution. The physical and chemical structure of the resulting catalyst is sensitive to the precipitation pH. Therefore, the precipitation process should be carried out in a continuously stirred system with pH control (Wang et al., 2012).

The co-precipitation method involves the simultaneous precipitation of both the support material and the active phase. This technique can lead to structural deviations and clay-like compounds in the prepared catalysts. Examples of such materials include smectite and hydrotalcites (Wang et al., 2016).

Unlike the co-precipitation method, the sol-gel method is a homogeneous process. It relies on the continuous transformation of the solution within the hydrated metal salt. This method is known for its flexibility, allowing control over the structural properties, homogeneity, and composition of the resulting product.

Ion exchange is a widely used method for introducing metal ions onto a support material. Ion exchange technique involves the adsorption of metal ions onto a support material through an excessively negatively charged framework. However, in the case of MCM-41, the efficient generation of excessive negative charge within the framework requires the incorporation of aluminum ions into the pore walls during synthesis. During ion exchange, equilibrium-charged cations (such as alkali ions, ammonium ions, or protons) are displaced by the desired metal ions. However, the ion exchange method is often diffusion-limited and requires long equilibration times. The loading capacity of metals is typically limited in this method.

MCM-41 exhibits poor resistance to mineralizing agents such as hydroxide ions, making the HDP or impregnation techniques insufficient for satisfactory results. In these methods, the delicate amorphous silica mesopore walls can dissolve, leading to structural collapse in the support and loss of desired properties. Moreover, the filling of solution into the mesopores of MCM-41 poses various challenges. The precipitation and co-precipitation methods are alternative approaches for MCM-41 catalysts supported on MCM-41. These methods involve the incorporation of metal ions into the silica pore walls during MCM-41 synthesis. However, the addition of hetero elements into the pore walls diminishes their stability, resulting in structural precipitates within the framework, even if the surfactant is removed.

A simple method used for catalyst preparation is the "spreading" technique. It involves mixing specific metal oxides (such as MoO_3 and V_2O_5) with the support material, which then spreads onto the surface of the high-temperature metal oxide support. However, the interaction between the support material and metal oxide is relatively weak, leading to a low

metal loading in the resulting catalyst. Moreover, this process causes a reduction in the surface area of the support material.

Chemical vapor deposition (CVD) is a catalyst synthesis method that relies on the adsorption of volatile metal salt compounds onto the surface of a support material. Through the interaction, the metal salt compounds undergo decomposition, leading to the deposition and accumulation of the desired metal on the support material. This technique enables precise control over the metal deposition process, allowing for the customization of catalyst properties and composition.

Organometallic metal salts are commonly used in the preparation of supported heterogeneous catalysts. This can be achieved through grafting or tethering processes. Grafting relies on the chemical reaction between the metal salt complex and hydroxyl groups on the surface of the support material. As a result, a covalent bond is formed between the support material and the metal ion/atom. Tethering, on the other hand, involves the use of both the metal complex and a bridging moiety. This bridging moiety, typically a small organic ligand, reacts with the hydroxyl groups on the support material, followed by the formation of a longer complex with the metal ion/atom. As a result, tethering yields a heterogeneous catalyst containing the metal complex.

By employing these modification techniques, catalyst materials can be tailored to exhibit enhanced catalytic activity, selectivity, and stability, thereby enabling their application in various chemical reactions.

2.3. Isobutane Dehydrogenation Reaction

Isobutene is a significant chemical compound utilized in the synthesis of various commercially important products, including methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), butyl rubber, polyisobutylene, methacrylate, isoprene, tertiary butylphenol, tertiary butylamine, 1,4-butadienol, and ABS resin (Luo et al., 2013) . Figure 2.6 provides examples of materials derived from isobutene.

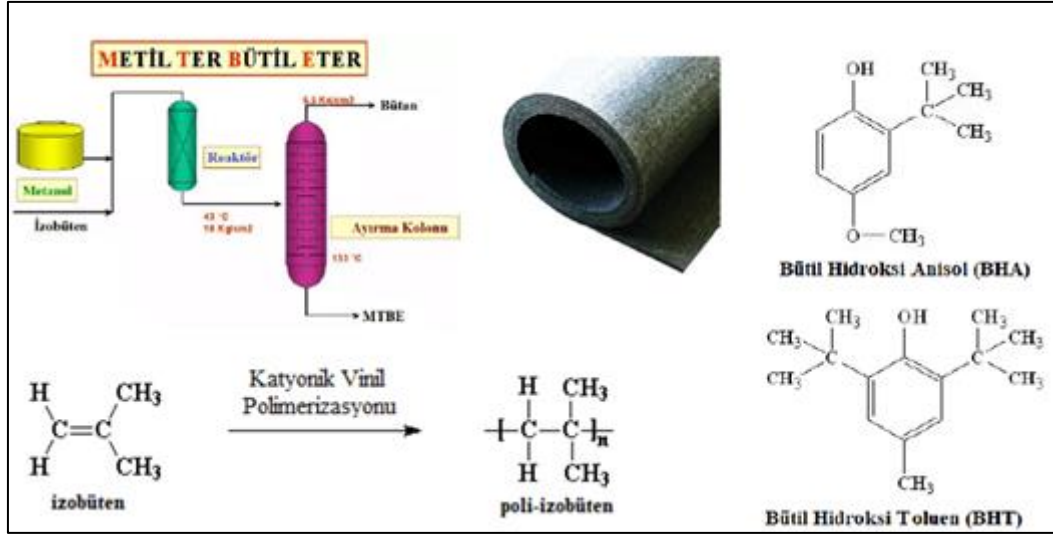


Figure 2.6. Isobutene-derived materials (Görseli, 2017)

The dehydrogenation of alkanes to olefins is a highly endothermic process, and the achievable conversion is constrained by thermodynamic equilibrium. This reaction requires an increase in the number of moles and specific conditions of high temperature and low pressure, given the low values of equilibrium constant (K_p). To achieve a conversion approximately 50%, temperatures ranging from 800 to 1000 K are typically required for C2-C5 paraffins, with higher temperatures needed for lower molecular weights. Notably, the reaction is observed to be influenced inversely by high pressures, contradicting the stoichiometry of the reaction.

During the process of isobutane dehydrogenation, high temperatures and prolonged residence times lead to the occurrence of side reactions such as thermal decomposition and coking. It was demonstrated that hydrogenation reactions are more prevalent as side reactions in this system. However, this dehydrogenation reaction exhibits certain drawbacks, including low selectivity towards isobutene due to the occurrence of side reactions, as well as high energy consumption associated with operating at elevated temperatures (Nawaz, 2015).

The equilibrium conversion of isobutane dehydrogenation is severely limited by thermodynamic constraints. To enhance this conversion, it is necessary to operate at temperatures above 450°C, where rapid catalyst deactivation due to coke formation occurs. Uncontrolled coke deposition on the catalyst surface results in a continuous decrease in catalytic activity. Addition of hydrogen to the feed stream helps mitigate coke formation;

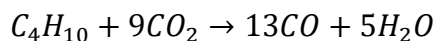
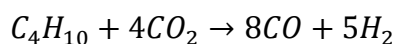
however, excessive hydrogen addition reduces the net dehydrogenation rate. In isobutane dehydrogenation reactions, the presence of acid sites on the catalyst support leads to increased coke formation rates and the occurrence of side reactions. This necessitates either a non-acidic catalyst support or modification of the support through alkaline addition (Nawaz, 2015).

The specific reactions associated with the endothermic and equilibrium-driven isobutane dehydrogenation can be found in Table 2.3.

Table 2.3. Main reactions and possible side reactions that occur during the oxidative dehydrogenation of isobutane (CO₂) (Gambo et al., 2021)

Main reactions	
$i-C_4H_{10} \leftrightarrow i-C_4H_8 + H_2$	$\Delta H_{298}^\circ = +117.28 \text{ kJ/mol}$
$H_2 + CO_2 \leftrightarrow H_2O + CO$	$\Delta H_{298}^\circ = + 41.13 \text{ kJ/mol}$
$i-C_4H_{10} + CO_2 \leftrightarrow i-C_4H_8 + H_2O + CO$	$\Delta H_{298}^\circ = + 158.41 \text{ kJ/mol}$
Side Reactions:	
$i-C_4H_{10} \leftrightarrow CH_4 + C_3H_6$	$\Delta H_{298}^\circ = +79.08 \text{ kJ/mol}$
$i-C_4H_{10} + H_2 \leftrightarrow C_3H_8 + CH_4$	$\Delta H_{298}^\circ = - 45 \text{ kJ/mol}$

The presence of hydrogen gas during the conversion of isobutane to isobutene leads to the undesired formation of propane and propene as byproducts. To prevent these side reactions, reducing the partial pressure of H₂ in the environment and utilizing H₂ in different reactions can enhance selectivity. One approach to achieve this is by utilizing CO₂, which exhibits low oxidation properties, to suppress the formation of CO₂ oxidation byproducts (Gambo et al., 2021). Co-feeding isobutane and CO₂ gas into the system has shown positive effects in reducing the formation of byproducts by utilizing H₂ in the process (Nowicka et al., 2018).



In recent years, the use of membrane reactors has gained attention for overcoming the equilibrium limitation by removing hydrogen from the environment in dehydrogenation reactions. Kinetic tests conducted using a CrO_x/MCM-41 catalyst in a membrane reactor have demonstrated close to 100% selectivity towards isobutene (Kılıçarslan et al., 2014).

Dehydrogenation of alkanes is a widely studied process, and it typically utilizes two types of catalysts: Pt-based catalysts and Cr-based catalysts. Commercial processes for dehydrogenation reactions were developed and implemented in various industries. Information regarding these processes (Catofin, Oleflex, STAR) is given below. Figure 2.7 shows a flow diagram of the Catofin process.

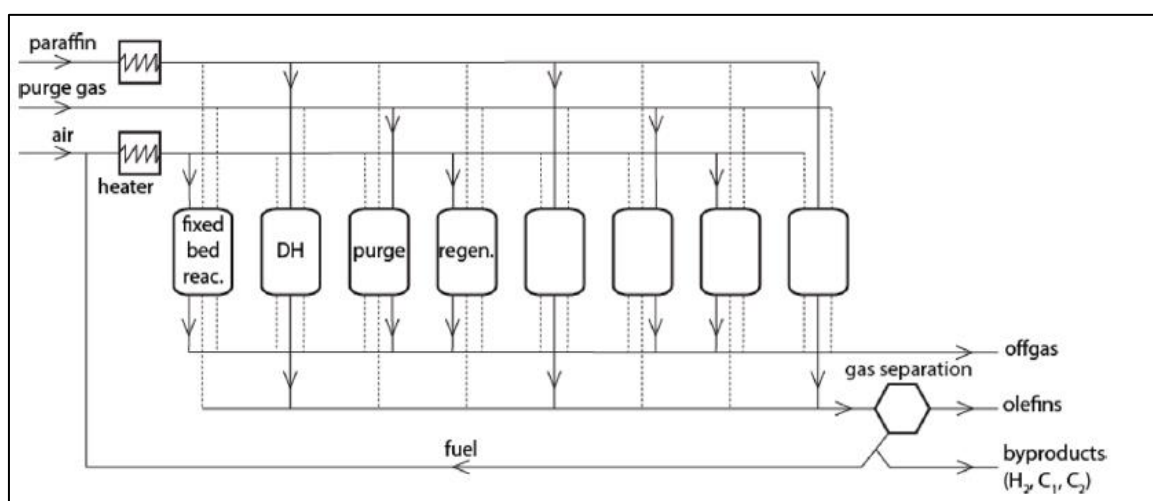


Figure 2.7. Catofin process flow diagram (Sattler et al., 2014)

Catadiene and Catofin processes are commercial processes used for the production of specific olefins. In these processes, a chromia-alumina catalyst is utilized in the form of cylindrical pellets. This process converts n-butane and isopentane into butenes and isopentenes. On the other hand, the Catofin process converts isobutane and propane into isobutene and propene. Both processes are conducted in parallel fixed-bed reactors, operating within a temperature range of approximately 550-650°C (Figure 2.7).

Figure 2.8 gives flow diagram for the Oleflex process.

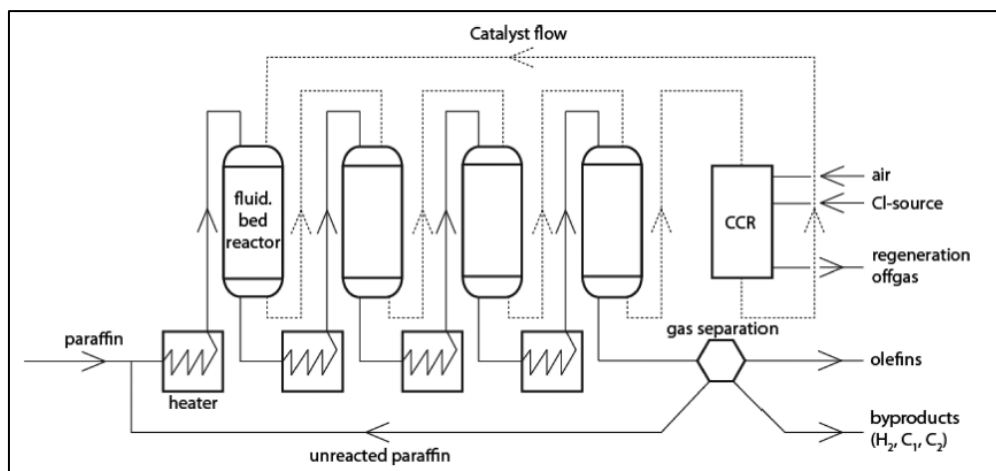


Figure 2.8. Oleflex process flow diagram (Sattler et al., 2014)

The Oleflex process is carried out using a Pt/alumina catalyst with Zn and Cu promoters. It is specifically designed for the dehydrogenation of C₂-C₄ olefins and isopentane feedstocks. The process operates in a series of fixed-bed reactors at temperatures ranging from 600 to 630°C, slightly above atmospheric pressure (Figure 2.8). Catalyst regeneration is accomplished using steam.

Figure 2.9 illustrates flow diagram of the STAR process.

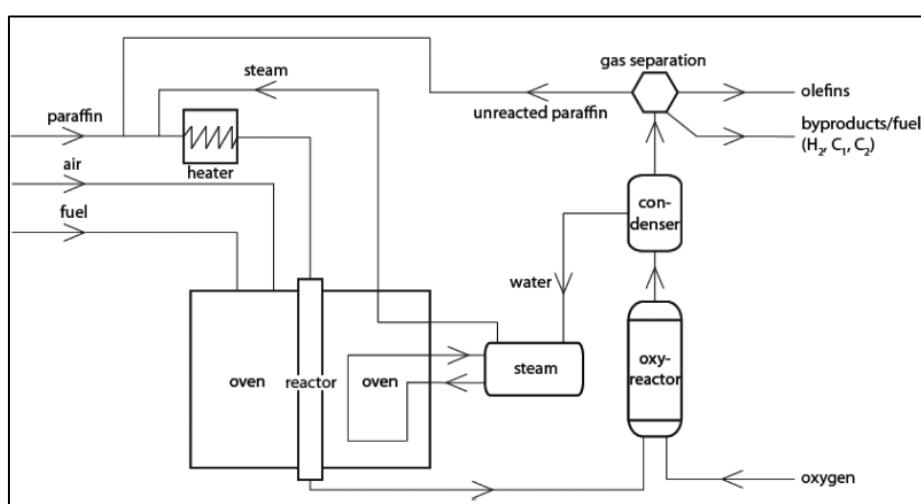


Figure 2.9. STAR process flow diagram (Sattler et al., 2014)

The STAR (Steam Active Reforming) process utilizes a Pt/Zn-alumina catalyst with Sn promoter. This process is conducted under isothermal conditions, using multiple catalyst bed tubes and high steam velocities. It is specifically designed for C2-C4 olefins, and operates at a temperature of 600°C and a pressure of 3.5 atm. In processes involving isobutane dehydrogenation, regeneration is commonly employed while avoiding excessively high temperatures (>650°C). This is crucial to prevent the conversion of high surface area δ -alumina to low surface area α -alumina in alumina-supported chromium oxide catalysts, which renders Cr₂O₃ inactive. Similarly, Pt/alumina catalysts experience a decrease in surface area and sintering (Figure 2.9).

3. LITERATURE REVIEW

Alkenes produced by the dehydrogenation reaction of alkanes are widely used in industrial applications. Typically, platinum and chromium-based catalysts are utilized in dehydrogenation reactions, but studies have also been conducted with different catalysts. The isobutane dehydrogenation is an endothermic and equilibrium-limited reaction. One or more reaction products are removed from the reaction medium to exceed the equilibrium conversion. In the case of isobutane dehydrogenation, the equilibrium limitation of the reaction can be overcome by removing hydrogen from the reaction medium. This can be achieved through oxidative reactions or by carrying out the reaction in a membrane reactor.

This section contains information about the different catalyst types used in dehydrogenation reactions. It also includes a review of various studies carried out using different catalysts. In general, the topics covered in this literature were categorized into three groups. These groups are the synthesis of MCM-41 and MCM-41 supported catalysts, catalyst synthesis and reaction applications for dehydrogenation reactions, and the role of carbon dioxide as a soft oxidant. The research findings are summarized below.

3.1. Synthesis of MCM-41 and MCM-41 Supported Catalysts

As well known, the mesoporous MCM-41 has an interesting property, such as uniform pore size distribution, low pores acidity, high porosity, high specific surface area, and good adsorption properties, all of which make it a good support for reaction catalysts. However, MCM-41 materials have low stability in the presence of water or steam, which limits their applicability. When the MCM-41 material is exposed to a water-containing environment, the pores are lost or modified, which has been related to the hydrolysis of the siloxane linkages (Si-O-Si), and the reduction of the material's mechanical resistance (Sangchoom and Mokaya, 2012).

In their study, Perez et al. (2016) suggested that the limited hydrothermal stability of MCM-41 was primarily due to a physical effect that occurs during the drying of the hydrothermally treated MCM-41, attributed to the intense capillary stress exerted by water. To prove this, they prepared three different samples with varying degrees of condensation. The hydrothermal test was carried out by mixing the samples with water at three different

temperatures (343K, 358K, and 373K) for 5 hours. Then, the samples were dried and characterized. In addition, more samples were prepared by repeating the hydrothermal test under the same process condition above. However, those samples were washed with n-butanol (99% extra pure), and after that, the formed samples were dried and characterized. The findings showed that when the material resulting from hydrothermal treatment was exchanged and dried using a low-surface tension solvent (n-butanol-based drying), the structure was preserved in good conditions. In contrast, the material dried in water exhibited damaged due to the capillary resulting from the high surface tension of water. The results also revealed that the capillary tension induced by the water contributes to structural damage following the hydrothermal treatment of calcined MCM-41. Particularly, the most remarkable results were observed for the un-aged MCM-41. Therefore, the collapse of the structure was associated with hydrolysis combined with loss of mechanical strength of the structure (López Pérez et al., 2016).

Chen et al. (2007) conducted a study to assess the thermal and hydrothermal stability of MCM-41 framework modified with titanium (Ti) or aluminum (Al), maintaining a Si/M molar ratio of 40 (where M= Al, Ti). The synthesized material remained its mesoporous structure when calcined in air at temperatures up to 800°C. However, the pore structure of both MCM-41 and Al-MCM-41 collapsed when subjected to calcination temperature exceeding 800°C, while pore collapse for Ti-MCM-41 occurred at approximately 100°C higher. MCM-41 materials were tested in pure distilled water at temperatures ranging from 25°C to 100°C for four hours, to assess hydrothermal stability. The test results showed a significant loss of BET surface area for MCM-41, while both Al-MCM-41 and Ti-MCM-41 demonstrated greater stability under these conditions. The addition of Ti to the MCM-41 structure improved its thermal and hydrothermal stability. All investigated samples were stable in an acidic solution (pH:2)but disintegrated rapidly in a strongly basic medium (pH:12) (Chen et al., 1997).

In Jiang et al.'s (2012) study, researchers synthesized mesoporous MCM-41 using the hydrothermal crystalline method. The synthesis involved using cetyltrimethylammonium bromide as a structural template, sodium silicate as a silica source, and sodium aluminate in an alkaline solution as an aluminum source. The molar ratio of silicon to aluminum (Si/Al) was varied for each sample. Characterization of the synthesized materials indicated that all samples had a hexagonal mesoporous structure. Additionally, the secondary restructured

materials had a well-defined structure and maintained a long-distance order within the mesopores structure. To test MCM-41's hydrothermal stability, prepared samples were mixed with distilled water and placed in a closed container for 12 hours at 105°C. According to the results obtained, the introduction of an Al atom into MCM-41 structure with Si/Al ratio of 25 provided optimal hydrothermal stability. These results clearly show that the hydrothermal stability of MCM-41 can be enhanced through secondary restructure (Jiang et al., 2012).

The use of titanium and titanium oxide-modified MCM-41 has recently gained wide attention in the industrial field due to its catalytic properties. According to Yao (2019), the modification of MnOx/CeO₂-ZrO₂ nanorod catalyst with TiO₂ enhanced its catalytic activity and tolerance to H₂O and SO₂. However, the mechanism of this enhancement was attributed to a significant amount of oxygen vacancies, an increased concentration of Ce³⁺, a higher ratio of Mn⁴⁺, and the presence of surface-adsorbed oxygen species, which also improved surface acidity. Catalytic test results showed that modification of TiO₂ effectively suppressed the non-selective oxidation of NH₃ to N₂O by reducing the redox property of the Mn/CeO₂-ZrO₂ catalyst, which enhances N₂ selectivity (Yao et al., 2019).

According to the research published by Kowalczyk et al. (2016), the template ion-exchange method was used to synthesize catalysts by loading FeOx (monomeric and aggregated iron species) on MCM-41 and Ti-MCM-41. FeCl₂ and [Fe₃(OAC)₆O (H₂O)₃]NO₃ solution were used as iron sources. Characterization tests show that the specific surface area and porosity of the mesoporous silica support slightly decreased when iron was deposited on MCM-41 and Ti-MCM-41. Moreover, in the case of using FeCl₂ solution, iron accumulates on the catalyst surface in the form of monomeric iron cations. Also, the increase of iron loading over 8.3% by mass in MCM-41 support led to an increase in aggregated iron oxide species. However, when Ti-MCM-41 was used as a supplement, the clustered FeOx species was higher. Additionally, it was discovered that when iron acetate oligo cations [Fe₃(OAC)₆O(H₂O)₃]NO₃ were deposited, monomeric iron, as well as micro-rods, were formed in Ti-MCM-41 surface. On the other hand, such an effect was not noticed when iron deposition was carried out using a solution of FeCl₂. It was discovered that MCM-41 and Ti-MCM-41, which had been iron-modified, were effective catalysts for the selective oxidation of NH₃ to N₂ (NH₃-SCO). The catalysts in this process functioned effectively at

high temperatures, exhibiting over 90% selectivity for dinitrogen at 550°C (Kowalczyk et al., 2016).

In another study carried out by Kowalczyk and his research group, The Template Ion-Exchange method (TIE) method was used in the synthesis of bimetallic catalysts supported on mesoporous MCM-41 as well as to deposit a single metallic component on MCM-41. Using methanol solutions of CuCl_2 , FeCl_2 , and MnCl_2 , metals (copper, iron, and manganese) were loaded on the MCM-41 support. Amorphous structures were observed when the Fe and Mn were doped on the support catalysts. On the other hand, when Cu was loaded into the MCM-41 structure, CuO crystals were formed. Such clumped crystalline types of copper oxide have not been detected in bimetallic samples containing copper and iron or copper and manganese. Catalysts prepared through the TIE method were found to show high activity in NH_3 oxidation. It was shown that the catalytic performance of catalysts depends mainly on the crystal structure of the loaded metal. Catalysts prepared with iron and manganese performed well at high temperatures, while catalysts containing copper performed well at low temperatures. The simultaneous incorporation of copper, iron, copper, and manganese into the MCM-41 support structure was noticed to give high selectivity values in NH_3 oxidation at low temperatures. This interesting effect is explained by the synergistic effects between the transition metals accumulating on the surface of MCM-41 (Kowalczyk et al., 2017).

Cr-MCM-41 catalysts were synthesized by Kılıçarslan et al. (2013) using hydrothermal synthesis and impregnation synthesis methods. The surfactants $\text{C}_{17}\text{H}_{38}\text{BrN}$, $\text{C}_{19}\text{H}_{42}\text{BrN}$, $\text{C}_{32}\text{H}_{68}\text{BrN}$, and $\text{C}_{19}\text{H}_{42}\text{BrN} + \text{C}_{17}\text{H}_{38}\text{BrN}$ were used in the synthesis. The best catalyst synthesis was achieved with $\text{C}_{19}\text{H}_{42}\text{BrN}$ surfactants. Catalytic tests for these catalysts were conducted at 600°C and atmospheric pressure. Characterization results verify well-dispersed chromium within the MCM-41 lattice. In all synthesized catalysts, Cr^{6+} was detected as chromates, while Cr^{3+} appeared in the form of CrOx or Cr_2O_3 . In catalysts prepared using hydrothermal synthesis, all chromate species (mono-, di-, and poly-) were present. The most active form for isobutane dehydrogenation were observed as monochromates. The catalyst deactivation mechanism occurs due to the transformation of the Cr(VI)O_4 chromate structure into the Cr_2O_3 crystal structure (Kılıçarslan et al., 2013).

Ajayi et al. (2013) reported the synthesizing of catalysts supported on X-MCM-41 (X is Cr, V, and Cr-V) using hydrothermal synthesis and impregnation synthesis methods. Metal sources such as chromium nitrate and ammonium metavanadate, surfactant cetyltrimethylammonium bromide, and silica source sodium metasilicate were used to prepare the catalysts. BET analysis revealed that the chromium/vanadium ratio had a reducing effect on the surface area of the catalysts. The catalytic tests showed that 1,2Cr₂,8V/MCM-41 catalyst had the highest conversion and selectivity values at 600°C. The study demonstrates the potential of these catalysts for n-butane dehydrogenation reactions under oxygen-free conditions (Ajayi et al., 2013).

In another study by Kılıçarslan et al. (2014), the calcium (Ca) metal was loaded onto Cr-MCM-41 catalysts structure. The catalysts were prepared using the hydrothermal synthesis method and impregnation method. The effects of Ca addition on the chromate distribution of the synthesized catalysts and the activity of the catalyst were investigated for the isobutane dehydrogenation reaction. The characterization tests showed that the addition of Ca in catalysts causes an increase in mono and dichromate structures in the catalysts prepared by the hydrothermal synthesis method. In the catalysts prepared by the impregnation method, the addition of Ca caused the formation of chromates that were not in the structure before. The catalytic test results declared that for a Ca/Cr ratio of 0.65, at 873K and atmospheric pressure, 100% isobutene selectivity was achieved (Kılıçarslan et al., 2014).

The impact of loading titanium and chromium on catalyst was investigated. Elias and others (2012), in their research work, studied the effect of the presence of Cr particles on the photocatalytic performance of the TiO₂-loaded Cr/MCM-41 catalyst, in addition they examined the presence of heterojunction effect between the titanium (Ti) and chromium (Cr) species.

The wet impregnation method was used to synthesize Cr/MCM-41(x) and TiO₂/Cr/MCM-41(x) where x shows the theoretical loading of Cr (X= 0.75, 1.5, 3.5, 5 and 10), the Ti loading 3.2 wt.% was kept constant. XRD, UV-vis DRS, ICP, TEM, SEM, EDX, N₂ adsorption-desorption and TPR -H₂ techniques were used to characterize the catalyst structure for the prepared samples. According to the characterization tests, all the prepared samples were typical of mesoporous MCM-41 materials. It is also shown that when the Cr loading is higher than 3.5 wt.%, the presence of α -Cr₂O₃ nano-particles was seen (by XRD at a high angle).

Additionally, all the titanium-modified catalysts contained TiO_2 in its anatase crystalline phase. It is also verified that after the Ti loading on Cr/MCM-41(x) , the samples with low Cr content displayed a better thickening of the pore walls. This fact demonstrates that Ti species have been able to diffuse inside the mesoporous channels due to the significant Cr^{6+} dispersion and the absence of $\alpha\text{-Cr}_2\text{O}_3$ nanoparticles. For Cr loadings more than 3.5 wt%, the result reveals an increasing presence of Cr^{3+} species (UV-vis DR absorption at wavelengths higher than 550 nm).

In particular, for $\text{TiO}_2/\text{Cr/MCM-41}$ samples with lower chromium (Cr) loadings exhibit absorption in the ranges of 370-500 nm and 650-850 nm, which is likely related to the formation of a heterojunction between Cr and Ti. In contrast, this behavior was not observed in $\text{TiO}_2/\text{Cr/MCM-41}$ samples with high Cr loadings. The reason for this difference is the presence of Cr^{3+} species in form of clusters and $\alpha\text{-Cr}_2\text{O}_3$ particles, which inhibit the formation of a heterojunction between the active Cr^{6+} and Ti species. Among all prepared samples, $\text{TiO}_2/\text{Cr/MCM-41}$ (containing 3.5wt.% Ti and 8wt.% Cr) catalyst has the most outstanding properties. Finally, because the homogeneous catalytic response by leached Cr ions was insignificant, they could demonstrate that the solids act as heterogeneous photocatalysts (Elías et al., 2012).

In the study conducted by Asghari et al. (2016), ethane dehydrogenation in the presence of carbon dioxide was investigated. CrOx/MCM-41 , prepared by the hydrothermal synthesis method, was used as the catalyst. The amount of chromium metal in the catalyst structure varied between 0-11% by mass. Sodium metasilicate was used as the silica source, and $\text{C}_{19}\text{H}_{42}\text{BrN}$ (cetyltrimethylammonium bromide) was used as the surfactant for hydrothermal synthesis. The CrOx/MCM-41 structure was found to contain Cr^{6+} , Cr^{3+} , and crystalline Cr_2O_3 forms after calcination. An increase in the amount of Cr_2O_3 crystals was observed when the chromium content exceeded 2% by mass. The $\text{Cr}^{6+}/\text{Cr}^{3+}$ ratio was found to be highest when the chromium content reached 8% by mass. The high conversion values determined for this catalyst were attributed to the high Cr^{6+} content. The advantages of carrying out the reaction in a carbon dioxide atmosphere were also demonstrated. At a temperature of 700°C, ethane conversion of 56% and ethylene selectivity of 94% were obtained (Asghari et al., 2016).

3.2. Catalyst Synthesis and Reaction Applications for Dehydrogenation Reactions

The dehydrogenation reaction over heterogeneous catalysts can be classified into direct (non-oxidative) dehydrogenation (DH) and oxidative dehydrogenation (ODH). In oxidative dehydrogenation (ODH), oxidants such as O_2 , CO_2 , and NO_2 are used to help in the removal of hydrogen from the reaction medium. This method not only promotes the dehydrogenation process but also helps mitigate the formation of by-products. The choice of oxidant and the reaction conditions are pivotal in determining the catalyst's performance, including its activity, and selectivity.

3.2.1. Non-oxidative dehydrogenation

Zhao et al. (2013), synthesized mesoporous chromium/alumina (CrO_x/Al_2O_3) catalysts and used them in isobutane dehydrogenation. The characterization test showed that the Cr species were present in the Cr^{6+} and Cr^{3+} states over the surface of the mesoporous catalysts. Also, it was shown that the activity of chromium catalysts is affected by the amount of Cr^{6+} and Cr^{3+} in the catalyst structure. Cr species were found to have a strong interaction with alumina support. High conversion and selectivity values were obtained on the synthesized catalysts (Zhao et al., 2013).

In the study conducted by Lou et al. (2013), alumina support catalysts were synthesized via ammonia precipitation and hydrochloric acid reflux methods, and subsequently used for isobutane dehydrogenation. $Pt-Sn-K/\gamma-Al_2O_3$ catalysts were then synthesized using impregnation method. Various characterization techniques were utilized to characterize the catalysts. The study aimed to investigate how the alumina support affected the performance of the $Pt-Sn-K/\gamma-Al_2O_3$ catalysts in the isobutane dehydrogenation reaction. It was determined that the particle sizes of $Pt-Sn-K/\gamma-Al_2O_3$ catalysts synthesized using the ammonia precipitation method were smaller, and their acidity distribution was weaker. The highest isobutane conversion and isobutene selectivity were achieved obtained with this catalyst. it demonstrated greater resistance to coke accumulation and exhibited high stability. 57% isobutane conversion and 94% isobutene selectivity were obtained on the catalyst synthesized using the support prepared by the ammonia precipitation method (Luo et al., 2013).

Fang et al. (2015) investigated the deactivation of CrOx/Al₂O₃ catalyst when used in isobutane dehydrogenation. It was shown that the deactivation was due to the carbon accumulating on the catalyst surface. It was determined that Cr²⁺ and Cr³⁺ forms remained in the catalyst structure after the reaction (Fang et al., 2015).

CrOx/Al₂O₃ catalyst contains five chromate groups in the pre-reaction structure. These mono, -di, -poly chromates are amorphous structures and Cr₂O₃ crystals. In addition to chromium-chromate (Cr⁶⁺) species on the surface of Cr₂O₃ clusters and aluminum-chromium-chromate (Cr⁶⁺) species coupled with Cr₂O₃ clusters (Fridman et al., 2016). In another study by Fridman and Xing (2017), CrOx/Al₂O₃ catalysts were studied to assess the relative activity of five chromium species in dehydrogenation processes of isobutane. Non-redox Cr³⁺ in the unreacted catalyst is non-functional in dehydrogenation reactions (Fridman and Xing, 2017).

A series of Cu and Zn-doped CrOx/Al₂O₃ catalysts were synthesized via wetness impregnation, which were then characterized to show how the modifiers affect the activity of the catalyst in isobutane dehydrogenation into isobutylene, which was conducted in a fixed-bed reactor. It was determined that the prepared support had high stability at high temperatures. Additionally, the loading of the active metal on the supporting surface did not significantly affect the surface area. The catalysts modified with Cu- and Cu-Zn showed higher catalytic activity in isobutane dehydrogenation in comparison with unmodified CrOx/Al₂O₃ and Zn-modified catalysts. It was observed that the addition of Zn modifier in catalyst synthesized adversely affected the catalytic activity by increasing the reduction temperature and decreasing the amount of Cr(VI) species. On the contrary, the use of Cu modifier in the catalyst synthesis increased the amount of redox chromium formed. The highest efficiency Cu-modified CrOx/Al₂O₃ catalyst was detected in the activity tests (Salaeva et al., 2019).

In another study, a chromium-based catalyst was synthesized via impregnation method for isobutane dehydrogenation. The support material used in the synthesis was commercial activated carbon (AC) treated with acid. The study demonstrated how the duration of contact between the metal salt solution and the support influenced both the structure and activity of the catalyst. When Ca was added to the catalyst structure, a decrease in monochromate amount was observed (Doğan et al., 2018).

Rodemerck et al. (2017) synthesized VOx/MCM-41 catalysts and evaluated their performance in the dehydrogenation of propane and isobutane. V^{+4} and V^{+3} groups were identified as the catalytically active sites. The Lewis acidity of the isolated VOx sites increased as the number of V-O-V bonds surrounding a central V cation decreased, which was associated with higher activity but lower selectivity in isobutane dehydrogenation. It was shown that V^{+3} sites were more resistant to deactivation. While VOx dimers facilitated coke formation and blocked active sites, isolated VOx sites exhibited high activity for cracking and isomerization reactions. Under the reaction conditions investigated, Lewis sites formed by the partial reduction of V^{+5} species was stronger than that of VOx species. The study suggested that isolated VOx sites with a balanced Lewis acidity sufficiently strong to activate the C-H bond of alkanes but not to catalyze cracking or isomerization reactions should be preferred (Rodemerck et al., 2017).

In addition to removing hydrogen with carbon dioxide, membrane reactors are also suggested in the literature. Kılıçarslan et al. (2016) aimed to investigate the contribution of a Pd membrane to the dehydrogenation of isobutane over a Cr-MCM-41 catalyst with a Cr weight percentage of 3%; the catalyst was synthesized by hydrothermal synthesis method. During the synthesis, the silica source and metal salt were added alternately. A Pd-membrane reactor was used for catalytic tests. It was found that the membrane tube became active in the reaction when the operating temperature was above 873K (Kılıçarslan et al., 2016).

3.2.2. Oxidative dehydrogenation

Compared to the extensive studies on the dehydrogenation of ethane and propane in CO_2 environments, there are fewer studies on the dehydrogenation of isobutane to isobutene. The search of the literature on the oxidative dehydrogenation of isobutane resulted in only 52 articles published since 2000. Additionally, approximately 190 different catalysts were developed and tested (Otroshchenko et al., 2021). Therefore, developing catalysts with enhanced catalytic activity for the dehydrogenation of isobutane using CO_2 as a soft oxidant is important.

Krasnobaeva et al. (2017) synthesized catalysts by adding different metals (Pr, Eu, Sm, In, or Ga) to the magnesium-aluminum hydrotalcite structure. The prepared catalysts were tested in the oxidative dehydrogenation reactions of ethane, propane, and isobutane. It was

found that the yield of isobutene increased with increasing temperature and oxygen concentration in the reaction environment. The experiment was conducted to determine the yield and selectivity of isobutene at different temperatures and feed ratios. At a temperature of 450°C, with the feed ratio $i\text{-C}_4\text{H}_{10}/\text{CO}_2/\text{O}_2 = 1/1/0$, the isobutene yield and selectivity were found to be 27% and 93%, respectively. When the oxygen concentration was increased to $i\text{-C}_4\text{H}_{10}/\text{CO}_2/\text{O}_2 = 1/1/1$, the isobutene yield and selectivity increased to 32% and 87%, respectively. At a higher temperature of 600°C, with the feed ratio $i\text{-C}_4\text{H}_{10}/\text{CO}_2/\text{O}_2 = 1/1/1$, the isobutene yield was found to be 45.9% with a selectivity of 74.0%. It was shown that the addition of praseodymium (Pr) to the catalysts increased the selectivity and yield in the ODH reactions of ethane and isobutane. The praseodymium addition improves reaction selectivity and yield in the studied multicomponent catalysts (Krasnobaeva et al., 2017).

Boron nitride (BN) catalysts were used in n-butane and isobutane oxidative dehydrogenation. It was found that CO_x selectivity was low in BN catalysts compared to Cr, V-based, and P-modified catalysts (Sheng et al., 2021). Another study using hexagonal boron nitride (h-BN) catalysts reported high olefin selectivity and CO_x selectivity below 1.2% (McDermott et al., 2020).

Silicon borides, though rarely utilized in catalysis, possess abundant boron sites and excellent oxidation resistance, making them promising catalysts for the oxidative dehydrogenation (ODH) of light alkanes. A recent study by Yan (2019) showed that oxygenated silicon borides, primarily composed of silicon boride (SiB₆) phases, exhibited remarkable catalytic performance in the ODH of light alkanes, including ethane, propane, and isobutane. The catalysts demonstrate high selectivity towards olefins. When the conversion of ethane, propane, and isobutane were 18.8%, 19.1%, and 6.0%, respectively, the selectivity values for olefins were 95.8%, 82.2%, and 77.1%. Additionally, the catalysts showed superior resistance to over-oxidation of olefins at high conversion values. The productivity of light olefins reached 1.2–2.6 $\text{g}_{\text{olefins}} \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$. Stability tests revealed that the silicon boride catalysts remained stable for over 100 hours of operation, showcasing their durability. Notably, most silicon boride materials exhibited relatively low specific surface areas, suggesting that synthesizing silicon borides with higher specific surfaces could further enhance their catalytic activity (Yan et al., 2019). Sheng et al. (2021) also investigated the ODH of light alkanes to olefins using metal-free catalysts. They found that certain carbon

materials showed promising catalytic performance, although further research is needed to optimize their properties (Sheng et al., 2021).

In the study conducted by Fan et al. (2019), VO_x-MCM-41 catalysts were synthesized using the impregnation technique. The dehydrogenation reaction of isobutane was examined under oxygen-free, oxygen-lean, and oxygen-rich conditions. Under oxygen-free conditions, the catalytic activity significantly decreased within the first 2 hours due to rapid coke formation. In contrast, under oxygen-rich conditions, a low selectivity of isobutene was observed, accompanied by a high amount of CO_x formation. However, in the studies conducted under oxygen-lean conditions, the formation of CO_x and coke was significantly inhibited. Also a 85% isobutene selectivity was obtained on isolated VO_x groups supported on MCM-41 (Fan et al., 2019).

VO_x/SBA-15 catalysts were synthesized by Wei et al. (2016) using the impregnation method. The V content was varied between 1% to 11% by mass. The activity of catalysts was investigated for the dehydrogenation of isobutane in the presence of CO₂. Catalytic activity studies showed that V metal was effective in dehydrogenation reactions, and catalytic activity was associated with the type of V structures dispersed over the SBA-15 support. The catalyst with 7% V by mass showed the highest isobutane conversion (41%). SBA-15 was shown to be good support for dehydrogenation reactions due to its well-distributed metal distribution and low acidity (Wei et al., 2016).

In the study conducted by Wei et al. (2017), chromium-ceria catalysts supported on SBA-15 were synthesized by the wet impregnation method. The catalytic performances of the catalysts for the dehydrogenation reaction of isobutane in CO₂ environment were tested. It was reported that the addition of cerium to the SBA-15-supported chromium structures improved the distribution of the chromium structures. The highest Cr⁶⁺ amount was determined in 3Cr-3Ce/SBA catalysts. The 3Cr-3Ce/SBA catalyst showed the highest activity with 35% isobutane conversion and 90% isobutene selectivity at 570°C (Wei et al., 2017).

Catalyst support plays a crucial role in dehydrogenation reactions. The paper published by Bugrova's research group explores the effects of different support materials (γ -Al₂O₃, ZrO₂, CeO₂, and CexZr1-xO₂) on CrO_x catalysts for the ODH of ethane with CO₂. The catalysts

were synthesized by impregnation and characterized, and activity tests showed that catalysts supported by γ -Al₂O₃ and ZrO₂ exhibit better performance (Bugrova et al., 2019).

In the study conducted by Asghari et al. (2016), The performance of Cr/MCM-41 nanocatalysts synthesized via hydrothermal and impregnation methods for CO₂ mediated ODH of ethane to ethylene were investigated. CeO_x was loaded onto ZSM-5 supports in varying ratios and then used to prepare CrO_x catalysts. The chromium content of the catalyst was found to affect its catalytic properties and performance significantly. The characterization test revealed that the addition of CeO₂ prevented the formation of α -Cr₂O₃. Moreover, the catalytic test results showed that at 700°C reaction temperature, the ethane conversion was 61%, and the ethylene yield was above 90% when 10 wt% CeO₂ was loaded. The appropriate acidity, redox properties, and homogeneous metal distribution facilitated ethylene desorption from the catalyst surface and prevented the accumulation of carbon. CrO_x/ZrO₂ catalysts were also synthesized and tested for CO₂ assisted ethane dehydrogenation. The catalysts prepared via co-precipitation exhibited the highest ethane conversion (48%) and ethylene yield (43%) at 700°C and remained stable after 300 hours of reaction. The high catalytic activity and stability were attributed to the well-distributed metal on the support surface (Asghari et al., 2016).

Some papers suggest that TiO₂ nanoparticle modification of Cr/MCM-41 catalyst can affect their catalytic performance. Al-Awadi and this research group (2019), prepared a series of TiO₂ loaded to the MCM-41 structure by the impregnation method (1.1, 1.9, 3.7, 6.6, 11.5, 15.5 and 19.5 wt.%). CrO_x/TiO₂-MCM-41 catalysts (with 8 wt.% Cr loading) were synthesized by the same method. The chemical and structural properties of the prepared Cr-TiO₂-MCM41 catalysts were studied and analyzed. The results demonstrated improved chromium dispersion, reducible chromium concentration, and chromium-support interaction. The catalytic performance of these prepared catalysts for the ODH of ethane with CO₂ was also investigated. The catalyst containing 8% Cr and 1.9% Ti by mass was determined as the optimum value. Ethylene yield of 48% and selectivity of 92.8%, and 51.87% ethane conversion were obtained at 700°C. The catalyst activity did not decrease during 500 minutes of the catalytic activity test. The presence of highly homogeneously dispersed and small-sized TiO₂ groups on the surface of MCM-41 contributed positively to increasing the concentration and stability of Cr⁶⁺ species (Al-Awadi et al., 2019).

Titania/silica mesoporous nanocomposites were synthesized and used as supports for CrOx catalyst by Al-Awadi. A series of Ti–MCM-41 supports were prepared with varying titanium contents, and the Ti loading was in the range of 1.3–9.2 wt. %. Chromium was then loaded onto these supports by impregnation method, the Cr content was 8 wt.%. The influence of titanium content, and chromium loading on the performance of the Cr/Ti–MCM-41 catalysts for oxidative C₂H₆ dehydrogenation using CO₂, was examined. The results showed that varying in the titanium loading affected the relative crystallinity and surface area of Ti–MCM-41 supports for the prepared catalysts. Specifically, Ti–MCM-41, with a 2.2wt.% titanium content exhibited improved crystallinity with good surface area and homogeneity, along with a higher Cr(VI)/Cr(III) ratio. Further, the existence of 2.2% titanium stabilized the reducible Cr species at a high oxidation number and improved chromium distribution and metal support interaction. Moreover, it was also discovered that the optimum chromium load for enhanced catalytic activity is 8wt%. The reaction was carried out in a packed bed reactor at atmospheric pressure and 700°C reaction temperature. The highest ethane conversions of 52.3% and ethylene yields of 48.0% were obtained for the Cr(8)/Ti(2.2)–MCM-41 catalyst. Furthermore, this nanocomposite catalyst showed good stability over 10 hours on the stream (Al-Awadi et al., 2020).

3.3. The role of Carbon Dioxide as a Soft Oxidant

CO₂ has recently gained much attention as a soft oxidant for the selective dehydrogenation of light alkanes into alkenes. CO₂ has more advantages than O₂ as an oxidant, such as improving selectivity toward targeted olefins and decreasing CO₂ emissions.

Du et al. (2015) investigated the Gibbs free energy associated with the dehydrogenation of light alkanes with CO₂ in a temperature range of 300–500°C. Among the light alkanes analyzed, ethane was found to have the highest Gibbs energy for ODH reaction with CO₂ (Figure 3.1).

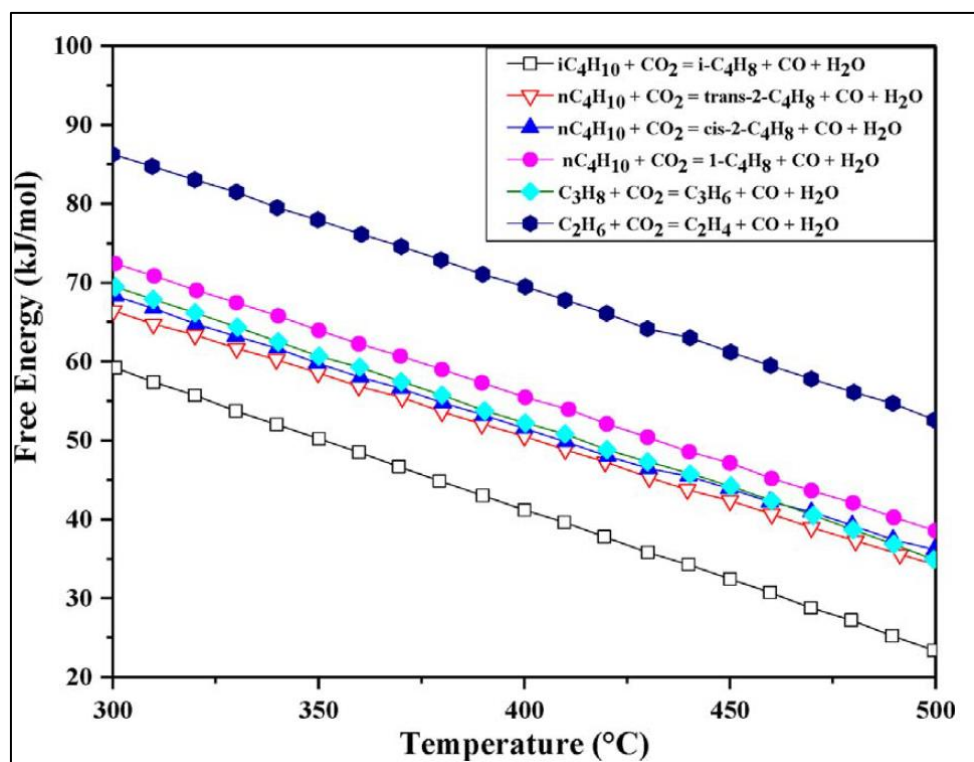


Figure 3.1. Gibbs energy for oxidative dehydrogenation of alkanes in CO₂ environment at a temperature range of 300–500 °C (Du et al., 2015)

Figure 3.1 indicates that operating the reaction at 300-500°C was much more difficult for ethane dehydrogenation compared to propane and butane dehydrogenation. The low value of Gibbs energy indicates a higher probability of cracking. In this study, the following conclusions were reached: (i) olefins showed greater probability of cracking than alkanes, (ii) propylene was more resistance to cracking than any isomer of butane, and (iii) the selectivity for target products was significantly affected by the increased cracking of olefins. Furthermore, it showed that activating ethane (breaking the carbon-hydrogen bonds in the ethane molecule) with CO₂ was difficult the reaction temperature below 500°C (Du et al., 2015).

Dehydrogenation reactions of alkanes with CO₂ are generally complex, and these reactions are thermodynamically limited at low temperatures and high pressures. Research showed that the dehydrogenation mechanisms and kinetics of ethane and butane were not very different from each other (Atanga et al., 2018).

Luo et al. (2019) prepared CrOx/Silicalite-1 catalysts via impregnation method and used them in the dehydrogenation reaction of isobutane assisted by CO₂. The catalyst with 3 wt%

Cr showed the highest conversion (37%) and selectivity (71%). The catalytic activity was strongly correlated with the Cr^{6+} content in the catalysts (Luo et al., 2019). In their study, the researchers proposed a mechanism for the dehydrogenation reaction of isobutane assisted by CO_2 (Figure 3.2).

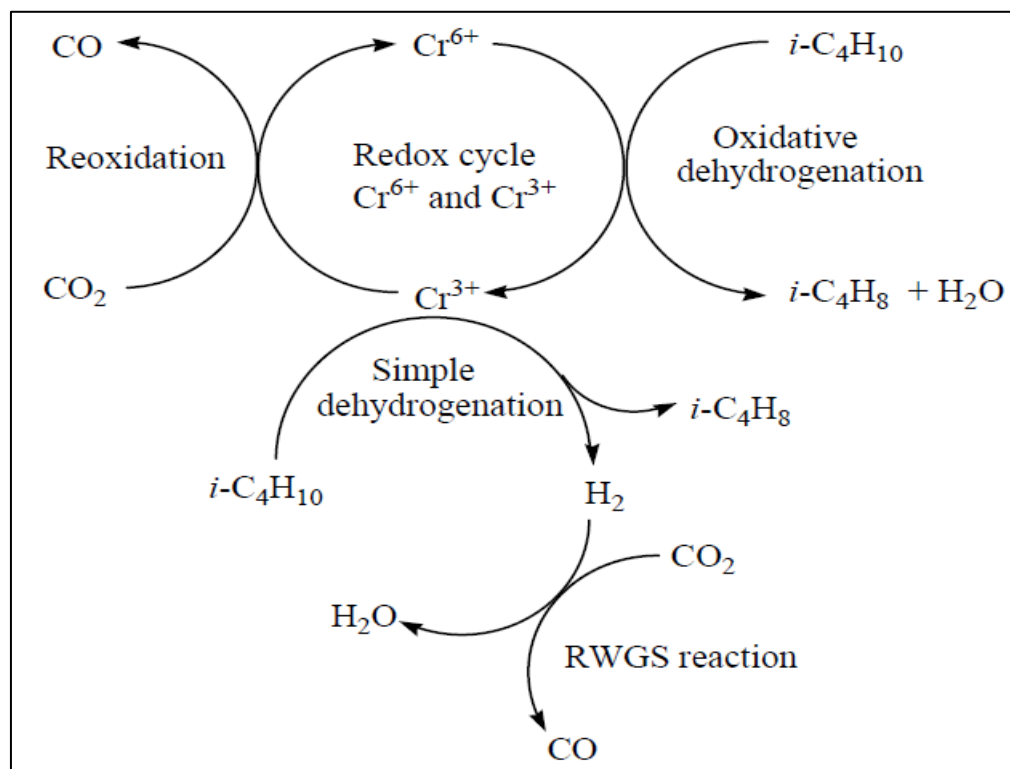


Figure 3.2. Proposed reaction mechanism for isobutane dehydrogenation in CO_2 media (over the CrOx/silicate-1 catalyst Scheme (Luo et al., 2019))

CO_2 has a promoting effect on the dehydrogenation of isobutane. It enhances this reaction through a redox mechanism, where the catalyst is first reduced by isobutane and then reoxidized by carbon dioxide. This process involves a coupling reaction between the direct dehydrogenation of isobutane and the reverse water-gas shift (RWGS) reaction, as illustrated in Figure 3.2.

Chromium oxide supported on active carbon (CrO_x/AC) catalyst that was utilized for the dehydrogenation of isobutane to produce isobutene in the presence of carbon dioxide by Ding et al. (2008). Incipient wetness impregnation was used for catalyst preparation. Isobutane dehydrogenation catalytic test was conducted in a fixed bed tubular reactor at atmospheric pressure. The study demonstrated that the presence of CO_2 in the reaction medium reduced the formation of coke and preserved the active forms of chromium on

CrOx/activated carbon catalysts. The results also showed that the isobutane equilibrium conversion increased from 82.1% in an inert atmosphere ($\text{Ar/IB} = 9$) to 94.4% in the presence of CO_2 ($\text{CO}_2/\text{IB} = 9$) at 550°C (Ding et al., 2008).

Another study used an incipient wetness method to synthesize supported ZnO catalysts on Silicalite-1 zeolites with various crystallite sizes (0.08, 0.35, 1, and $1.7\mu\text{m}$) and 5% Zn. CO_2 -assisted isobutane dehydrogenation was carried out to investigate the effect of Silicalite-1 crystallite size on the catalytic performance of selected catalysts. It was confirmed that the catalytic activity of ZnO/Silicalite-1 was highly influenced by the crystallite size of the support. Among the tested catalysts, the one with crystallite size of $0.35\mu\text{m}$ showed the best activity, enabling high isobutane conversion of 51.0% and isobutene selectivity of 74.5%. This was due to a majority of acid sites on this catalyst and a greater number of silanols, which enhanced the dispersion and stability of active metal oxide species (Luo et al., 2020).

The catalytic activities of zeolite-supported metal catalysts for the dehydrogenation of different alkanes, including isobutane, butane, and n-butane is presented in Table 3.1

Table 3.1. The catalytic activities over various zeolite-supported metal catalysts for alkane dehydrogenation reactions (Sun et al., 2021)

Catalyst	Metal loading [wt%]	Metal size [nm]	T [$^\circ\text{C}$]	WHSV [h^{-1}]	Feed [ml/ml]	Time [h]	Con [%]	Sel [%]
Cr/silicalite-1	3.00	-	570	4.1	i-C ₄ H ₁₀ /N ₂ =50/50	6	31.0-20.0	67-71.2
PtSn/Al ₂ O ₃ -SAPO-34	0.46	-	590	5.6	C ₄ H ₁₀ /N ₂ =5/1	8	42.6-23.1	87-98
ZnO/ silicalite-1	5.00	-	570	4.1	i-C ₄ H ₁₀ /N ₂ =2.9/2.9	6	51.0-49.0	74.5-79.0
PtSn/SAPO-34	0.43	2	585	2.8	C ₄ H ₁₀ /N ₂ =4/1	8	36.0-11.0	44-80
PtSn/ZSM-5	0.49	3	585	3.0	n-C ₄ H ₁₀ /N ₂ =4/1	8	38.7-26.6	34-40

The chemical equilibria of one-step and two-step oxidative dehydrogenation of propane with CO_2 were investigated by Zangeneh et al. (2015). The study carried out a detailed thermodynamic analysis of the oxidative dehydrogenation of propane reaction (ODHP) via CO_2 . The constrained Gibbs free energy minimization method was applied, and side reactions such as coke formation and dry reforming were considered. Different reaction networks representing various catalytic systems were simulated. The effects of the CO_2 : C_3H_8 molar ratio, temperature range, and various pressures on equilibrium conversion and product composition were investigated. Incorporating these side reactions in the

thermodynamic model significantly impacted the equilibrium conversion values, where the equilibrium conversion of propane increased at the expense of propene equilibrium selectivity. The results showed that at higher temperatures, propane dry reforming was preferred, whereas coke formation was preferred at lower temperatures and lower CO_2 : C_3H_8 ratios. It was also observed that the data obtained from experiments showed conversions that were far less than the equilibrium, due to catalyst deactivation. According to this study, in order to increase propene yield, kinetic control of dry reforming and coke forming processes is necessary to avoid the deactivation of the catalysts for CO_2 –ODHP. In addition to that, it is preferred to shift the equilibrium forward by the removal of hydrogen. Therefore, instead of hydrogen, water is generated as a primary oxidative dehydrogenation product or as a byproduct of direct dehydrogenation of propane DDH, followed by the RWGS reaction. As shown below, "Eq. (3.1)" is the direct catalytic dehydrogenation reaction of propane, "Eq. (3.2)" is the reverse water–gas shift reaction (RWGS), and "Eq. (3.3)" is the direct oxidation of propane to propylene (one-step pathway):

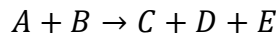


Table 3.2 shows all possible reactions among reactive species, as well as their components and additional constraint.

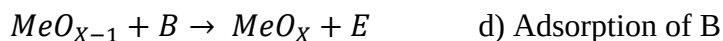
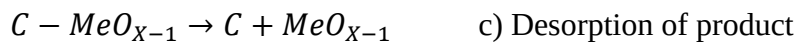
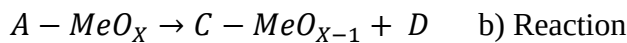
Table 3.2. Components and additional constraints for different reaction systems (Zangeneh et al., 2015)

Reaction system	component	Additional constraint
Simple (reaction 3-1)	C_3H_8 , C_3H_6 , H_2 (or inert diluent)	None
One-step (reaction 3-3)	C_3H_8 , CO_2 , C_3H_6 , CO , H_2O	$(n_{\text{C}_3} + n_{\text{C}_3})_{\text{initial feed}} = (n_{\text{C}_3} + n_{\text{C}_3})_{\text{equilibrium}}$
Two-step (reaction 3-1+ reaction 3-3)	C_3H_8 , CO_2 , C_3H_6 , CO , H_2 , H_2O	$(n_{\text{C}_3} + n_{\text{C}_3})_{\text{initial feed}} = (n_{\text{C}_3} + n_{\text{C}_3})_{\text{equilibrium}}$
Two-step + propane reforming	C_3H_8 , CO_2 , C_3H_6 , CO , H_2 , H_2O	None
Two-step + propane reforming + coke formation	C_3H_8 , CO_2 , C_3H_6 , CO , H_2 , H_2O	None

The Mars-Van Krevelen (MVK) model is commonly used to describe reaction kinetics. It was originally developed by Mars and Van Krevelen in 1954 to explain the kinetics of sulfur dioxide (of SO₂) oxidation over a molten vanadium-potassium (V/K) salt supported on a porous silica (Mars and Van Krevelen, 1954). In recent years, this model has transcended its original scope and found application in diverse reactions, such as hydrodesulfurization. (Liu et al., 2017), COV removal (Guo et al., 2021), dehydrogenation (Bai et al., 2015; Jibril, 2004; Sharma et al., 2015), and oxidative dehydrogenation reactions (Bhasin et al., 2001). According to this model, the catalyst's lattice provides the oxygen required for the reaction. The reduced catalyst is then reoxidized by gaseous oxygen (Grabowski, 2006). The redox mechanism can occur even in the presence of weak oxidizing agents, such as carbon dioxide. According to the Mars-Van Krevelen mechanism, carbon dioxide can reoxidize the catalyst surface that reduced by hydrocarbons. Therefore, it is essential to include CO₂ in the feed to maintain active metal oxide in a high oxidation state (Michorczyk et al., 2008; Ogonowski and Skrzyńska, 2008). The possible redox mechanism for the oxidative isobutane dehydrogenation was shown below:



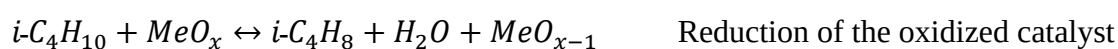
It is assumed that the reaction occurs according to the following steps. (Ross, 2019), where "MeO_x" represents an empty site on the surface of the catalyst:



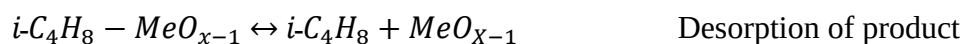
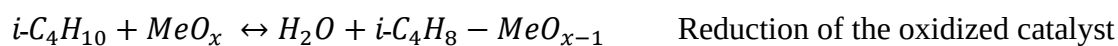
The adsorption of B (step d) is presented last since the empty site is created by the reaction rather than being present on the fresh catalyst. In a kinetic relationship, steps (a) and (b) are combined, assuming that the product is formed as soon as A interacts with catalyst's lattice. Additionally, it is assumed that the desorption step (c) is rapid compared to either this

combined reaction or step (b). Consequently, the reaction is effectively considered to occur in two steps: the adsorption of B with a rate constant k_2 (step (d)); and a second step (a combination of all the other steps), involving the formation of an empty site as well as the products through the reaction. In some cases, the mechanism might be simplified into a two-step process, while in others, a more detailed three-step mechanism may be proposed (Sharma et al., 2015).

Two stage mechanism



Three stage mechanism



This study introduces several novel contributions to the field of isobutane oxidative dehydrogenation. A review of existing literature reveals that chromium-based catalysts supported on titanium-modified MCM-41 had not been previously investigated for this reaction before this research. Additionally, this work marks the first application of K_2TiF_6 as a titanium source for modification of MCM-41, with the presence of potassium in this metal source expected to provide catalytic advantages. Furthermore, a reaction rate expression for the oxidative dehydrogenation of isobutane was developed, representing a significant advancement in the kinetic modeling of this process. The Mars–van Krevelen mechanism was systematically examined for this reaction over the selected catalysts, addressing a crucial requirement for catalysts with redox properties to meet industrial productivity demands. The study also investigated heat and mass transfer limitations, including both internal and external diffusion as well as the temperature gradient within the catalyst particles.

4. EXPERIMENTAL

The synthesis of MCM-41 support, the synthesis of Cr-based catalysts, the hydrothermal stability tests, the characterization analysis, and the catalytic activity test are the main headlines in this section.

In the oxidative dehydrogenation of alkanes, water vapor is produced as a side product. To utilize mesoporous MCM-41 as a support for chromium-based catalysts effectively, its hydrothermal stability must be enhanced. In this study, MCM-41 was modified with titanium to investigate the effect of Ti loading on the hydrothermal stability of the MCM-41 structure. Titanium loading was 2.5 wt%. After that, chromium-based catalyst was synthesized by hydrothermal method and wet impregnation synthesis method. The titanium amount was kept constant (2.5 wt.%) and different amount of chromium was loaded in the catalyst (3%, 6% and 10 wt.%). Additionally, catalytic activity tests of all prepared Cr-based catalysts were investigated for the oxidative dehydrogenation of isobutane. The oxidative dehydrogenation reaction of isobutane was performed at different reactor temperatures and at different weight hourly space velocities (WHSV) to investigate the effect of temperature and WHSV on isobutane conversion and isobutene selectivity. Finally, the reaction rate expression was developed over 10Cr/Ti-MCM-41 catalyst.

4.1. Synthesis of Pure MCM-41 and Titanium-modified MCM-41 Materials

In this study, titanium was loaded on MCM-41 to investigate its effect on increasing the hydrothermal stability of the MCM-41 by supporting its thin and weak walls. The chemical and structural properties of Ti-MCM41 were examined.

First of all, pure MCM-41 was synthesized by hydrothermal method. The main substances used in the synthesis of MCM-41 are silica source, surfactant, and solvent.

The chemicals used in the synthesis are:

- The surfactant: $C_{19}H_{42}BrN$ (N-cetyl-N, N, N-trimethyl ammonium bromide).
- Silica source: sodium silicate solution (27% by mass SiO_2 + 8% by mass Na_2O + 65% by mass H_2O).

- Solvent: deionized water.
- pH adjuster: sulfuric acid (4N H₂SO₄).

C₁₉H₄₂BrN (N-cetyl-N, N, N-trimethyl ammonium bromide) were used as surfactant due to its ability to direct the formation of well-ordered mesoporous structures (Kılıçarslan et al., 2013)

The surfactant/Si (mol/mol) ratio was chosen as 0.5 for the synthesis of pure MCM-41. The hydrothermal synthesis steps are shown below:

- As a start, the amount of the surfactant required for the synthesis was determined. As a result of the calculations, it was regulated that a 12.76 g of C₁₉H₄₂BrN should be used to keep the surfactant/Si (mol/mol) ratio at 0.5. Calculation of the amount of surfactant required is shown in Appendix-1.
- A 12.76 g of C₁₉H₄₂BrN (surfactant) and 87 mL of deionized water were mixed at magnetic stirrers under a temperature of 30°C until a clear colorless mixture was obtained. As shown in Image 4.1.

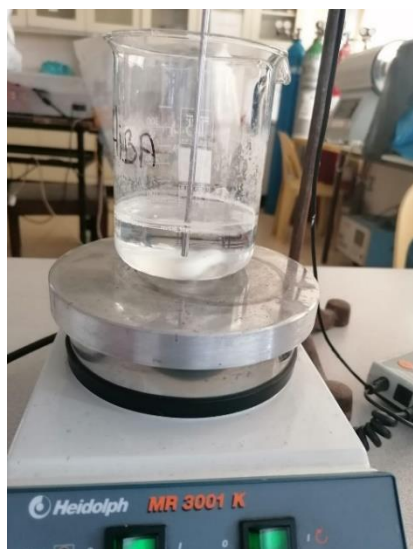


Image 4.1. Photograph of the dissolving process of the surfactant in the deionized water at 30 °C using a magnetic stirrer

- After that, 11.3 mL of sodium silicate solution (silica source) was added dropwise to the surfactant solution.
- Then, the pH of the resulting mixture was adjusted to 11 by adding acid 4N H₂SO₄.

- Consequently, the mixture (which its pH was adjusted to 11) was taken into a Teflon-steel autoclave and kept in an oven at a temperature of 120°C for four days (96 hours). Image 4.2 shows the mixture when placed into the Teflon-steel autoclave



Image 4.2. Photograph of the mixture taken into a Teflon-steel autoclave

- At the end of the fourth day, the sample was removed from the autoclave and taken into a beaker. Then, deionized water was added instantly to reach a total of 400 ml. The sample was mixed and left for a night to cool down. The sample that was removed from the autoclave is shown in Image 4.3.

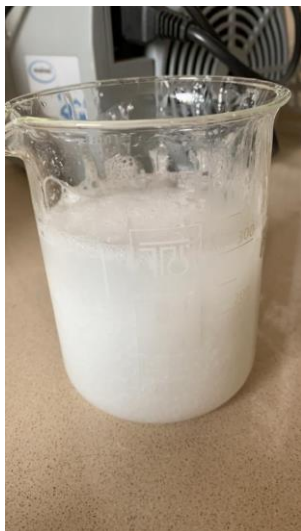


Image 4.3. Photograph of the sample removed from the autoclave after the sample volume was completed to 400 mL with deionized water

- The next day, the washing process was carried out until the pH of the sample filtrate was stabilized (pH~7). The washing system can be seen in Image 4.4.



Image 4.4. Photograph of the washing process for the prepared sample

- At the end of the washing process, the sample accumulated on the filter paper was dried at room temperature (~48 hours). Then, the dried sample was crushed into powder (in a mortar) and kept in a container. In Image 4.5, the shape of the dried sample can be seen.

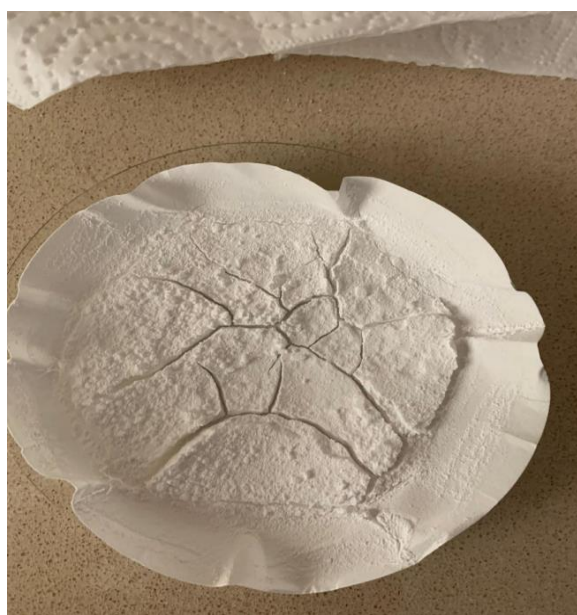


Image 4.5. Photograph of the dried sample after the washing process was completed

- After that, the dried sample was subjected to a calcination process to remove the organic compounds in the pores of MCM-41 structure. The calcination was done by placing the dried sample in a quartz reactor containing a porous sieve glass tube 1.5 m long, with a 1cm diameter. The glass tube was placed in a furnace. The furnace temperature was 600°C, and the heating speed was 1°C/min. After the system temperature reached 600°C,

the sample was left for 6 hours in a dry airflow (130 ml/min). The photograph of the calcination system is given in Image 4.6.

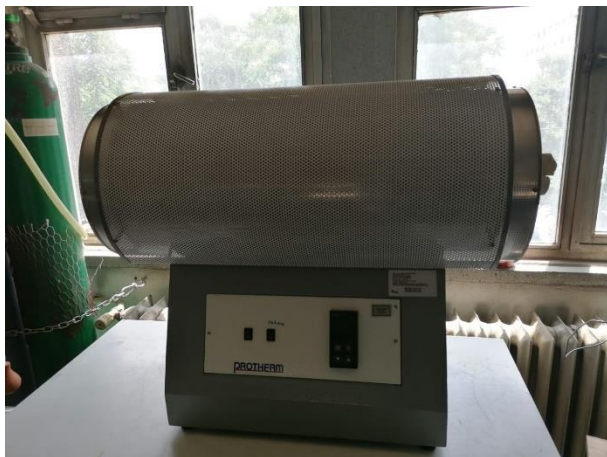


Image 4.6. Photograph of the calcination system

The synthesis of pure MCM-41, explained in detail above, was completed in three stages: hydrothermal treatment, washing, and calcination. The synthesis steps of pure MCM-41 are given in Figure 4.1.

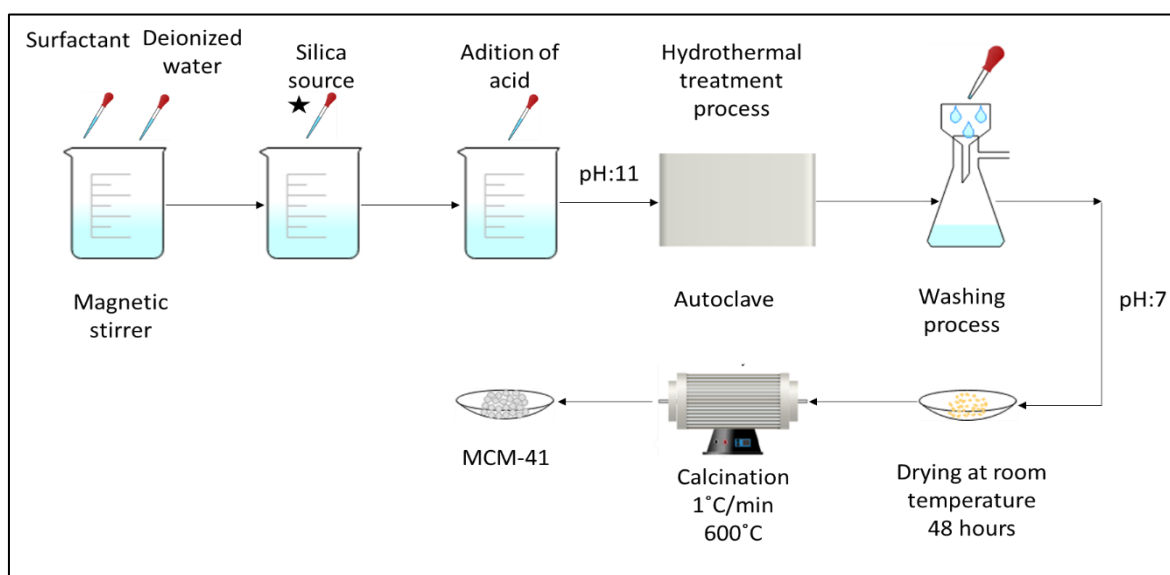


Figure 4.1. Synthesis steps of pure MCM-41

Second of all, the titanium-doped mesoporous MCM-41 materials were synthesized. The main ingredients used in the synthesis are silica source, surfactant, titanium source, and solvent.

The chemicals used in the synthesis are:

- The surfactant: $C_{19}H_{42}BrN$ (N-cetyl-N, N, N-trimethyl ammonium bromide).
- Silica source: sodium silicate solution (27% by mass SiO_2 + 8% by mass Na_2O + 65% by mass H_2O).
- Solvent: deionized water.
- Metal source: K_2TiF_6 (Dipotassium titanium hexafluoride).
- pH adjuster: sulfuric acid (4N H_2SO_4), sodium hydroxide (1N $NaOH$).

In the synthesis studies carried out, the surfactant/Si (mol/mol) ratio was chosen as 0.5, and titanium metal was 2.5% by mass in Ti-doped MCM-41 material.

The dipotassium titanium hexafluoride (K_2TiF_6) is a white leaflet powder soluble in hot water, slightly soluble in cold water, and inorganic acid (National Center for Biotechnology Information 2022). Two solutions of K_2TiF_6 were prepared, one with hot water (TiW-MCM-41) and the other with sulfuric acid (TiA-MCM-41), to assess the effect of the different solutions on the structural properties of the prepared titanium-modified MCM-41.

As a start, the amount of dipotassium titanium hexafluoride required for the synthesis was determined (Appendix-1).

The hydrothermal synthesis steps of both titanium-doped mesoporous MCM-41 support are like shown for pure MCM-41. The only difference is in the step that is marked with the star (★) in Figure 4.1. In that step, the sodium silicate and K_2TiF_6 solutions were added dropwise and alternately to the surfactant solution.

4.2. Hydrothermal Stability Test

In this study, Cr-based catalysts were used in the oxidative dehydrogenation reaction of isobutane into isobutene in CO_2 environment. During this reaction, water is expected as a by-product. That is why the use of catalysts with high hydrothermal stability is preferred for this reaction. In fact, one of the disadvantages of the MCM-41 is that its walls are vulnerable to moisture, the hydrothermal stability of the MCM-41 should be improved to increase the conversion and selectivity toward isobutene in this reaction.

The hydrothermal stability was tested to investigate the role Ti in enhancing the improvement of the hydrothermal stability of the synthesized MCM-41 materials (MCM-41, TiA-MCM-41, and TiW-MCM-41).

To carry out the test hydrothermal stability, samples were mixed with water. The samples were dispersed in 30 ml water and gently stirred while being heated at 110°C for 5 hours. Hot water was added when necessary to maintain a constant amount of water. The experiments were conducted using 100 ml beakers, thermometers, and magnetic stirrers. As shown in Image 4.7.

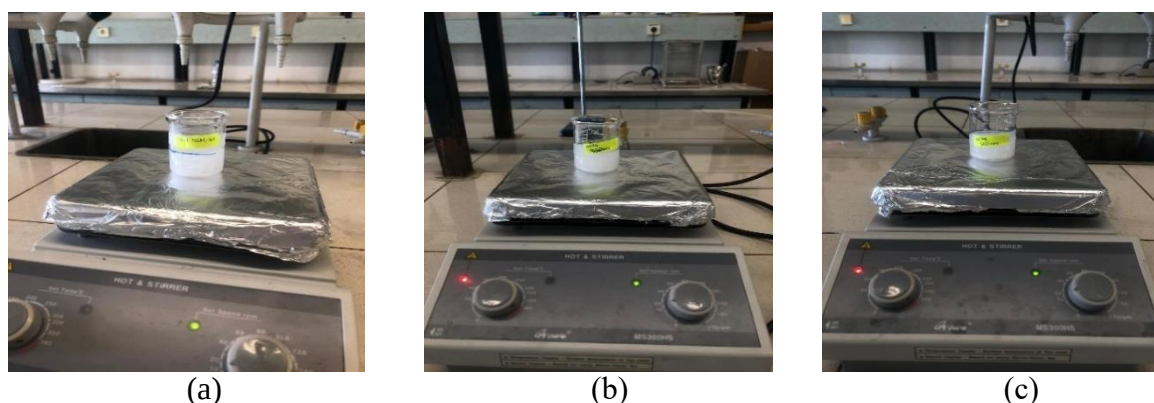


Image 4.7. Picture of the samples through hydrothermal stability test where (a) Pure MCM-41 (b) TiW-MCM-41 (c) TiA-MCM-41

The samples were filtered and left to dry at room temperature for three days. Once dry, the samples were weighed, labeled, and stored in a container. The labeling for the samples before and after the hydrothermal stability test (HT) is shown in Table 4.1.

Table 4.1. Labeling of the prepared samples before and after hydrothermal treatment

Sample description	Before HT	After HT
Pure mesoporous MCM-41	MCM-41	MCM-41-HT
Titanium-modified MCM-41 in which K_2TiF_6 dissolved in hot water	TiW-MCM-41	TiW-MCM-41- HT
Titanium-modified MCM-41 in which K_2TiF_6 dissolved in acid water	TiA-MCM-41	TiA-MCM-41-HT

4.3. Synthesis of Chromium-Based Catalyst

Chromium-based catalysts supported on titanium-doped mesoporous MCM-41 were synthesized by both the hydrothermal method and the impregnation method. The titanium loading was kept constant (2.5 wt.%), and different amount of chromium was used in the catalyst (3, 6, and 10 wt.%).

The chemicals used in the synthesis are:

- The surfactant: $C_{19}H_{42}BrN$ (N-cetyl-N, N, N-trimethyl ammonium bromide).
- Silica source: sodium silicate solution (27% by mass SiO_2 + 8% by mass Na_2O + 65% by mass H_2O).
- Solvent: deionized water.
- Titanium source: K_2TiF_6 (dipotassium titanium hexafluoride).
- Chromium source: $Cr(NO_3)_3 \cdot 9H_2O$ (chromium nitrate),
- pH adjuster: sulfuric acid (4N H_2SO_4), sodium hydroxide (1N $NaOH$).

4.3.1. Synthesis of chromium-based catalysts by the hydrothermal synthesis method

First, chromium-based catalysts supported on titanium-doped mesoporous MCM-41 (xCr/Ti-MCM-41) were synthesized by the hydrothermal method (x is the Cr content). The steps of the synthesis are shown below:

The synthesis of a Cr-based catalyst is an attempt to keep chromium content at 3 wt.% and titanium doped at 2.5 wt.% (3Cr/Ti-MCM-41).

- As a start, the Cr/Ti ratio is 1.2. The amount of chromium and titanium needed for the synthesis was determined based on that. As a result of the calculations, it was regulated that 1.024g of the chromium nitrate ($Cr(NO_3)_3 \cdot 9H_2O$) should be used, and 0.556 g of the dipotassium titanium hexafluoride (K_2TiF_6) must be used in the preparation of 3Cr/Ti-MCM-41. Calculations of the Cr/Ti ratio and the amount of Ti and Cr used are shown in Appendix 2.

- A 12.76 g of $C_{19}H_{42}BrN$ (surfactant) and 87 mL of deionized water were mixed using magnetic stirrers at a temperature of 30°C until a clear colorless mixture was obtained. As shown in Image 4.8.



Image 4.8. Photograph of the surfactant's dissolving process in the deionized water at 30 °C using a magnetic stirrer

- After that, 11.3 mL of sodium silicate solution (silica source), K_2TiF_6 (titanium source), which was dissolved in approximately 10 drops of deionized water, and $Cr(NO_3)_3 \cdot 9H_2O$ (chromium source) that was dissolved in 0.5 ml of deionized water, were all added drop wisely and alternately to the surfactant solution. Image 4.9 shows the prepared mixture.



Image 4.9. The prepared mixture

- Then the pH of the resulting mixture was adjusted to 11 by adding acid (4N H_2SO_4).
- Consequently, the mixture, which its pH was adjusted to 11, was taken into a Teflon-steel autoclave and kept in an oven at a temperature of 120°C for four days (96 hours).
- On the fourth day, the sample was taken out of the autoclave and put into a beaker. Then, deionized water was added immediately till the volume reached a total of 400 ml. The mixture was left to cool overnight. The resulting sample is shown in Image 4.10.

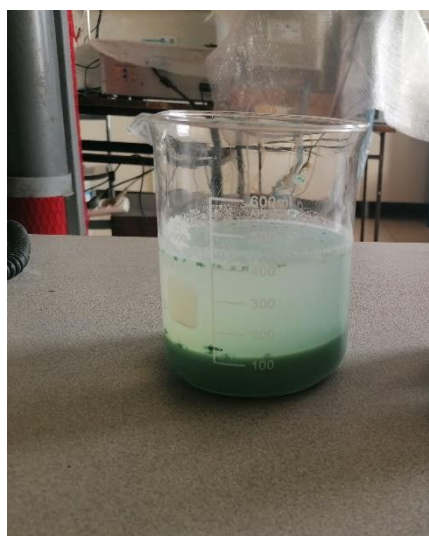


Image 4.10. Photograph of the sample removed from the autoclave after the sample volume was completed to 400 mL with deionized water

- The next day, the washing process was carried out until the pH of the sample filtrate was stabilized (pH~7).
- After the washing process, the sample was dried at room temperature for approximately 48 hours. Once dried, the sample was crushed into a powder and stored in a container.
- Once the sample drying process was complete, the obtained sample was further treated through a calcination process. To carry out the calcination process, the dried sample was placed in a quartz reactor that contained a porous sieve. The temperature was increased at a rate of 1°C per minute until it reached 600°C , where it was held for 6 hours. The entire process was conducted in a dry airflow of 130 ml/min.

The synthesis process of the 3Cr/Ti-MCM-41 catalyst is completed in three stages: hydrothermal treatment, washing, and calcination, with detailed steps shown in Figure 4.2.

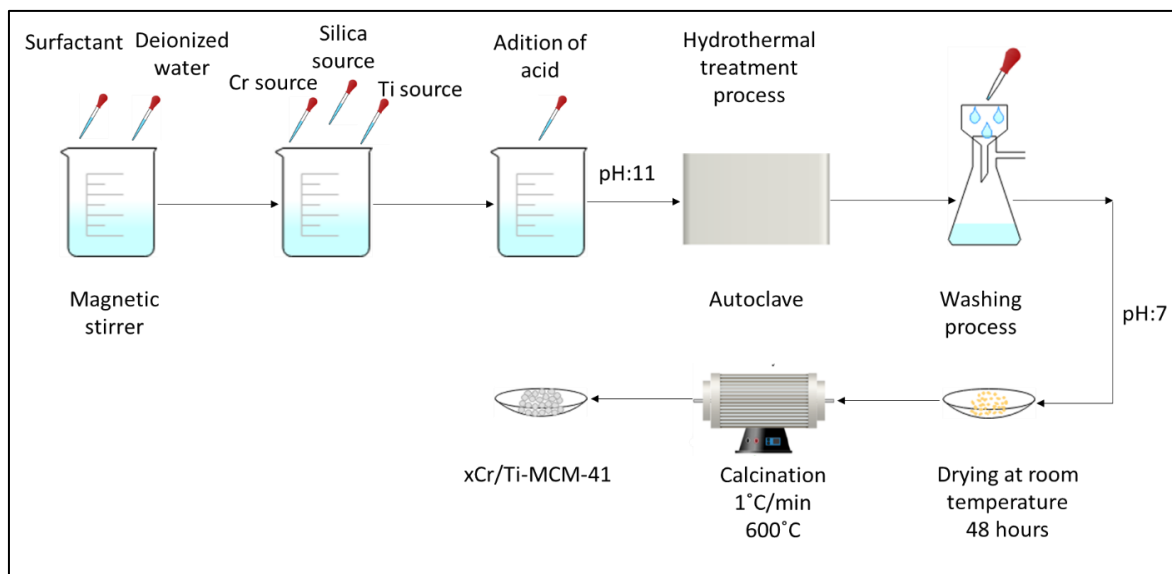


Figure 4.2. Synthesis steps of xCr/Ti-MCM-41

Similarly, catalysts containing 6% and 10% chromium by mass were prepared by hydrothermal synthesis.

In addition, a Cr-based catalyst containing 10 wt.% Cr (10Cr/MCM-41) was synthesized by the same method described above, and this catalyst's support was not modified with titanium (Ti content: 0 wt.%).

4.3.2. Synthesis of chromium-based catalysts by the impregnation synthesis method

The impregnation method was also used to synthesize a chromium-based catalyst supported on titanium-doped mesoporous MCM-41. This method involves dissolving the metal source in a solvent and then placing it within the structure of the support material, which in this case, is the TiW-MCM-41 material. Chromium metal loading on the titanium-doped mesoporous MCM-41 is 3wt.%, 6wt.%, and 10wt.% (xCr@Ti-MCM-41), where x is the Cr content.

The chemicals used in the synthesis are:

- The titanium doped MCM-41 support (TiW-MCM-41): 0.5 gram.
- Solvent: deionized water: 10 ml.
- Metal source: chromium nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$).

Next, the preparation steps of the synthesized catalysts containing 3% by mass of Cr is explained.

- To synthesize the catalyst, the required amount of chromium nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) required for the synthesis was determined. After performing the necessary calculations, it was determined that 0.12 grams of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ must be used to maintain a concentration of 3 wt.% of chromium. The calculated amount of chromium nitrate required is provided in Appendix-2.
- 0.5 g of TiW-MCM-41 material and 10 mL of deionized water were mixed in magnetic stirrers, and the mixture temperature was increased slowly to reach 40°C,
- When the mixture temperature reaches 40°C, chromium nitrate $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution was added dropwise to the solution.
- After the addition of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution, the temperature of the mixture was gradually increased to 60°C, and continued mixing until the water evaporated.
- Then, the remaining sample was scraped, placed in a container, and left to dry in an oven at 100°C for 24 hours.
- Last, the dried sample was subjected to a calcination process under the same conditions applied to the catalyst prepared by the hydrothermal synthesis method.

The synthesis steps of the $x\text{Cr}@$ Ti-MCM-41 catalyst is given in Figure 4.3.

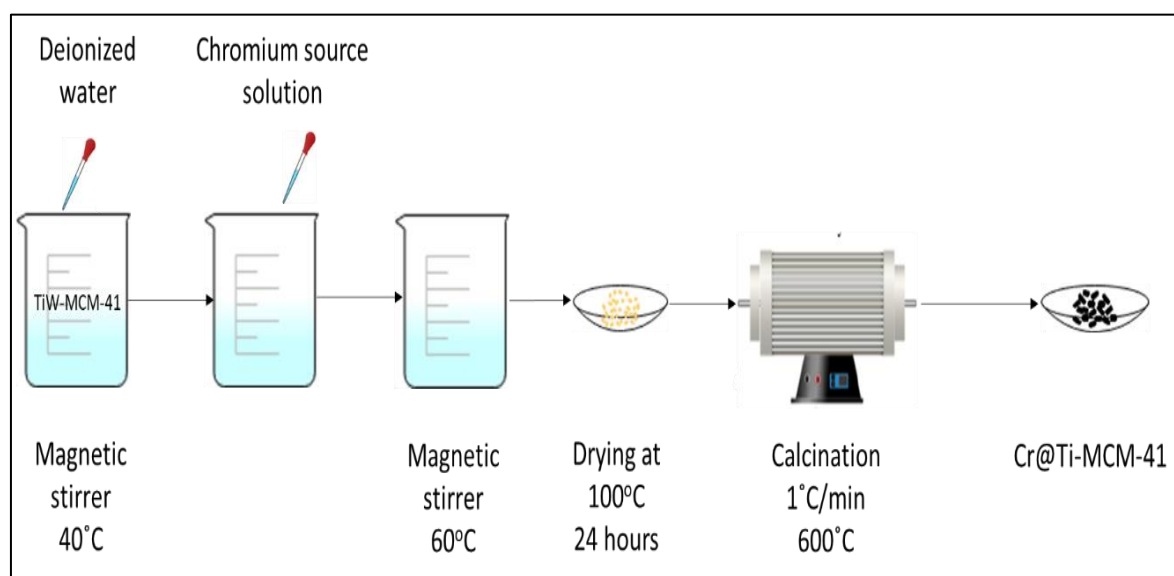


Figure 4.3. Preparation of $x\text{Cr}@$ Ti-MCM- catalysts by impregnation synthesis method

The wet impregnation synthesis steps of Cr-based catalyst for Cr content of 6 and 10wt.% are similar to those for 3wt.% Cr.

Table 4.2 displays the names of the prepared supports and catalysts.

Table 4.2. Description and coding of prepared supports and catalysts

Sample description	Sample name
Pure mesoporous MCM-41	MCM-41
Titanium-modified MCM-41 in which K_2TiF_6 dissolved in hot water (before hydrothermal stability test)	TiW-MCM-41
Titanium-modified MCM-41 in which K_2TiF_6 dissolved in acid water (before hydrothermal stability test)	TiA-MCM-41
Chromium-based catalyst supported on titanium-modified MCM-41 synthesized by hydrothermal method	xCr/Ti-MCM-41
Chromium-based catalyst supported on MCM-41 synthesized by hydrothermal method	10Cr/MCM-41
Chromium-based catalyst supported on titanium-modified MCM-41 synthesized by wet impregnation method	xCr@Ti-MCM-41

In this study, a total of six Cr-based catalysts were synthesized using the hydrothermal method and the impregnation method. It was observed that the catalysts, which were green after synthesis, turned yellow after the calcination process. The color changes due to the oxidation of chromium by the calcination process. The yellow color indicates the presence of a monochromate in the catalyst structure, and the orange color shows polychromates in the structure. The appearance of the chromium-based catalyst is given in Image 4.11.

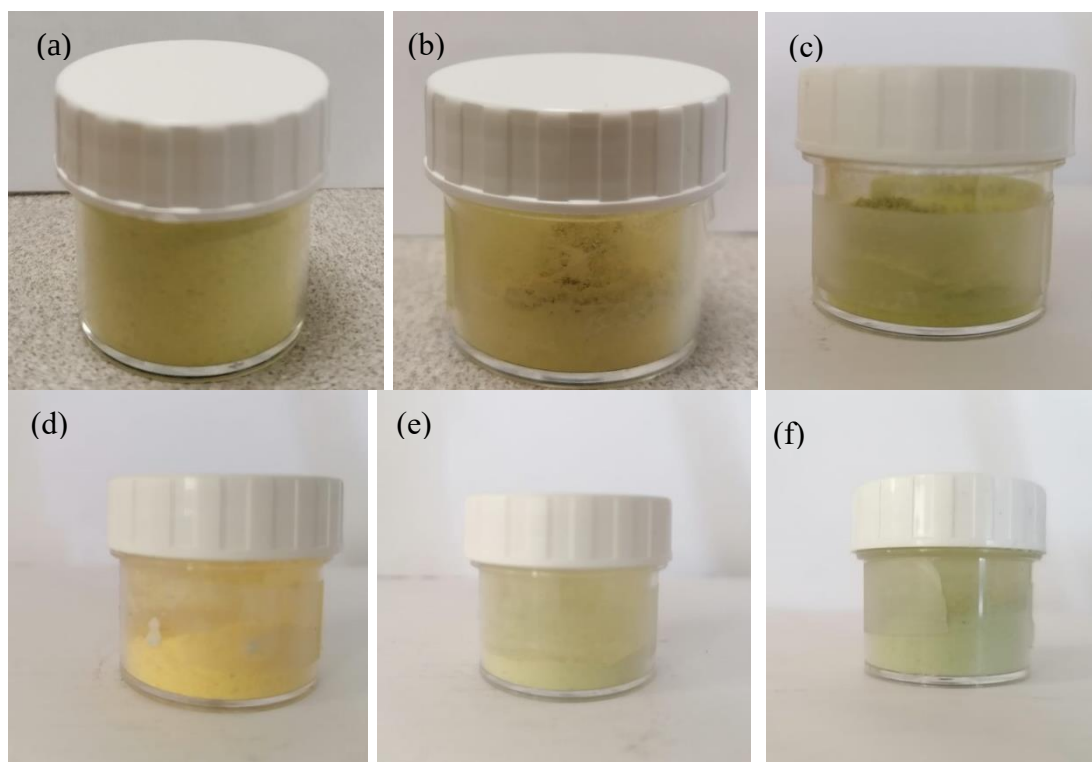


Image 4.11. Appearance of chromium-based catalysts with different chromium content, where: (a) 3Cr/Ti-MCM-41, (b) 6Cr/Ti-MCM-41, (c) 10Cr/Ti-MCM-41, (d) 3Cr@Ti-MCM-41, (e) 6Cr@Ti-MCM-41, (f) 10Cr@Ti-MCM-41

4.4. Catalytic Activity Tests

Catalytic activity tests were carried out on Cr-based catalysts for the oxidative dehydrogenation of isobutane. The tests were performed in a fixed-bed reactor at 600°C and atmospheric pressure for 120 minutes. The catalyst was placed in a quartz glass reactor (1 m long and 0.65 cm in diameter) and then installed inside the tube furnace. In all catalytic activity tests, an amount of 0.1 g of catalyst was used.

To start the experiment, the temperature of the furnace was first adjusted. Nitrogen gas was then passed through the quartz glass reactor until the desired reaction temperature was achieved. After that, the flow rates of isobutane and carbon dioxide gases were adjusted and then fed to the reactor at the same time as the cutting of the N₂ flow (which passed through the reactor). Throughout the reaction, gas samples were collected from the reactor outlet at different intervals (at 5, 10, 15, 30, 45, 60, 75, 90, 105, and 120 minutes) until the reaction was completed. At the end of the reaction time (120 min), the gas feed (isobutane and CO₂) was cut off. At the same time, N₂ gas was allowed to flow through the reactor until the reactor

temperature cooled down to 200°C. After that, the system was shut down, and the catalyst was collected the next day. Subsequently, the composition of product streams was determined by analysis of taken gas samples on a gas chromatography (GC) instrument (SRI 8610C). GC analyses were performed with 1mL sample injections. Schematic representation of the experimental setup used in oxidative dehydrogenation in carbon dioxide environment is given in Figure 4.4.

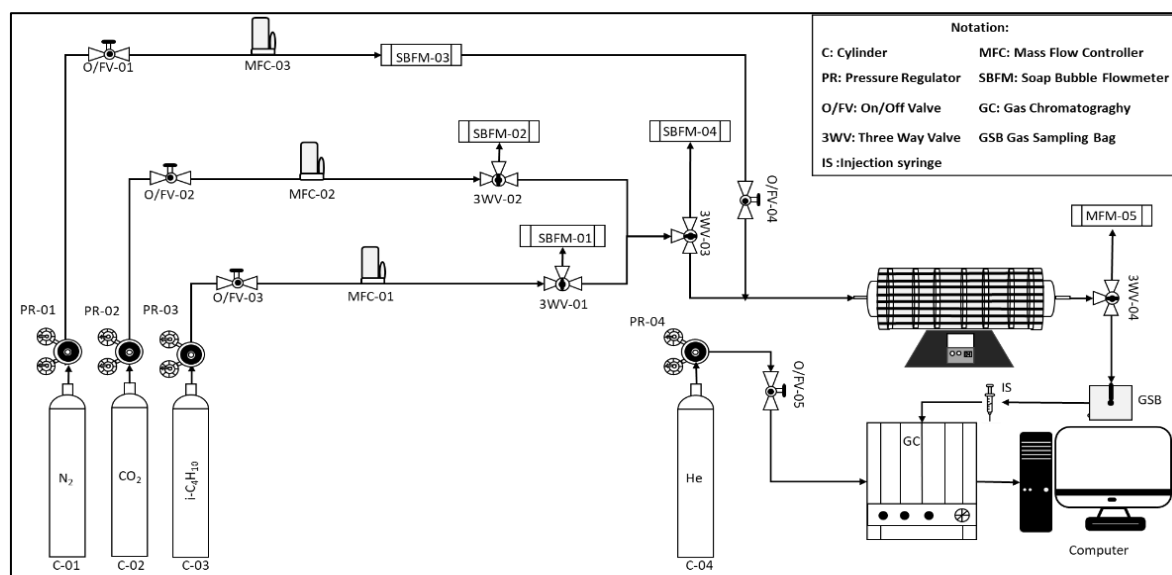


Figure 4.4. Experimental set-up for performing catalytic activity test system

Furthermore, by using the data obtained from GC analysis, isobutane conversion, and isobutene selectivity values were determined with the help of the following equations. Selectivity values of products of side reactions were also determined

$$\text{Isobutane conversion (\%)} = \frac{(i\text{-C}_4\text{H}_{10,\text{initial}} - i\text{-C}_4\text{H}_{10,\text{exit}})}{(i\text{-C}_4\text{H}_{10,\text{initial}})} \times 100 \quad (4.1)$$

$$\text{Isobutene selectivity (\%)} = \frac{(i\text{-C}_4\text{H}_8,\text{exit})}{(i\text{-C}_4\text{H}_{10,\text{initial}} - i\text{-C}_4\text{H}_{10,\text{exit}})} \times 100 \quad (4.2)$$

The catalytic activity of the 3Cr/Ti-MCM-41 catalyst was tested to determine the optimal $i\text{-C}_4\text{H}_{10}/\text{CO}_2$ molar ratio. The experiments involved testing different feed ratios of $i\text{-C}_4\text{H}_{10}$ and CO_2 (1/9 and 1/5). The total flow rate of the mixture of feed gases was 50 ml/min (WHSV=51 h⁻¹) for both experiments. The reaction was conducted at temperature 600°C and atmospheric pressure.

Additional catalytic activity tests were performed on the 10Cr/Ti-MCM-41 catalyst, which exhibited the highest catalytic activity. To thoroughly investigate the effect of weight hourly space velocity (WHSV) on conversion and selectivity over the 10Cr/Ti-MCM-41, two catalytic tests were carried out. In the first one, the total feed mass flow rate was 50 mL/min (WHSV=51 h⁻¹), while in the second one, the total feed mass flow rate was 70 mL/min (WHSV=72 h⁻¹). For both experiments, i-C₄H₁₀/CO₂ molar ratio was 1/5, temperature 600°C, and atmospheric pressure.

Catalytic tests were performed to analyze the effect of temperature change on selectivity and conversion. The catalytic tests were conducted at two different temperatures: 500°C and 600°C, with a total feed flow rate of 50 mL/min (WHSV=51 h⁻¹), i-C₄H₁₀/CO₂ molar ratio was 1/5, and under atmospheric pressure.

All catalytic tests carried out in this thesis are summarized in Table 4.3.

Table 4.3. Catalytic tests carried out in this study

Parameter Experiment	Catalyst	i-C ₄ H ₁₀ /CO ₂ molar ratio	T [°C]	P [atm]	WHSV [h ⁻¹]	Catalyst amount [g]
Optimal i-C ₄ H ₁₀ /CO ₂ molar ratio	3Cr/Ti-MCM-41	1/5 1/9	600	0.901	51	0.1
Effect of Chromium Content	3Cr/Ti-MCM-41 6Cr/Ti-MCM-41 10Cr/Ti-MCM-41 3Cr@i-MCM-41 6Cr@i-MCM-41 10Cr@Ti-MCM-41	1/5	600	0.901	51	0.1
Effect of Titanium Modification	10Cr/Ti-MCM-41 10Cr/MCM-41	1/5	600	0.901	51	0.1
Effect of Reactor temperature	10Cr/Ti-MCM-41	1/5	600 500	0.901	51	0.1
Effect of WHSV	10Cr/Ti-MCM-41	1/5	600	0.901	51 72	0.1

4.5. Development of Reaction Rate Expression

The reaction rate expression was developed on the 10Cr/Ti-MCM-41 catalyst. The kinetic measurements for oxidative dehydrogenation of isobutane with CO₂ were obtained from the catalytic tests. The apparent reaction orders were determined within the range partial pressure of 5 kPa to 20 kPa for both isobutane and CO₂. Differential reactor assumptions were considered during the development of the reaction rate expression. The reaction was

carried out in a quartz reactor with a diameter of 0.65cm and a length of 100cm at atmospheric pressure at different temperatures. A 0.05 g catalyst was utilized. The reactant mixture consists of isobutane, carbon dioxide, and helium. The gas samples were taken at the 15th minute of the experiment.

Two sets of reaction conditions were designed to obtain the reaction rate expression. In the first set of reactions, catalytic tests were carried out at different isobutane partial pressures (5, 10, 15, 20 kPa), while carbon dioxide partial pressure was kept constant at 5 kPa. In the second set of reactions, catalytic tests were performed at different CO₂ partial pressures (5,10,15,20 kPa), while i-C₄H₁₀ partial pressure was kept constant at 5 kPa.

Catalytic test conditions for the first set of reactions:

- Catalyst amount (0.05g)
- The feed composition consists of isobutane, carbon dioxide, and helium.
- Various isobutane partial pressure (5, 10, 15, and 20 kPa) and constant CO₂ partial pressure at 5 kPa.
- Temperatures: 500°C, 550°C, and 600°C.
- Reaction time :15 minutes.

The catalytic test conditions for the second set of reactions are similar to those in the first set, with the only difference being the variation of the gas feed composition.

In a multi-reaction system, determining the reaction orders for each reaction is not as straightforward as in a single-reaction case. Experimental data cannot provide direct access to these orders for each reactant. Instead, the kinetic orders for the different reactants can be calculated by examining the overall reactions and expressing them in terms of a power law kinetic formalism. The observed rate of reaction (R_A) can be expressed in terms of the following equation.

$$-R_A^* = k P_{i-C_4H_{10}}^\alpha P_{CO_2}^\beta \quad (4.3)$$

The kinetic orders for isobutane and carbon dioxide are α and β respectively. The reaction orders of isobutane were calculated from experiment data obtained from set 1 (varying

partial pressure of i-C₄H₁₀). On the other hand, the reaction orders of carbon dioxide were calculated from experiment data obtained from set 2 (varying partial pressure of CO₂).

$$-R_A^* = B P_{i-C_4H_{10}}^\alpha \quad (4.4)$$

When taking the natural logarithm of both sides of the rate equation (for set 1),

$$\ln(-R_A^*) = \ln B + \alpha \ln P_{i-C_4H_{10}} \quad (4.5)$$

$\ln(-R_A^*)$ was plotted against $\ln P_{C_4H_{10}}$, the slope gives the α . Similar steps were applied for set 2 and β was determined. Then, the reaction rate constant k value was calculated from the rate equation. After finding k value at different temperatures, activity energy (E_A) was calculated.

4.6. Characterization Studies

Catalyst characterization and analysis play a key role in catalyst development, and it is critical not only for the design and development of novel catalysts but also for process development. This section provides a detailed explanation of the XRD analysis and N₂ adsorption/desorption, SEM /EDS, and FTIR analysis used in the characterization studies.

4.6.1. XRD analysis

XRD analysis was carried out to determine the characteristic features (the structural, physical, and chemical properties) of synthesized materials. XRD analyses were performed with 0.02digit variation using CuK α radiation (wavelength 1.5406 $\text{\AA}$) in Rigaku Brand D/MAX 2200 instrument at METU Department of Metallurgical Engineering. In this term, detailed information about XRD analyses is presented below.

X-ray diffraction patterns are commonly used to determine the crystal structure and size of materials, as well as its regular pore arrangement. This technique can also provide information about the material's chemical composition and unit cell sizes. However, X-ray powder diffraction is mainly used for phase identification of crystalline materials Bragg's law is used to explain the solid structure of the X-rays of the materials, which calculates the

distances (d) between layers of materials (Epp, 2016). Figure 4.5 provides a visual representation of Bragg's law diffraction.

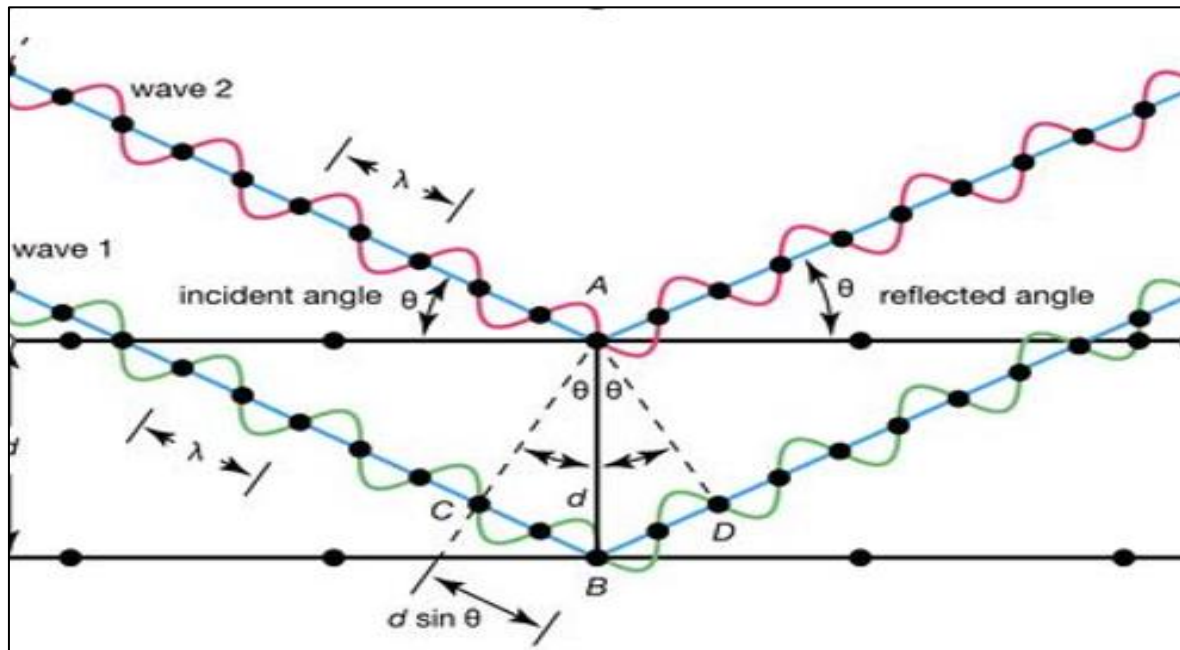


Figure 4.5. Bragg law diffraction

Bragg's law equation is given below:

$$\lambda n = 2d \sin \theta \quad (4.6)$$

Where:

λ : The wavelength of the beam used (nm)

n : A constant that depends on the instruments used to obtain X-ray diffraction patterns and the sample being analyzed (accepted as 1.0 in the interpretation of XRD patterns)

d : The distance between layers of the material (nm)

θ : reflected angle.

Bragg's law explains how the angle of a diffracted X-ray beam varies with the wavelength of the X-rays and the spacing of the atoms and molecules in the material.

XRD analysis has a great advantage in determining the phase of unknown samples. This is done by comparing the results with a relevant database and identifying the phases contained in the sample. Additionally, methods like Rietveld analysis can be used to determine the relative quantitative ratios of the compounds present in the unknown sample. The Rietveld refinement technique is used to determine the crystal structure, chemical composition, and physical properties of the sample by monitoring the intensity of X-rays refracted from the sample. The observations are based on variables like diffraction angle, polarization, wavelength, or energy.

Scherrer equation was developed in 1918, to calculate the nano-crystallite size (L) by XRD radiation of wavelength λ (nm) from measuring the full width at half maximum of peaks (β) in radian located at any 2θ in the pattern. The shape factor of n can be 0.62 - 2.08 and is usually taken as about 0.89. Scherrer equation is given below:

$$L = \lambda n / \beta \cos \theta \quad (4.7)$$

N₂ adsorption-desorption analysis

N₂ adsorption-desorption analysis determines the surface area, pore size distribution, and pore volumes of materials. N₂ adsorption-desorption analysis of the synthesized materials was obtained by using the Quantochrome Autosorp 6 Physical Adsorption Device located in the Central Laboratory of Middle East Technical University.

Prior to conducting the analysis of the materials, a de-gassing process was conducted to empty the pores at a temperature of 250°C for 2 hours. Once the de-gassing process was completed, the sample was subjected to N₂ adsorption-desorption analysis.

The specific surface area of a sample can be measured by determining the volume of gas, usually N₂, that is needed to create a monomolecular monolayer (film) using the Brunauer-Emmett-Teller (BET) method. This method is based on the physical adsorption of gas to determine the single-layer capacity. The BET equation is used to describe the relationship between the volume adsorbed at a given partial pressure and the volume adsorbed at the single-layer scope. Using the physical adsorption values, the specific surface areas of the materials can be calculated.

BET equation:

$$\frac{X}{V(1-X)} = \frac{1}{V_m \cdot C} + \frac{(C-1)X}{V_m \cdot C} \quad (4.8)$$

Where:

V: The volume of the gas adsorbed at pressure P.

V_m : The volume of gas required to form the single layer.

C: Constant of the BET equation.

$X: \frac{P}{P_0}$: relative pressure of the adsorption.

The surface area, pore size, and pore volume values of the synthesized materials were calculated using relative pressure values.

The most commonly used methods for calculating surface areas

- The single point BET surface area value is obtained from the adsorbed volume at relative pressure $P/P_0 = 0.35$.
- The multipoint BET surface area value is obtained from the adsorbed volume at the relative pressure $0.05 < P/P_0 < 0.35$.
- The Barrett-Joyner-Halenda (BJH) surface area value is obtained from the adsorbed volume at the relative pressure $P/P_0 > 0.35$.

Using the XRD main peak, and the N_2 adsorption-desorption results, the crystal size of the material can be calculated with the help of Scherrer's law. The interlayer distance value of the material (d) is determined using the Bragg law (Sing, 2001).

Scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM/EDS)

The scanning electron microscopy method is used to visualize the surface of materials while providing information about their topography, morphology, composition, and

crystallographic structure. An EDS analysis was performed to determine the amounts and distribution of metals added to the structure of the prepared catalysts. These analyses were performed using the QUANTA 400F Field Emission SEM high-resolution scanning electron microscope instrument at the Central Laboratory of Middle East Technical University.

The SEM/EDS technique operates on the principle of directing an electron beam onto the sample, where interactions result in backscattered electrons and secondary electrons being emitted from the sample surface. These emitted electrons are then converted into images. The interaction of primary electrons with the sample's atoms induces orbital transitions that result in the emission of characteristic X-rays. These X-rays possess energy signatures specific to the elements present in the sample. EDS (Energy Dispersive X-ray Spectroscopy) detects and measures the energy of these X-rays to perform elemental analysis. This technique provides rapid qualitative and quantitative analysis of the elemental composition within a depth of 1-2 microns. Additionally, X-rays can be used to generate elemental distribution maps or line profiles on the sample surface, offering a detailed spatial analysis of the elemental composition (Abd Mutalib et al., 2017).

Fourier transform infrared spectroscopy (FTIR)

FTIR (Fourier transform infrared spectroscopy) analysis was conducted on the synthesized materials to identify their functional groups. The analysis was carried out using a Jasco Fourier Transform Infrared Spectroscopy device in the Laboratory of the Department of Chemical Engineering, Gazi University.

FTIR is an analytical technique widely used for identifying both inorganic and especially organic materials. Through FTIR analysis, an absorption spectrum is obtained, providing detailed information about the molecular structure and chemical bonds within the material. This analysis is based on the characteristic vibrational frequencies of chemical bonds and bond groups. When a molecule is exposed to infrared radiation, it absorbs energy at frequencies characteristic of its molecular structure. During FTIR analysis, an infrared beam is directed at the sample, and the absorption and reflection of infrared radiation at various frequencies are measured. The resulting IR absorption spectrum, composed of inverted peaks, reflects these interactions. The FTIR spectrum obtained is then analyzed and compared with known reference spectra from the FTIR library to identify the material's

molecular structure and chemical composition accurately. This comparative analysis ensures precise identification of the functional groups and bonds present in the sample(Giraldo and Marin, 2025).

5. RESULTS AND DISCUSSION

In this study, equilibrium calculations were performed for the oxidative dehydrogenation of isobutane with CO₂. The variation of isobutane equilibrium conversion values with temperature at different *i*-C₄H₁₀/CO₂ ratios (mol/mol) under atmospheric pressure were estimated. Also, pure MCM-41 and titanium-modified MCM-41 materials were synthesized using hydrothermal synthesis method. The effect of Ti addition on the hydrothermal stability of MCM-41 was investigated by applying hydrothermal stability test. The synthesized materials were characterized before and after hydrothermal stability test. Chromium-based catalysts supported on titanium-modified MCM-41 were synthesized and characterized. The catalytic activity of the synthesized Cr-based catalysts was investigated. Catalytic activity test was also carried out with Cr-based catalyst supported on pure MCM-41 to assist the effect of titanium addition on the activity of Cr-based catalysts. In addition, reaction rate expression was developed over the selected catalyst followed by reactor modeling studies. All the results and discussion of the carried out studies are presented in this section.

5.1. Equilibrium Calculations

The equilibrium calculations were carried out for the isobutane oxidative dehydrogenation reaction.

Isobutane oxidative dehydrogenation occurs according to the following equation.



Reaction 1 represents the direct dehydrogenation reaction, reaction 2 states the water gas shift reaction (WGSR), and reaction 3 clarifies the oxidative dehydrogenation reaction of isobutane. As noted, the summation of reactions 1 and 2 led to reaction 3. According to the reaction pathways, reaction 3 is considered a one-step reaction pathway, while reactions 1 and 2 are taken as a two-step reaction pathway.

Equilibrium calculations for the isobutane oxidative dehydrogenation (i-BOD) reaction were performed, considering the chemical reaction pathways. The first method involved calculating the equilibrium conversion through mathematical equations, while the second method utilized the GASEQ program. The data and equations used in calculations are given in Appendix-3.

Variation of heat capacity (kJ/mol.K) with temperature was obtained as following "(5.1)".

$$\Delta C_{p_{rxn}} = 45.033 \times 10^{-3} - 11.0312 \times 10^{-5} \times T + 6.6932 \times 10^{-8} \times T^2 - 12.696 \times 10^{-12} \times T^3 \quad (5.1)$$

The temperature dependence of the reaction enthalpy (kJ/mol) was determined as following "Eq. (5.2)".

$$\Delta H_T = 149 + 45 \times 10^{-3} \times T - 05.52 \times 10^{-5} \times T^2 + 2.23 \times 10^{-8} \times T^3 - 3.17 \times 10^{-12} \times T^4 \quad (5.2)$$

The temperature dependence of the equilibrium constant was calculated

The temperature dependence of the equilibrium constant was calculated using the Van 't Hoff equation, which relates the equilibrium constant (K_e) of a chemical reaction to the temperature (T) based on the standard enthalpy change (ΔH_T) of the reaction. The resulting equation is provided below.

$$\ln K_e = -17944,69 \ T^{-1} + 5417.18 \times 10^{-3} \times \ln T - 663.5 \times 10^{-5} T + 134.19 \times 10^{-8} \times T^2 - 127.270 \times 10^{-12} \times T^3 - 12 \quad (5.3)$$

K_e values determined at some temperatures are given in Table 5.1.

Table 5.1. K_e values determined at some temperatures (i-C₄H₁₀/CO₂: 1, P: atmospheric)

T (K)	K_e
773	2.4×10^{-2}
823	1.1×10^{-1}
873	4.2×10^{-1}
923	1.37
973	3.96

After determining the equilibrium constant values at different temperatures, the equilibrium conversion of isobutane was calculated. The calculations were conducted for different $i\text{-C}_4\text{H}_{10}/\text{CO}_2$ ratio (mol/mol) at a range of temperature from 300 to 1000 K under atmospheric pressure.

In addition to that, equilibrium calculations for the isobutane oxidative dehydrogenation reaction based on the one-step reaction pathway were also accomplished by the GASEQ program. The results for the equilibrium conversion of isobutane were shown in Figure 5.1.

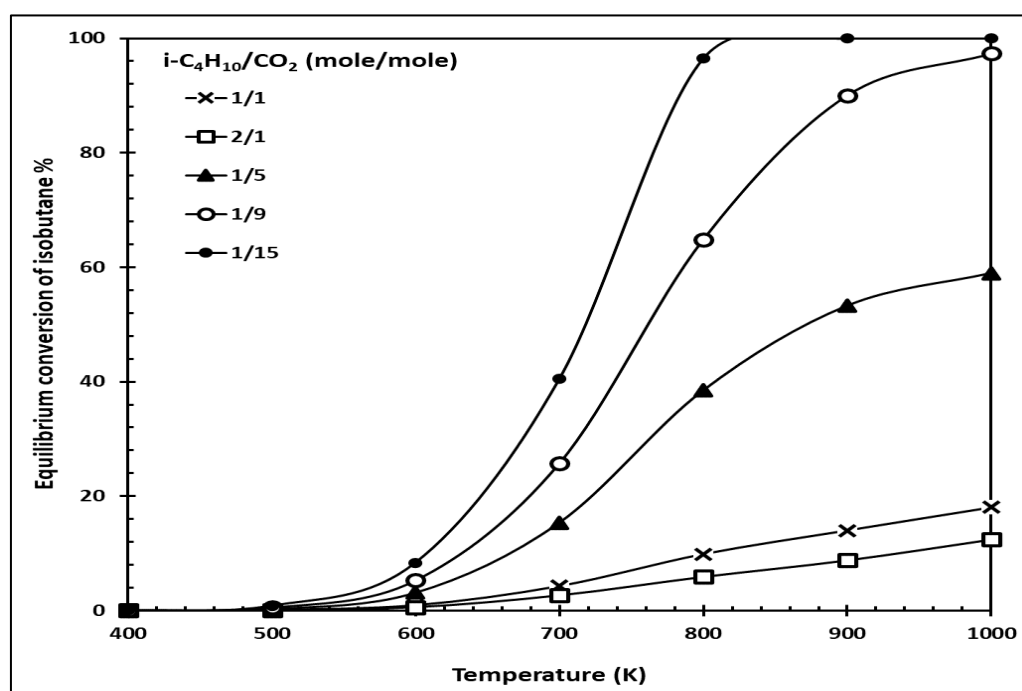


Figure 5.1. Variation of isobutane equilibrium conversion with temperatures at different $i\text{-C}_4\text{H}_{10}/\text{CO}_2$ ratio molar based on one-step pathway (P: 1 atm)

The equilibrium conversion values of isobutane under different $i\text{-C}_4\text{H}_{10}/\text{CO}_2$ molar ratios were analysed, according to the results, the value of the equilibrium conversion of isobutane that calculated by using mathematical equations are typically matches the results found in the calculation carried out by GASEQ program. Table 5.2 shows the equilibrium conversion X_{Ae} values obtained using mathematical equations and accomplished by the GASEQ program at different temperatures.

Table 5.2. Equilibrium conversion X_{Ae} values obtained by different calculation methods (i-C₄H₁₀/CO₂ molar ratio: 1, P: 1 atm)

Temperature (K)	X_{Ae} % by calculations	X_{Ae} % by GASEQ program
700	3.8	4.2
800	10	9.8
900	15	14
1000	20	18

By examining the results for the equilibrium conversion, it can be noted that increasing the number of moles of isobutane in the feed affected the equilibrium. It was observed that the when the molar ratio of i-C₄H₁₀/CO₂ was 2/1 the conversion decreases by 35% in comparison to the conversion value when the i-C₄H₁₀/CO₂ molar ratio was 1 at the same temperature of 900 K. That means increasing the number of moles of isobutane in the feed shifts the equilibrium of isobutane oxidative dehydrogenation reaction toward reactants.

The data also shows that increasing the number of moles of CO₂ in the feed had a positive effect on the equilibrium. The results reveal that, at a temperature of 900 K, when i-C₄H₁₀/CO₂ molar ratios are 1/5, 1/9, and 1/15, isobutane conversion values were 53.25%, 97.90 %, and 99.99%, respectively. This indicates that increasing the number of moles of CO₂ shifts the equilibrium of the isobutane oxidative dehydrogenation reaction into completion.

Although CO₂ is a good source of oxygen, unfortunately, it also has disadvantages; when CO₂ is adsorbed to the catalyst surface, the surface acidity increases, which leads to undesirable side reactions. Besides that, when CO₂ is adsorbed to the catalyst surface, the adsorption of the alkanes becomes difficult. That is why, the increasing of CO₂ in the feed is preferred to be limited to some extent (Ansari and Park, 2012; Mukherjee et al., 2016). Based on that, an i-C₄H₁₀/CO₂ molar ratio of 1/15 was excluded.

5.2. Characterization Results of Pure MCM-41 and Titanium-modified MCM-41

It is aimed to investigate the effect of Ti loading into MCM-41 structure on the hydrothermal stability of the material, therefore, hydrothermal stability tests were performed. Results of the characterization studies before and after the tests are presented in this section.

5.2.1. Before hydrothermal stability tests

Pure MCM-41, and titanium-modified MCM-41 were characterized by the XRD analyzer. Figure 5.2 shows the XRD patterns for pure MCM-41, TiW-MCM-41 and TiA-MCM-41 before the hydrothermal stability test.

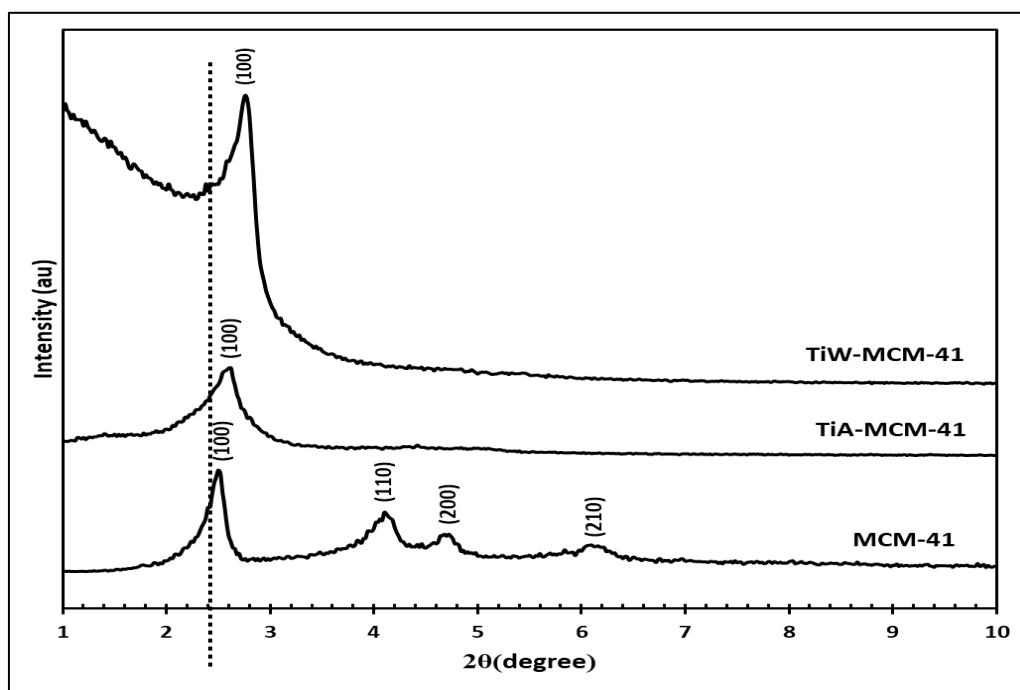


Figure 5.2. XRD patterns for pure MCM-41, TiW-MCM-41, and TiA-MCM-41 materials

In the performed studies, the XRD pattern for the MCM-41 shows 4 peaks in the range between 1° and 10° (where the Bragg angle was 2θ). The XRD data obtained for the pure MCM-41 basically matches the literature (Kılıçarslan et al., 2013). The XRD pattern of titanium-modified MCM-41 materials were investigated as well to identify the effect of titanium loading on the MCM-41 support structure. For TiW-MCM-41, the XRD shows that only one peak was detected at 2.76° . For TiA-MCM-41 only one peak was detected at 2.56° . Likening these results to pure MCM-41 XRD patterns, it was found that the detected peak for TiW-MCM-41 and TiA-MCM-41 shifts to the right. The fact that the main peak characterizing of MCM-41 is still present after titanium modification indicates that the hexagonal structure of MCM-41 is preserved.

In addition, structural features of the analyzed materials (Distance between layers (d), crystallite size (L), and pore wall thickness δ) were calculated. All the calculations are in

Appendix-3. Table 5.3 gives the corresponding structural characteristics properties of the prepared samples.

Table 5.3. Structural characteristics of the prepared materials

Sample	d, Å	δ , Å	L, Å
Pure MCM-41	28.0	12.9	-
TiW-MCM-41	32.0	15.0	177.9
TiA-MCM-41	34.5	17.9	203.8

When the obtained data were compared with the literature data, it was seen that the mesoporous MCM-41 material was successfully synthesized. It was also noted that the distance between layers (d), increased when Ti was added to the structure of MCM-41. The distance between layers calculated for titanium-modified MCM-41 matched the literature (Al-Awadi et al., 2019). It was also seen that titanium-modified MCM-41 has higher pore wall thickness (δ) compared to the unmodified MCM-41. This means the presence of titanium species supported the pores of the structure. The crystallite size (L) for TiA-MCM-41 is bigger than TiW-MCM-41, according to the literature materials with high crystallite size are not preferred due to the presence of species blocking the pores of the structure (Niphadkar et al., 2014).

N₂ adsorption-desorption isotherms and pore size distribution of pure MCM-41 and titanium-modified MCM-41 supports are expressed graphically. Surface area, pore volume, and pore diameter of the materials were also obtained by N₂ adsorption-desorption analysis data.

The N₂ adsorption-desorption isotherms are given in Figure 5.3.

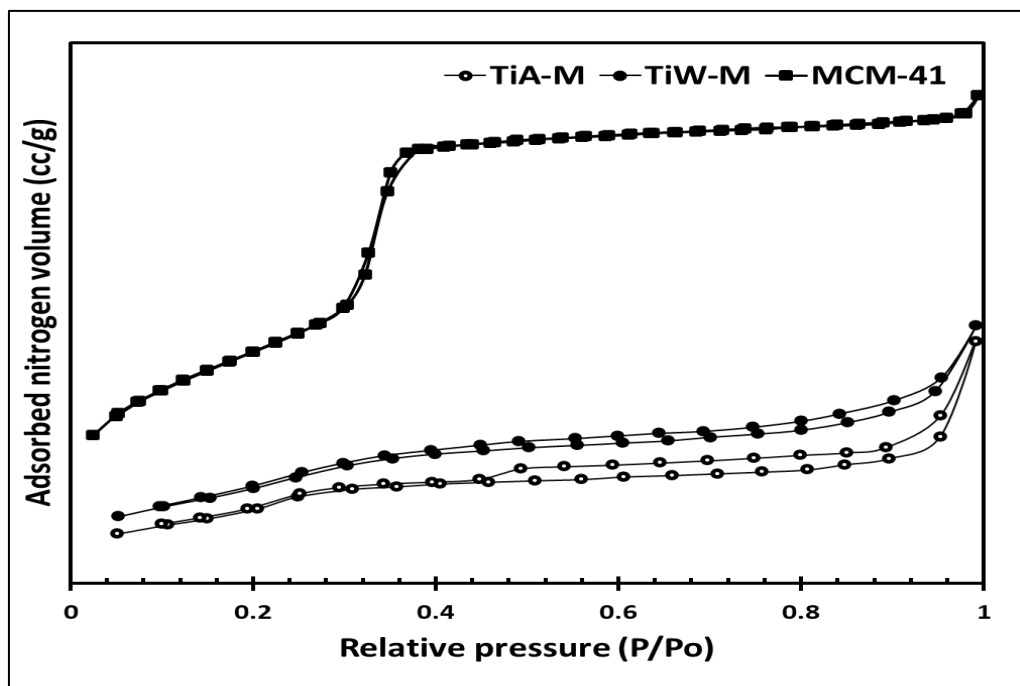


Figure 5.3. N₂ adsorption-desorption isotherms of MCM-41 and titanium-modified MCM-41 materials

It was determined that the N₂ adsorption-desorption isotherms of the titanium-modified MCM-41 were compatible with Type IV. and Hysteresis I according to IUPAC classification. Type IV isotherm shows that supports are in the mesoporous structure, Hysteresis 1 (H1- type according to IUPAC) shows that the formed structure is quite regular, homogeneous and the pore sizes are narrow (Sotomayor et al., 2018; Thommes et al., 2015).

When the isotherm given in Figure 5.3 was examined, monolayer adsorption of nitrogen molecules occurred on the titanium-modified MCM-41 surface at low relative pressure values ($P/P_0 < 0.2$). As the relative pressure increases, hysteresis formation and an increase in adsorption volume after 0.1 indicate the capillary condensation inside the mesoporous (Al-Awadi et al., 2019). Also, it was noted that when the relative pressure approached 1, the mesoporous were completely saturated, and the macropores were partially saturated.

Researchers often use the desorption branch to determine pore size distribution due to its aesthetic appeal and connection to the equilibrium phase transition during pore condensation. Desorption typically results in an abrupt emptying of mesoporous, in which produces a narrower pore size distribution (Dudek, 2016; Gregg et al., 1967; Villarroel-Rocha et al., 2014). However, some researchers argue in favor of using the adsorption branch

to obtain the complete pore size distribution, including information on neck sizes that play a role during desorption (Kruk et al., 1999; Sing and Williams, 2004; Sotomayor et al., 2018; Thommes et al., 2015). In this study, adsorption data was used to determine pore size distribution, as shown in Figure 5.4.

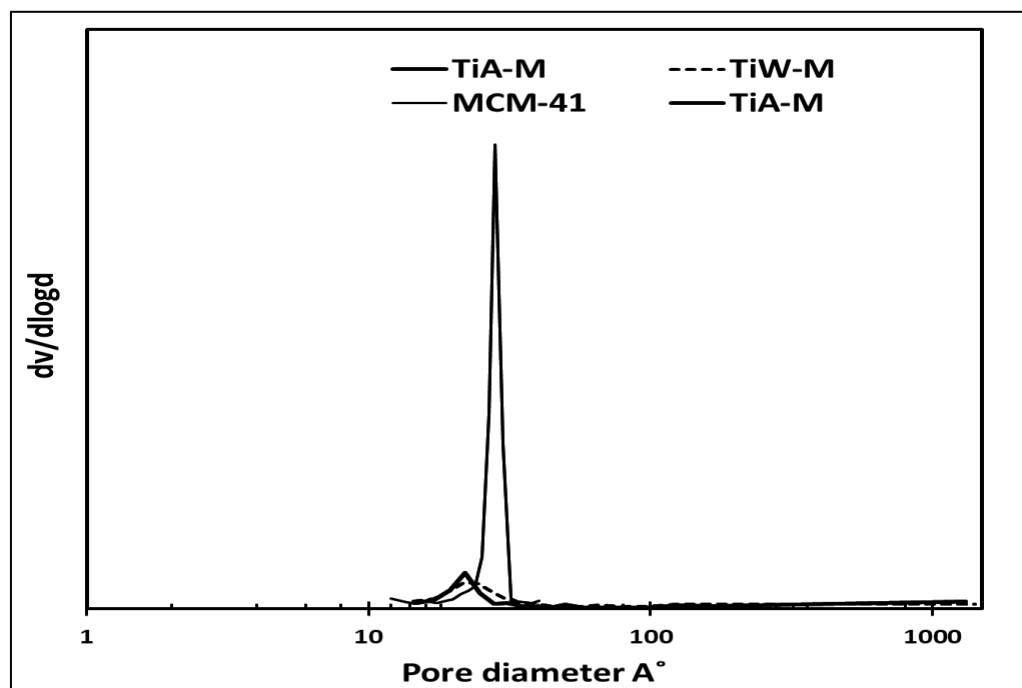


Figure 5.4. Pore size distribution of MCM-41, TiW-MCM-41 and TiA-MCM-41 materials

Figure 5.4 shows that the synthesized titanium-modified MCM-41 has pores within the 20-500 Å range, confirming its mesoporous nature. Also, the presence of sharp, narrow peak indicates uniform pore structure of the synthesized titanium-modified MCM-41. This aligns with the characteristics of MCM-41, which is known for its ordered mesoporous structure (Sing et al., 2002).

The structural and physical properties of the prepared MCM-41 and titanium-modified MCM-41 support materials obtained by N₂ adsorption-desorption analysis are given in Table 5.4.

Table 5.4. Physical properties of the prepared titanium-modified MCM-41 materials

Sample	S_{BET} m^2/g	Pore volume (BJH) cm^3/g	Pore diameter $\text{\AA}$
Pure MCM-41	1250	1.2	28
TiW-MCM-41	554	0.59	22
TiA-MCM-41	473	0.57	22

The N_2 adsorption-desorption isotherms show that all samples have significantly high pore volumes and BET-specific surface areas (S_{BET}). The MCM-41 mesoporous silica shows high BET surface area ($1250 \text{ m}^2/\text{g}$) and a very narrow size distribution, centered at $28 \text{ \AA}$ (Kılıçarslan et al., 2013). The BET surface area and pore volume of the TiW-MCM-41 was found to be $554 \text{ m}^2/\text{g}$ and $0.59 \text{ cm}^3/\text{g}$, respectively. Also, for TiA-MCM-41, the BET surface area was specified as $473 \text{ m}^2/\text{g}$, and the mean pore volume was determined as $0.57 \text{ cm}^3/\text{g}$. The average mesoporous diameter of TiW-MCM-41 and TiA-MCM-41 was found to be identical ($22 \text{ \AA}$).

The results presented that for pure MCM-41 catalyst, the values of calculated surface area (m^2/g), pore volume (cm^3/g), and pore diameter ($\text{\AA}$) typically match the literature reviews (López Pérez et al., 2016). Both titanium-modified MCM-41 supports, in comparison with MCM-41, exhibit a decrease in the values of surface area and pore volume. This can be associated with the presence of highly dispersed titania species and bigger size TiO_2 particles that could be blocking the pores of the structure. All N_2 adsorption-desorption isotherm data are provided in Appendix-4.

In a research carried out by Gil et al., they prepared the TiO_2 -MCM-41 using colloidal TiO_2 nanoparticles as the titanium source. For Ti loading of 4.8wt.%, BET area was $1085 \text{ m}^2/\text{g}$; pore volume was $0.58 \text{ cm}^3/\text{g}$, and the pore diameter was 3.0 nm . Taking those data in comparison to data optioned from Table 5.4, it can clearly be seen that the BET area is for TiW-MCM-41 and TiA-MCM-41 is almost 50% less than TiO_2 -MCM-41, also the pore diameter for TiO_2 -MCM-41 is bigger than TiW-MCM-41 and TiA-MCM-41, this can be on account of preparation method and silica and titanium source used. Also, it is found that the pore volume of TiO_2 -MCM41 is all similar to TiW-MCM-41 and TiA-MCM-41 (Gil et al., 2012).

In the study by Clercq et al., it was found that the pore volume (cm^3/g) for the $\text{TiO}_2/\text{MCM-41}$ decreased from 0.59 to 0.55 as the TiO_2 loading increased from 1wt% to 5wt% (De Clercq et al., 2018). According to the paper published by Niphadkar et al., a decrease in band gap energy was observed with the increase in TiO_2 loading, this may be caused by an increase in TiO_2 crystallite size. Therefore, a smaller crystallite size is preferred. The smaller crystallite size at lower TiO_2 loading may be attributed to higher surface area of MCM-41, which prevents agglomeration of particles and leads to uniform dispersion of smaller-size titanium crystals (Niphadkar et al., 2014).

As a result of the data obtained from XRD, and N_2 adsorption-desorption characterization studies, there is no major difference in structural and physical properties of the prepared titanium-modified MCM-41 materials. However, TiW-MCM-41 support is preferable because it has a lower crystallite size and higher surface area.

The TiW-MCM-41 was selected to be used in the synthesis of Cr-based catalysts. Therefore, the sample was analyzed by FTIR spectrum. The Fourier transform infrared (FTIR) spectrum of the synthesized TiW-MCM-41 material is given in Figure 5.5.

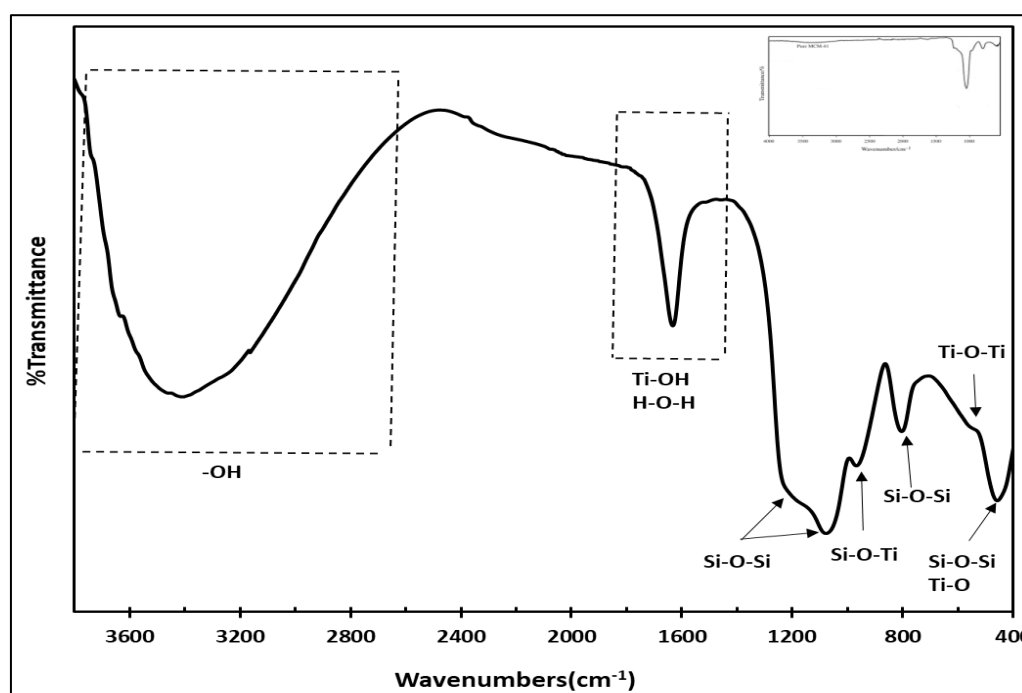


Figure 5.5. FTIR spectra of TiW-MCM-41 material

The 3440 cm^{-1} band is associated with the presence of hydroxyl groups (-OH) on the framework. The band at a range of 1645 cm^{-1} corresponds to bending vibrations of the Ti-OH and H-O-H. The band within the $1000\text{--}1245\text{ cm}^{-1}$ range is assigned to the presence of Si-O-Si bonds, which are inherent to the siliceous structure and serve as a distinctive characteristic. The band at 800 cm^{-1} is also related to the bending vibrations of the Si-O-Si groups. The presence of the 960 cm^{-1} band in the materials is associated with the isomorphic substitution of Si by Ti ions and is attributed to the stresses of the Si-O-Ti polar bonds (Roy et al., 2018; Wróblewska et al., 2019). The absorption peak at 690 cm^{-1} is associated with the infrared vibrations of Ti-O in the anatase phase (Talati et al., 2016). The bands at 455 cm^{-1} are ascribed to the bending vibrations of the Si-O-Si groups and Ti-O metal oxides.

5.2.2. After hydrothermal stability tests

After the hydrothermal stability test was performed, the samples were weighted to measure the dissolution. The sample dissolution was quantified using the weight difference, as shown in Table 5.5.

Table 5.5. Sample dissolution data after the hydrothermal stability test

Sample	Sample dissolution %
MCM-41-HT	46%
TiW-MCM-41-HT	5%
TiA-MCM-41-HT	6%

According to sample dissolution data, pure MCM-41 suffered from the largest dissolution about 46% of the material was gone by the end of the test, while for TiW-MCM-41-HT, and TiA-MCM-41-HT the dissolution was 5% and 6%, respectively. To inquire whether the dissolution data of the samples is related to the stability of the prepared material, XRD characterization analysis were conducted.

Figure 5.6 shows the XRD patterns for pure MCM-41, TiW-MCM-41, and TiA-MCM-41 after hydrothermal stability test.

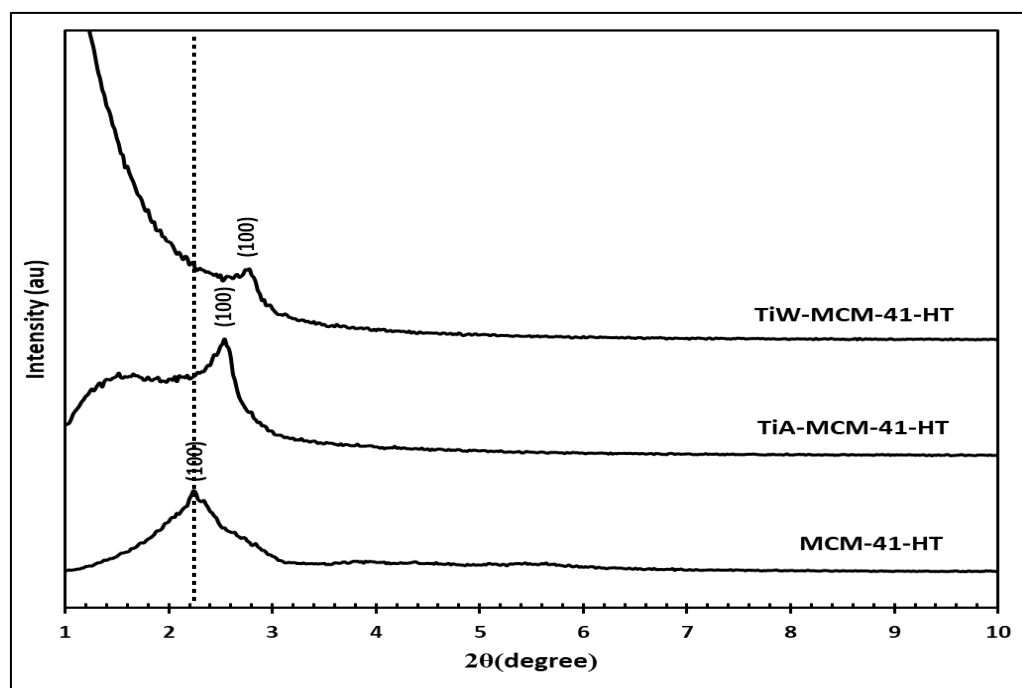


Figure 5.6. XRD patterns for pure MCM-41, TiW-MCM-41, and TiA-MCM-41 materials after hydrothermal stability test

When analyzing the data for pure MCM-41 material, after being subjected to the hydrothermal stability test (MCM-41-HT), all the characterization peaks between 3° - 7° were lost, and only the main peak was preserved at 2.20° . This means, the hexagonal structure of the MCM-41-HT was not completely lost.

It can be seen from Figure 5.6, that both TiW-MCM-41-HT and TiA-MCM-41-HT have the main characteristic peak, which means hexagonal structure is still preserved.

The characterization results demonstrate that the addition of titanium increases the hydrothermal stability of the MCM-41, improves the resistance to collapse, and helps maintain the ordered mesoporous structure of MCM-41. This can be explained by the type of bonds that assist with each material. It is well known that pure MCM-41 contains Si-O-Si bonds in its structure, forming a highly ordered mesoporous structure that can collapse under hydrothermal conditions. titanium-modified MCM-41 is different from pure MCM-41 because it contains Ti-O-Si and Ti-OH bonds. These bonds are a result of the incorporation of titanium into the material. When applying a hydrothermal stability test with water, it is thought that the interaction of Ti-OH bonds is deferred from the Si-O-Si bonds. In their recaches, Liu et al. and López et al. confirmed that when Si-O-Si bonds interact with

water, the capillary occurs in the pores, which causes structural damage.(Liu et al., 2023) . In contrast, the presence of Si-O-Ti bonds effectively prevents MCM-41 walls of sinterization when subjected to hydrothermal condition (Gaidau et al., 2017; López Pérez et al., 2016). Titanium is capable of creating strong bonds with oxygen atoms (Ti-OH and Ti-O). These bonds play a crucial role in stabilizing the titanium-modified MCM-41 structure, making it highly resistant to structural changes, even in the presence of water at high temperatures (Bourikas et al., 2014). According to literature, Ti-OH and Ti-O bonds are stronger than Si-O-Si. This could contribute to the higher hydrothermal stability observed in titanium-modified MCM-41. The study results showed that the modification of the MCM-41 with Ti to be used in oxidative dehydrogenation is necessary.

5.3. Characterization Studies for Cr-Based Catalysts

The Cr-based catalysts supported on titanium-modified MCM-41, containing 3%, 6%, and 10% Cr by mass, and Ti loading was kept at 2.5wt.%, were prepared by wet impregnation and hydrothermal synthesis methods. Characterization studies of the prepared catalysts were carried out with catalysts containing 3% and 10% Cr by mass.

The XRD patterns of the synthesized Cr-based catalysts prepared by impregnation and hydrothermal synthesis methods are presented in Figure 5.7 and Figure 5.8. The analysis was conducted in the range of 20-80° (wide-angle XRD).

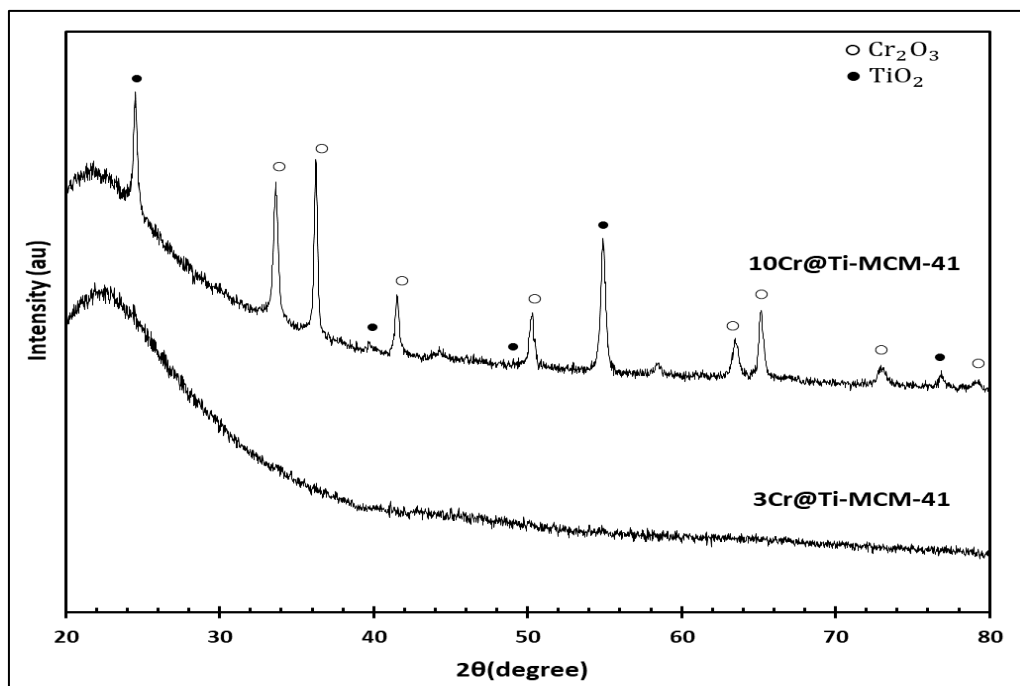


Figure 5.7. XRD patterns of Cr-based catalysts synthesized by impregnation method

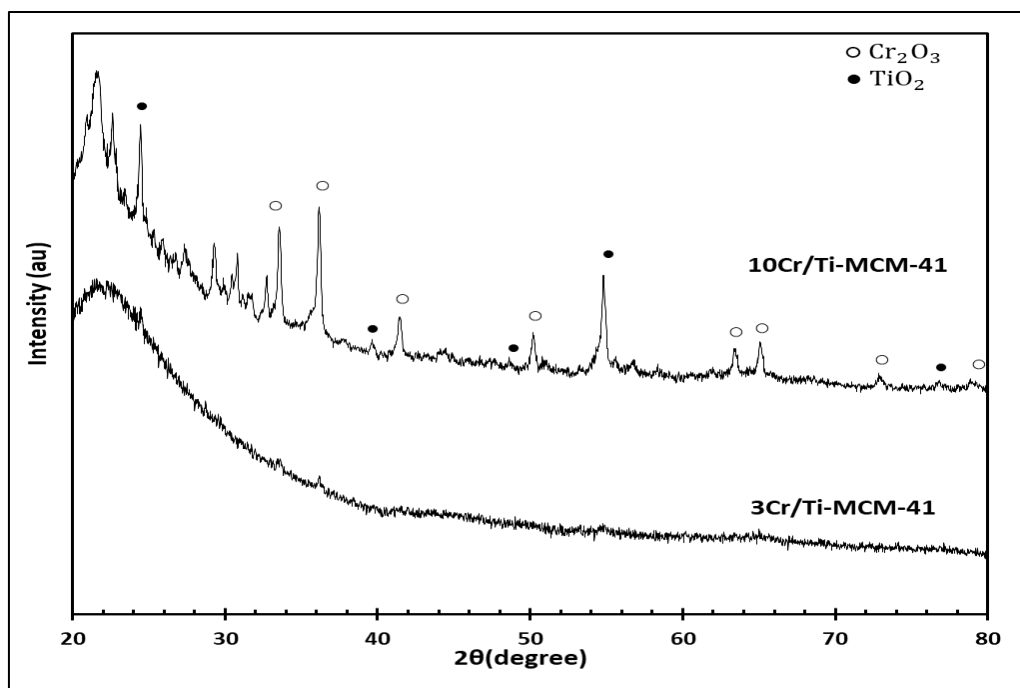


Figure 5.8. XRD patterns of Cr-based catalysts synthesized by hydrothermal method

When examining the XRD patterns of the catalysts, a wider peak was observed in all Cr-based catalysts at $2\theta = 22^\circ$, which is a distinctive feature of amorphous silica structure. No peaks corresponding to chromium oxides were observed on the wide-angle XRD patterns of 3Cr/Ti-MCM-41 and 3Cr@Ti-MCM-41, corresponding to the lower Cr content. This fact

could indicate that CrOx particles, are too small to be detected by XRD and well dispersed. These observations are in consistent with the findings reported by Elías et al. (2012), they found that samples with low Cr loading exhibited a thickening of the pore walls after Ti loading, which indicates the diffusion of Ti species inside the mesoporous channels, this diffusion was facilitated by the high dispersion of Cr^{6+} ions and the absence of $\alpha\text{-Cr}_2\text{O}_3$ particles (Elías et al., 2012),

As proven by the XRD results in Figure 5.7, nine peaks (at 2θ : 33.574° , 36.193° , 41.505° , 50.233° , 58.46° , 63.43° , 65.09° , 72.79° , and 79.1°) were observed in the pattern of 10Cr@Ti-MCM-41, which indexed to crystal rhombohedral $\alpha\text{-Cr}_2\text{O}_3$ phase (JCPDS 00-006-0504). Also, from the reference patterns, the peaks at $2\theta = 24.448^\circ$, 39.62° , 54.811 , and 76.83° indexes the TiO_2 anatase phase (JCPDS No.21–1272).

As shown in Figure 5.8, peaks at 2θ : 33.534° , 35.58° , 36.17° , 41.393° , 49.79° , 50.18° , 56.8° , 63.378° , 65.075° and 79.85° , corresponded to the diffraction rhombohedral $\alpha\text{-Cr}_2\text{O}_3$ (JCPDS 00-006-0504), and the peaks at $2\theta = 24.481^\circ$, 39.62° , 54.8° , and 68.19° indexes phase of TiO_2 anatase (JCPDS No.21–1272) were detected for 10Cr/Ti-MCM-41.

Figure 5.9 displays the XRD patterns of 10wt.% Cr-based catalysts synthesized by impregnation and hydrothermal methods.

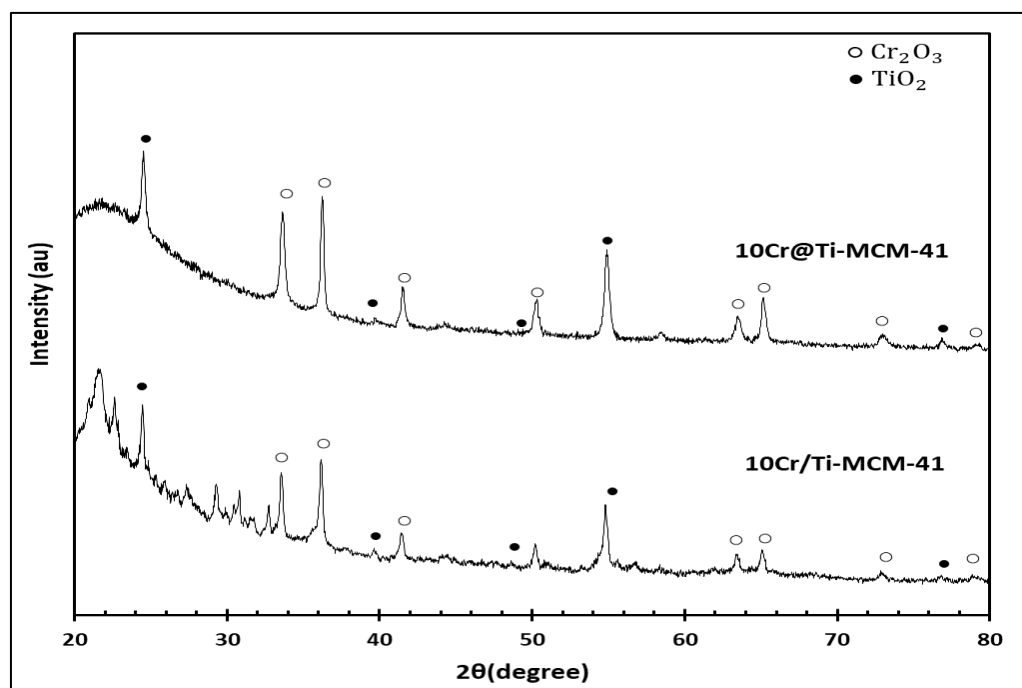


Figure 5.9. XRD patterns of 10Cr@Ti-MCM-41 and 10Cr/Ti-MCM41 catalysts

When comparing the XRD patterns of 10Cr@Ti-MCM4 and 10Cr/Ti-MCM41, the formation of the anatase phase of TiO_2 and $\alpha\text{-Cr}_2\text{O}_3$ were observed for both catalysts. Also, it was found that the intensity of diffraction peaks for titania in 10Cr/Ti-MCM41 catalysts were weaker than 10Cr@Ti-MCM41. Table 5.6 shows the structural properties of the catalysts.

Table 5.6. Structural properties of the prepared catalysts

Catalyst	d(Å)	L (Å)Cr	L (Å)Ti
3Cr@Ti-MCM-41	3.9	9.4	-
10Cr@Ti-MCM-41	2.7	259	278
3Cr/Ti-MCM-41	4.0	13	-
10Cr/Ti-MCM-41	2.7	116	126

d: distance between layers, L: crystallite size. Calculations are given in Appendix-5.

By examining the structural properties data for catalysts containing 10wt.% Cr, the hydrothermal method effectively creates smaller CrO_x and TiO_2 crystals. Furthermore, the crystallite sizes of $\alpha\text{-Cr}_2\text{O}_3$ and titania anatase are exactly match the literature for the catalysts prepared by impregnation synthesis methods (Al-Awadi et al., 2020).

SEM/EDX analysis was conducted on Cr-based catalysts in order to determine catalyst morphology and bulk composition. SEM images of catalysts synthesized by hydrothermal method are demonstrated in Image 5.1.

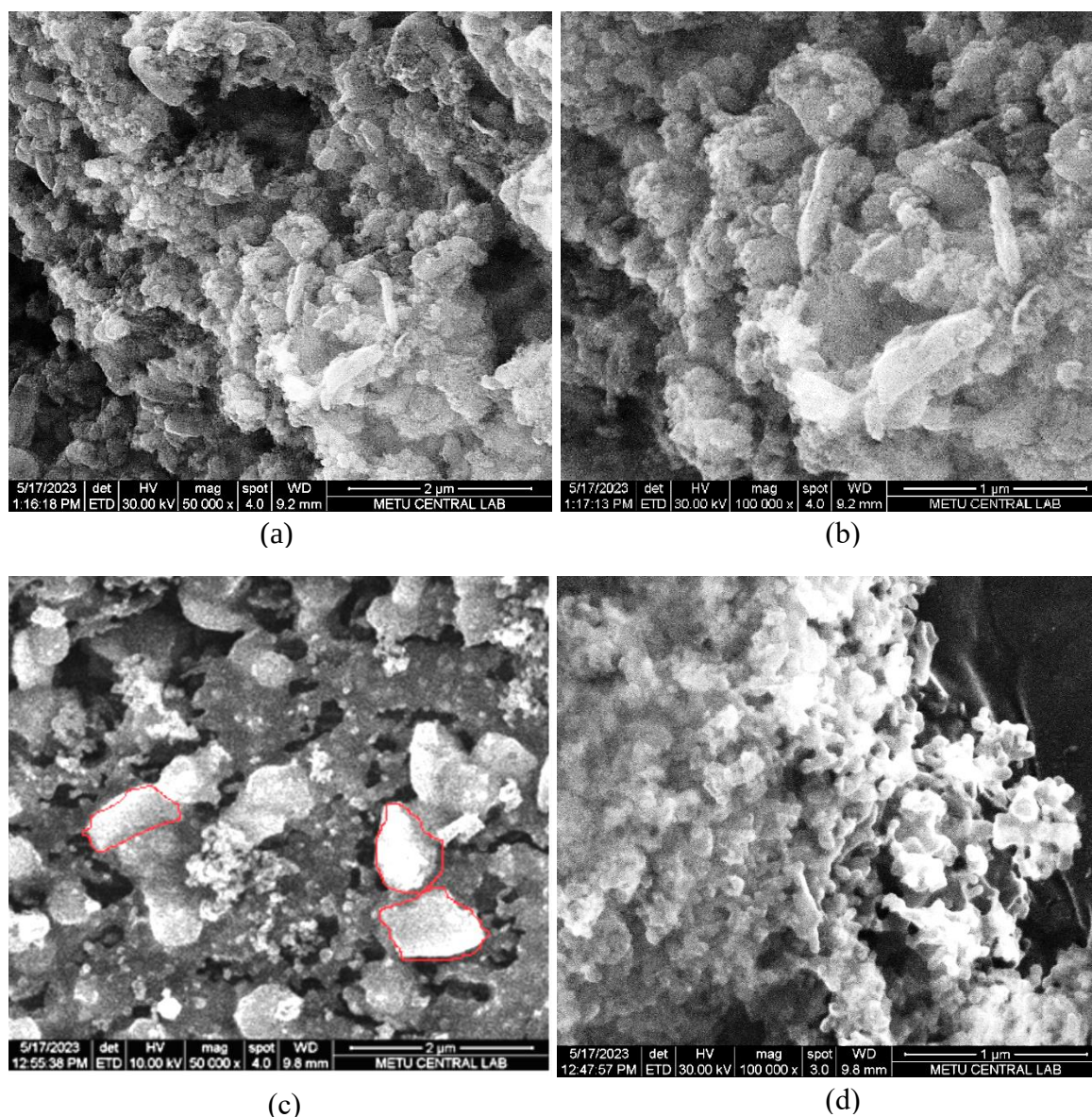


Image 5.1. SEM images of the catalysts synthesized by hydrothermal method ((a): 3Cr/Ti-MCM-41 x 50000, (b): 3Cr/Ti-MCM-41 x 100000, (c):10Cr/Ti-MCM-41 x 50000, (d): 10Cr/Ti-MCM-41 x 50000)

SEM images in Image 5.1 confirmed the homogeneous structure of the catalysts, the highly ordered structure of the MCM-41 support is clear, and also the surface has a smooth appearance, this indicates that the incorporation of the metal oxides into the mesopores was successful. It is important to note that for 10wt.% Cr catalyst, smaller pores are indeed seen. Those findings were supported by observation reported in the literature (Elías et al., 2012)

(Al-Awadi et al., 2019). Also, it was defined that the CrO_x density was higher in the bright regions observed in the SEM photograph.

Image 5.2 shows SEM image of MCM-41 supported Cr-based catalysts (3wt.%) prepared by hydrothermal method (Saliha Çetinyokuş - 2014)

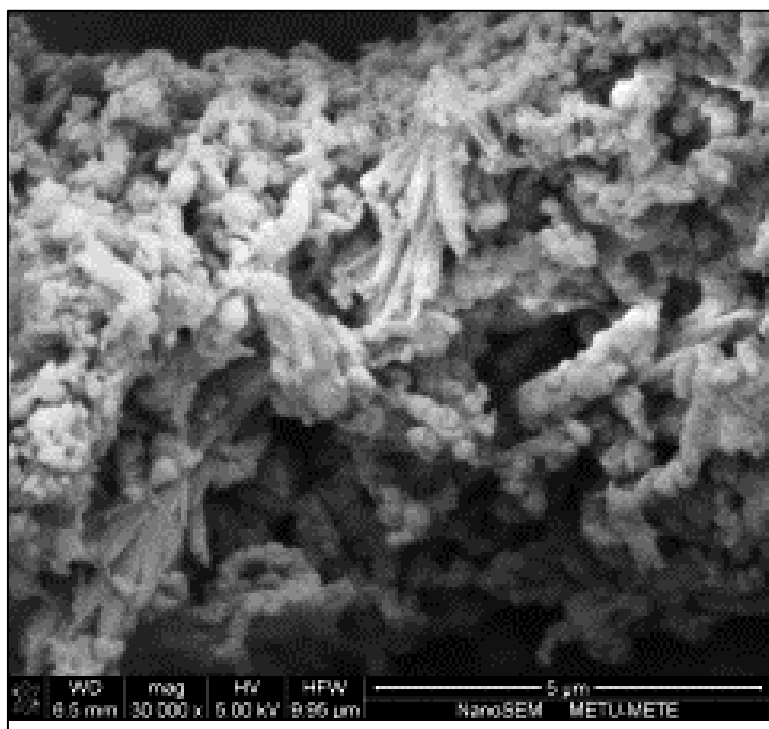


Image 5.2. SEM images of Cr-based catalysts supported on MCM-41 synthesized by hydrothermal method (Çetinyokuş -2014)

When comparing Cr/Ti-MCM-41 samples prepared for this study to Cr/MCM-41 catalyst prepared by Saliha Çetinyokuş (2014), it can be said that the ordered structure of the MCM-41 support was retained even after the loading of Ti.

SEM images of catalysts synthesized with impregnation method are given Image 5.3.

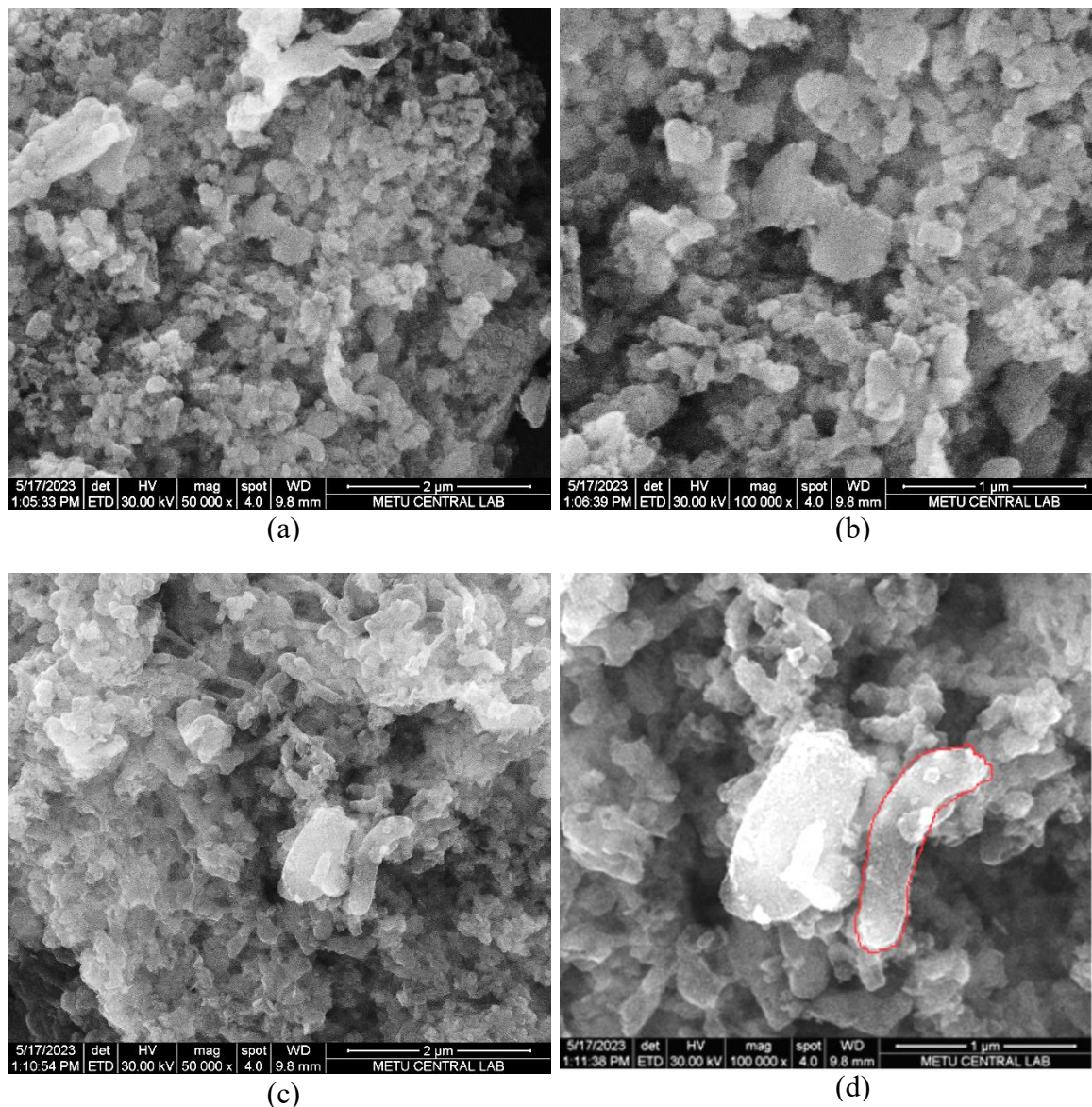


Image 5.3. SEM images of the catalysts synthesized with impregnation method ((a): 3Cr/Ti-MCM-41 x 50000, (b): 3Cr@Ti-MCM-41 x 100000, (c):10Cr@Ti-MCM-41 x 50000, (d): 10Cr/Ti-MCM-41 x 100000)

When Image 5.3 was examined, it was seen that the catalyst containing 10% chromium by mass had larger pores.

EDX analyses were carried out to determine bulk components of the catalyst structure, EDX spectra are presented in Figure 5.10.

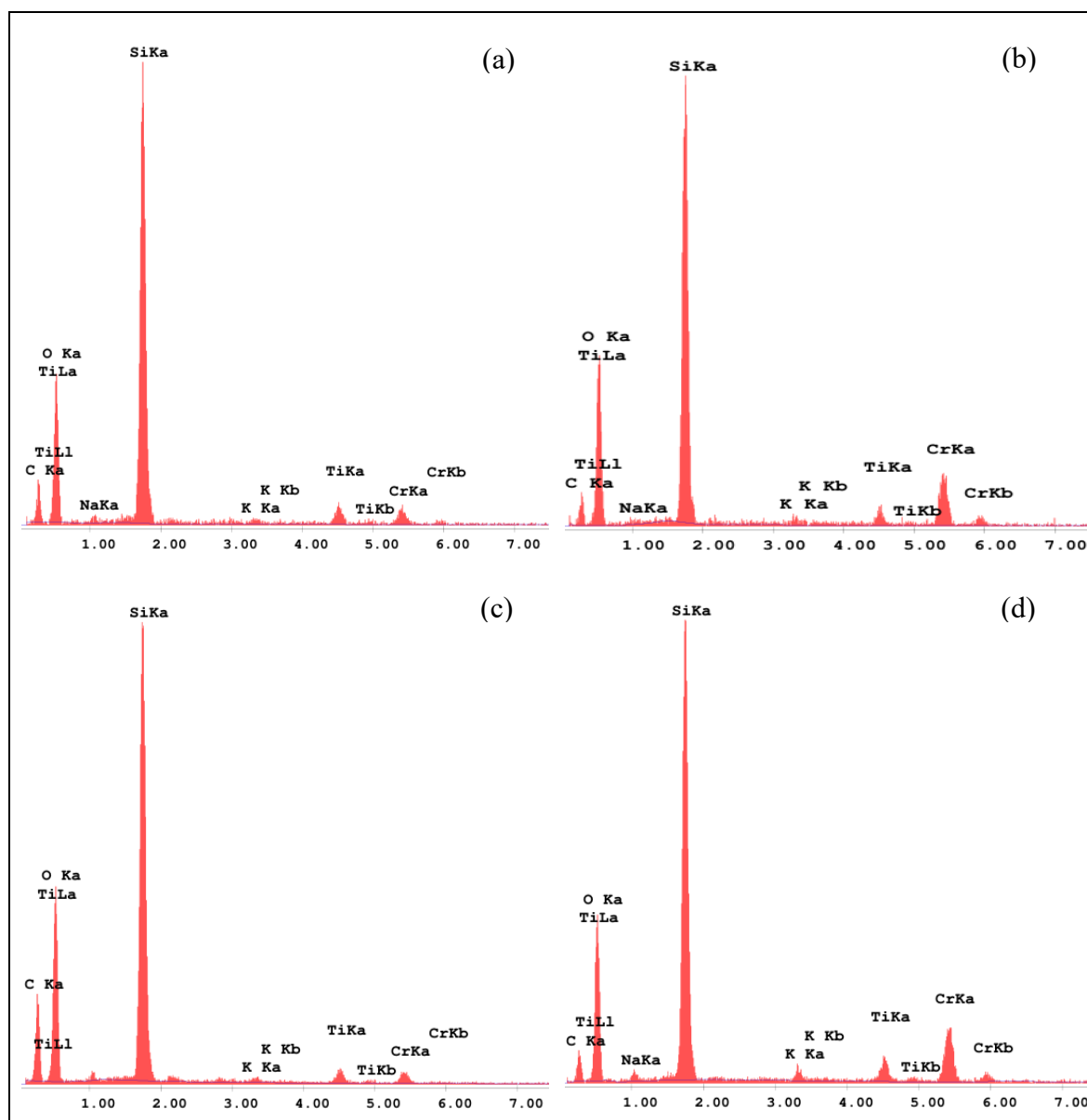


Figure 5.10. EDX analysis of synthesized Cr-based catalyst (a): 3Cr@Ti-MCM-41, (b): 10Cr@Ti-MCM-41, (c): 3Cr/Ti-MCM-41, (d): 10Cr/Ti-MCM-41

EDX analysis showed that Cr and Ti were distributed homogeneously on the catalyst surface. Bulk compositions determined by EDX analysis are given in Table 5.7.

Table 5.7. Bulk compositions of the catalysts (EDX)

Catalyst \ Element	Oxygen (O)	Sodium (Na)	Silica (Si)	Potassium (K)	Titanium (Ti)	Chromium (Cr)
3Cr/Ti-MCM-41	67.53	-	29.17	0.38	1.35	1.57
10Cr/Ti-MCM-41	54.10	1.69	32.79	0.92	2.45	8.10
3Cr@Ti-MCM-41	58.39	1.31	35.1	0.46	2.18	2.56
10Cr@Ti-MCM-41	56.52	0.75	32.73	0.69	1.73	7.59

A comparison between the Cr/Ti ratio (by mass) obtained from EDX results and synthesis is given in Table 5.8.

Table 5.8. Comparison between the values of the Cr/Ti (wt./wt.) ratio obtained from EDX analysis and synthesis

Catalyst	EDX Cr/Ti (wt./wt.)	Synthesis Cr/Ti (wt./wt.)
3Cr/Ti-MCM-14	1.16	1.20
10 Cr/Ti-MCM-14	3.31	4.00
3Cr@Ti-MCM-14	1.17	1.20
10Cr@Ti-MCM-14	4.38	4.00

It can be said that the ratios determined from EDX and synthesis are very close to each other.

EDX is a surface-sensitive technique that primarily analyzes the composition of the sample's surface or near-surface regions (Liou et al., 2022). The observation is because the EDX analysis does not measure the element on the intrinsic part (channels) of the catalyst's particles. However, most Ti and Cr particles are loaded within the ordered channels of the support, as discussed in the research carried out by Liou et al,2022.

Furthermore, potassium was found in the catalysts structure. It was shown that the addition of potassium significantly enhanced the catalytic activity of Cr-based catalysts. Potassium and chromium lead to the formation of K_2CrO_4 and $K_2Cr_2O_7$ species, which act as anchors for active monochromate species, enhancing the overall catalytic performance the addition of potassium results in the presence of more low-coordinated oxygen species, enhancing the basicity of the catalysts and contributing to their improved catalytic activity (Zhao et al., 2019). The presence of potassium in the metal source used in this study is thought to provide an advantage.

5.4. Catalytic Activity Tests

Oxidative dehydrogenation of isobutane was investigated over Cr-based catalysts prepared by hydrothermal and impregnation synthesis method, (Cr loading: 3, 6, and 10 wt.%) using carbon dioxide as oxidant. Isobutane oxidative dehydrogenation occurs according to the following equation.

Main reactions:



Side reactions:



The effect of the $i\text{-C}_4\text{H}_{10}/\text{CO}_2$ molar ratio on catalytic activity was investigated on 3Cr/Ti-MCM-41 to determine suitable feed ratios. According to the thermodynamic equilibrium calculation, $i\text{-C}_4\text{H}_{10}/\text{CO}_2$ molar ratios of 1/5 and 1/9 both showed promising conversion.

The catalytic activity of 3Cr/Ti-MCM-41 catalyst was studied under two different $i\text{-C}_4\text{H}_{10}/\text{CO}_2$ (1/9 and 1/5) molar ratios. In both experiments, the total flow rate of the reactant was maintained at 50 ml/min, at a temperature of 600°C, and under atmospheric pressure. Figure 5.11 shows the isobutane conversion and isobutene selectivity values for two different molar ratios of $i\text{-C}_4\text{H}_{10}/\text{CO}_2$.

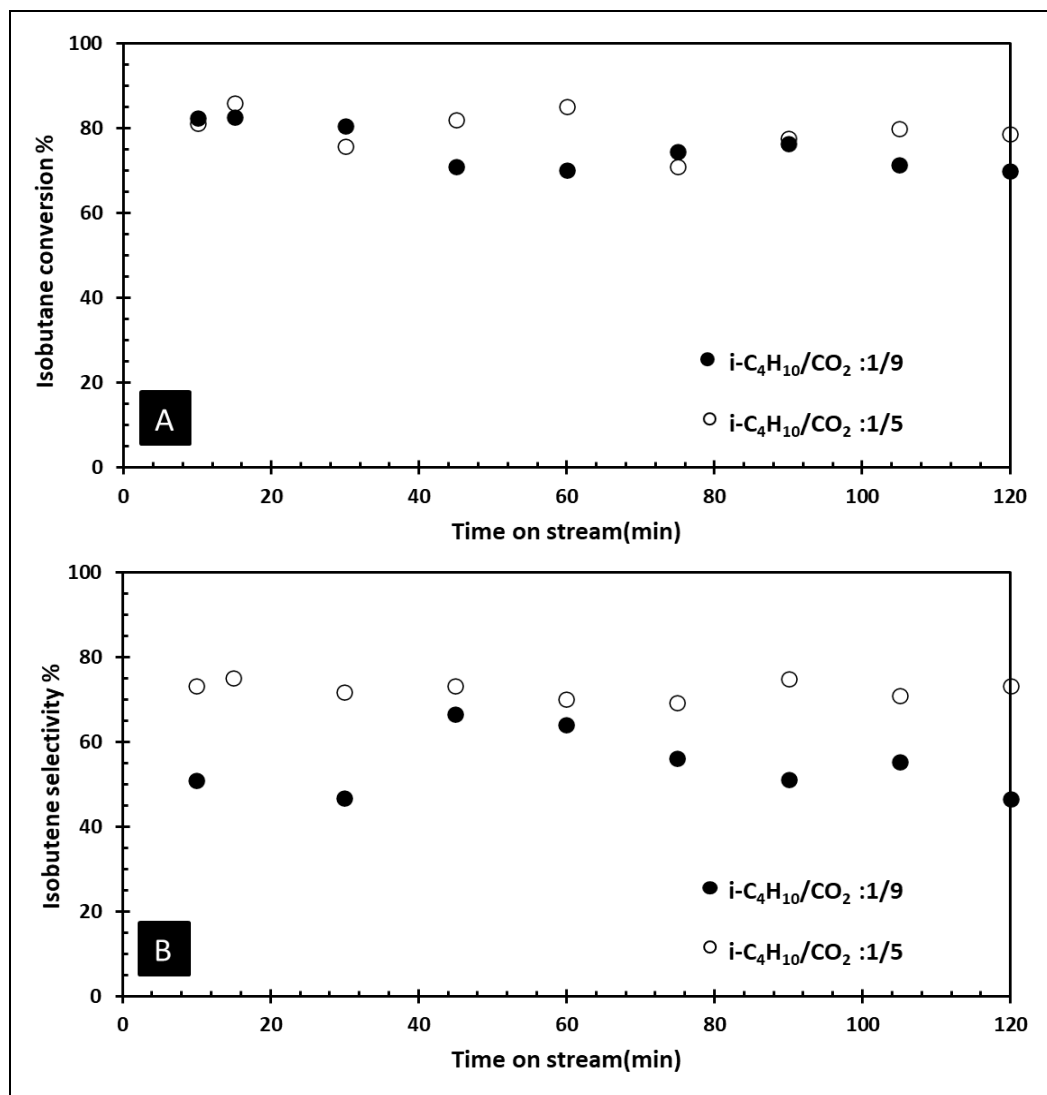


Figure 5.11. Isobutane conversion and isobutene selectivity values for different $i\text{-C}_4\text{H}_{10}/\text{CO}_2$ molar ratios (catalyst: 3Cr/Ti-MCM-41, T: 600°C, P: atmospheric, WHSV: 51 h^{-1})

The results demonstrated in Figure 5.11 show that the isobutane conversion values are almost similar for both the $i\text{-C}_4\text{H}_{10}/\text{CO}_2$ molar ratios. The highest isobutene selectivity values were achieved when the $i\text{-C}_4\text{H}_{10}/\text{CO}_2$ molar ratio was 1/5. Lower isobutene selectivity values obtained at molar ratio of 1/9 can be explained by the excessive presence of CO_2 . The isobutane conversion and isobutene selectivity values when the $i\text{-C}_4\text{H}_{10}/\text{CO}_2$ molar ratio was 1/5 did not exhibit a massive decrease through the reaction time. It was thought that carbon accumulation and formation of inactive Cr forms were not significant.

The propane, propene, and methane selectivity values for different $i\text{-C}_4\text{H}_{10}/\text{CO}_2$ ratios are given in Figure 5.12.

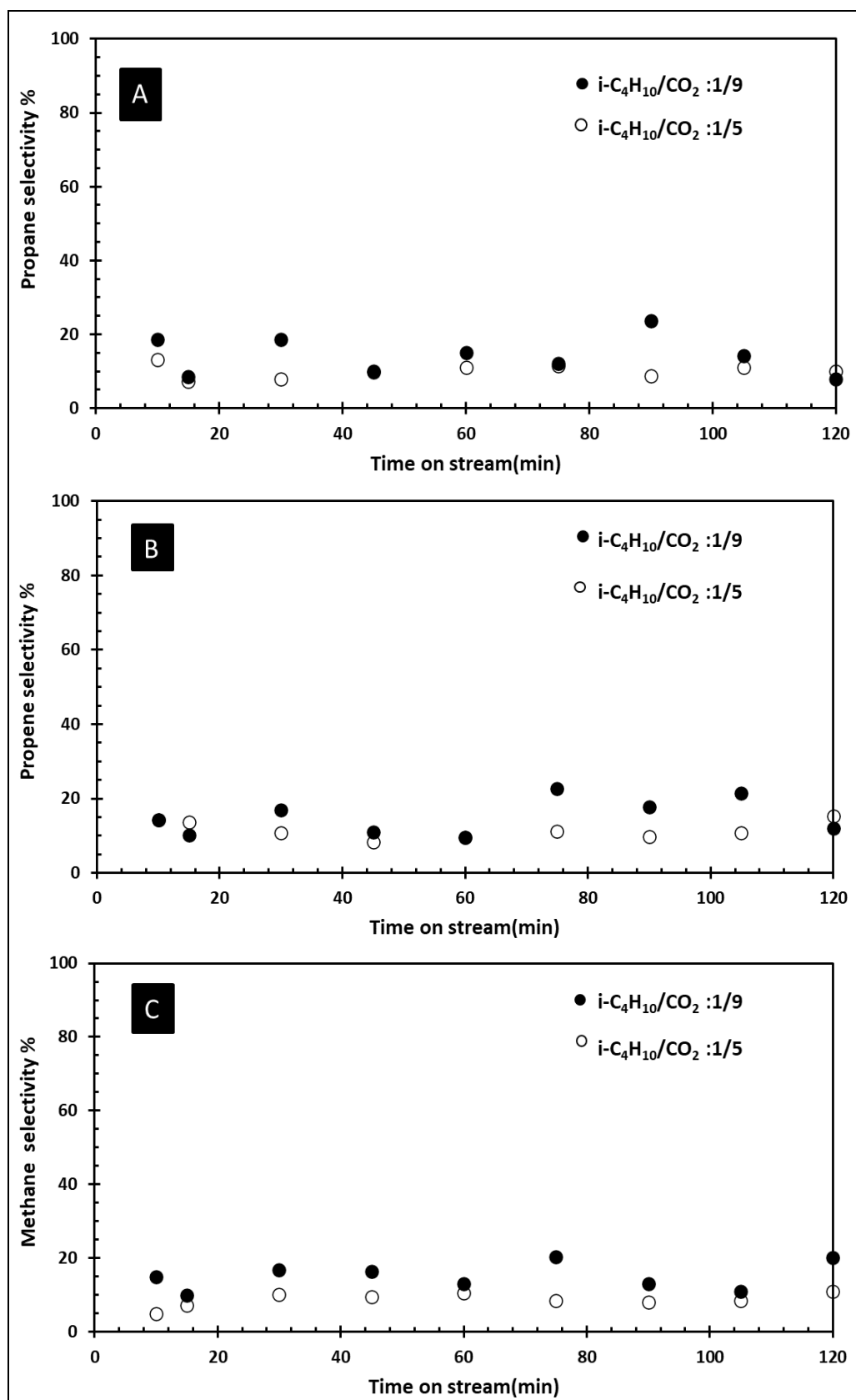


Figure 5.12. Selectivity values of propane, propene, and methane for different $i\text{-C}_4\text{H}_{10}/\text{CO}_2$ molar ratios (catalyst: 3Cr/Ti-MCM-41, T: 600°C, P: atmospheric, WHSV: 51 h⁻¹)

As can be seen, propane, propene, and methane were observed in both $i\text{-C}_4\text{H}_{10}/\text{CO}_2$ molar ratios, which means that side reactions have occurred (R.4 and R.5).



Isobutene selectivity values were lower at a 1/9 molar ratio. It is thought that the excess CO_2 gas affected the acidity of the catalyst surface, leading to reduced isobutene selectivity.

As a result, the $i\text{-C}_4\text{H}_{10}/\text{CO}_2$ molar ratio of 1/5 was found more suitable for subsequent catalytic activity tests due to its higher isobutene selectivity. That is why it was chosen to be utilized for the following catalytic test.

In addition to determine whether the reaction over the synthesized Cr-based catalyst occurs according to the one-step reaction or two-step reaction pathway. The hydrogen selectivity values were analysed at different $i\text{-C}_4\text{H}_{10}/\text{CO}_2$ molar ratios. The hydrogen selectivity values were about zero which means the reaction over Cr/Ti-MCM-41 catalyst follow one-step pathway as conformed by literature (Zangeneh et al., 2015).

5.4.1. Effect of chromium content on catalytic activity

The catalytic activity tests for Cr-based catalyst synthesized by hydrothermal and impregnation methods were carried out for the oxidative dehydrogenation of isobutane with CO_2 . Isobutane conversion and isobutene selectivity values for Cr-based catalyst prepared by hydrothermal synthesis are given in Figure 5.13.

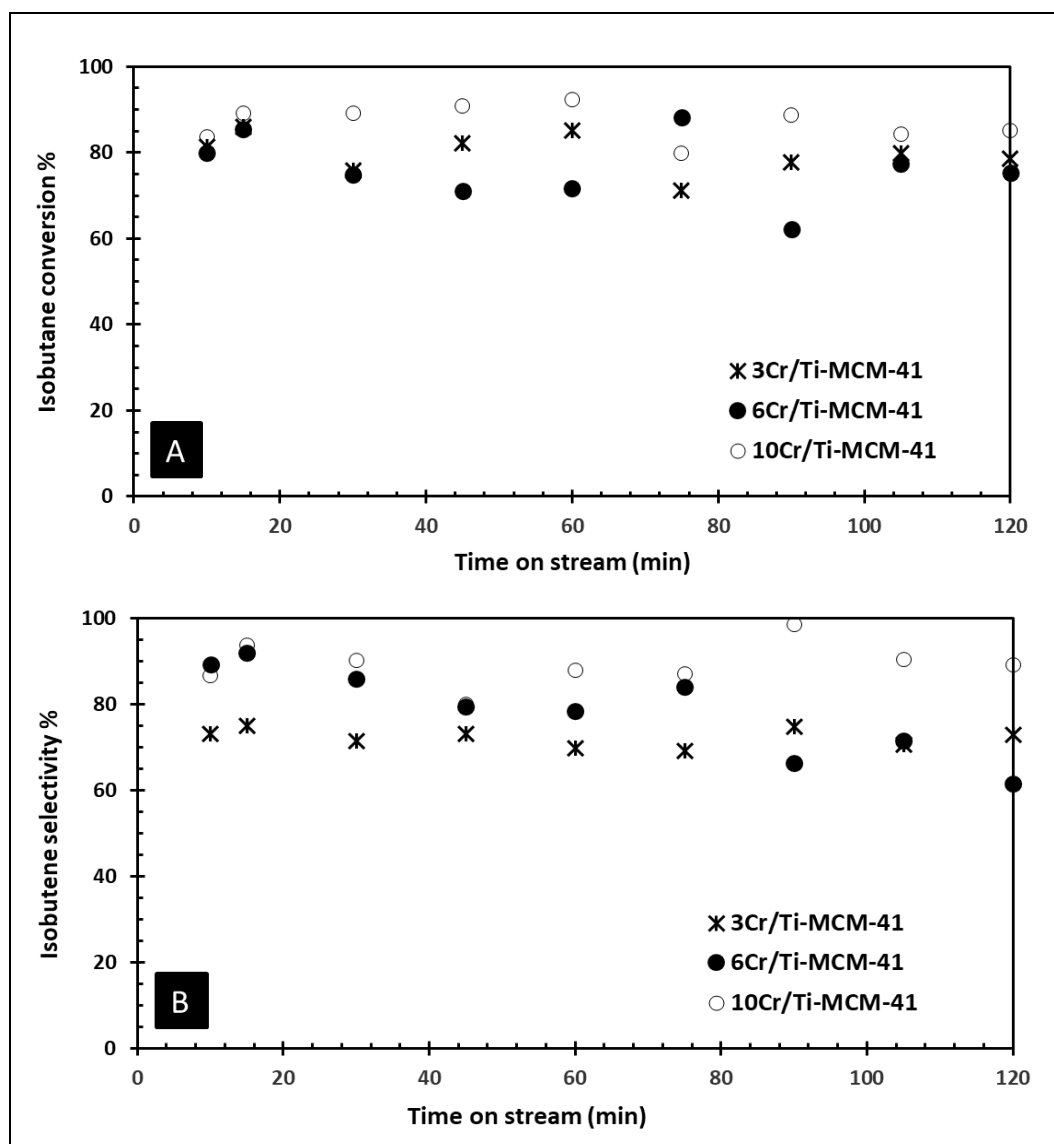


Figure 5.13. Isobutane conversion and isobutene selectivity values over Cr-based catalysts prepared by hydrothermal synthesis ($i\text{-C}_4\text{H}_{10}/\text{CO}_2$: 1/5, T: 600°C, P: atmospheric, WHSV: 51 h⁻¹)

It is observed that the 10Cr/Ti-MCM-41 catalyst exhibits the highest isobutane conversion and isobutene selectivity. The conversion and selectivity values of the 10Cr/Ti-MCM-41 and 6Cr/Ti-MCM-41 catalysts exhibit close proximity. However, the isobutene selectivity after 75-minute reaction period is higher for the 10Cr/Ti-MCM-41 catalyst and 10Cr/Ti-MCM-41 catalyst demonstrates good stability.

The propane, propene, and methane selectivity values over Cr-based catalysts prepared by hydrothermal are given in Figure 5.14.

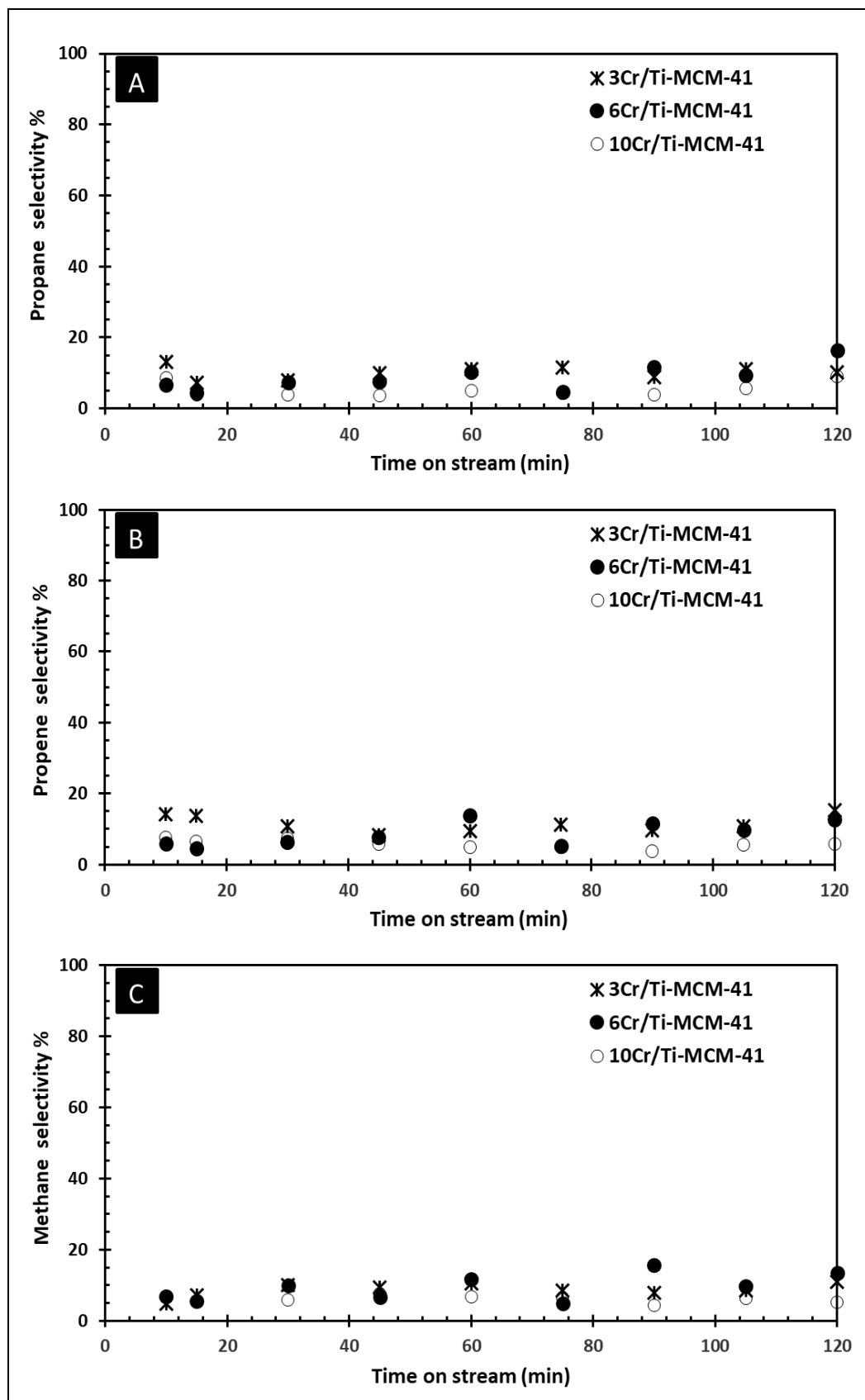


Figure 5.14. Selectivity values of propane, propene, and methane over Cr-based catalysts prepared by hydrothermal method ($i\text{-C}_4\text{H}_{10}/\text{CO}_2$: 1/5, 600°C , P: atmospheric, WHSV: 51 h^{-1})

The data presented in Figure 5.14 demonstrates that 10Cr/Ti-MCM-41 catalyst had the lowest selectivity values, with propane selectivity of 9%, propene selectivity of 7.7%, and methane selectivity of 7.6%.

In general selectivity values for propane, propene, and methane were consistently low and do not change significantly with time which means the chemical decomposition reactions (R.6, R.7, and R.8) have not taken place.



Isobutane conversion and isobutene selectivity values for Cr-based catalysts prepared by the impregnation synthesis method is shown in Figure 5.15.

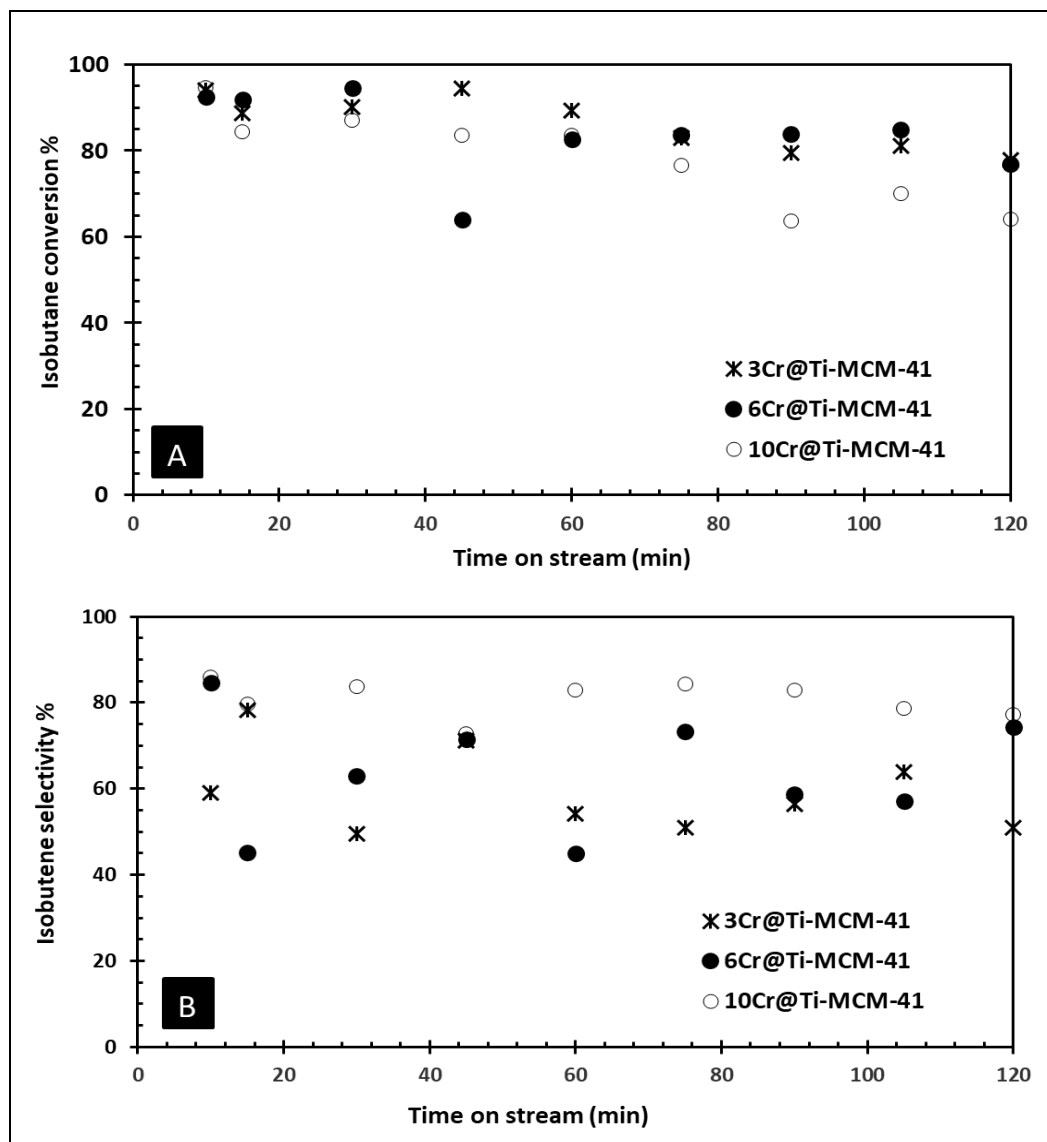


Figure 5.15. Isobutane conversion and isobutene selectivity values over Cr-based catalysts prepared by impregnation synthesis ($i\text{-C}_4\text{H}_{10}/\text{CO}_2$: 1/5, T: 600°C, P: atmospheric, WHSV: 51 h⁻¹)

By analyzing the isobutane conversion data presented in Figure 5.15, the 3Cr@Ti-MCM41 and 6Cr@Ti-MCM41 catalysts demonstrate high isobutane conversion. However, it is clear that the 10Cr@Ti-MCM-41 catalyst exhibits the highest isobutene selectivity.

The selectivity values for propane, propene, and methane on Cr-based catalysts prepared by the impregnation method are shown in Figure 5.16.

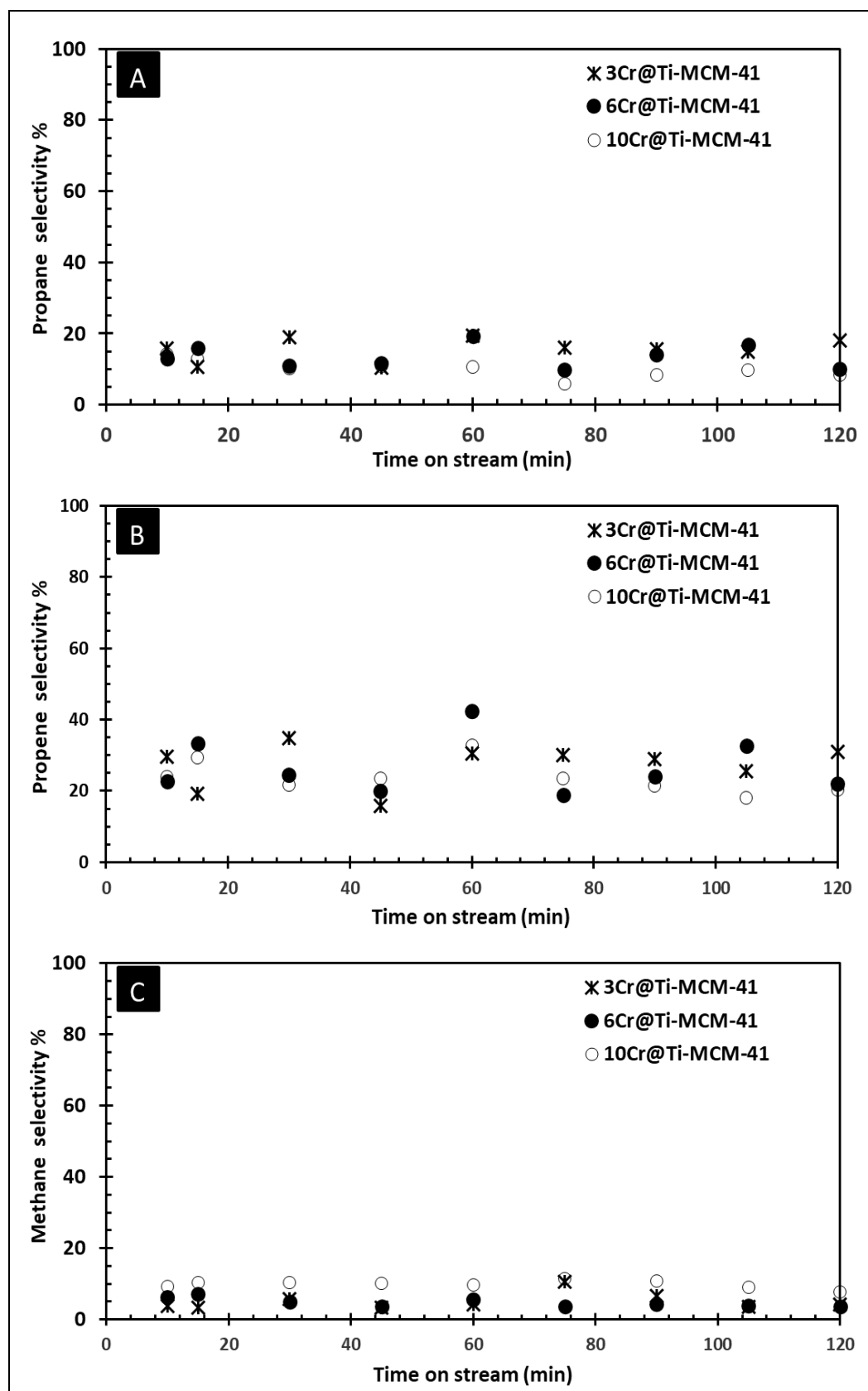


Figure 5.16. Selectivity values for propane, propene, and methane over Cr-based catalysts prepared by impregnation method ($i\text{-C}_4\text{H}_{10}/\text{CO}_2$: 1/5, T: 600°C, P: atmospheric, WHSV: 51 h⁻¹)

The results show that propane and propene selectivity values were high over all catalyst. This implies the occupation of side reactions (R.4 and R.5).



Selectivity values for methane were not as high as expected, indicating that the chemical decomposition reaction (R.8) occurred.



Figure 5.17 displays the conversion and selectivity values of 10Cr/Ti-MCM-41 and 10Cr@Ti-MCM-41 catalysts.

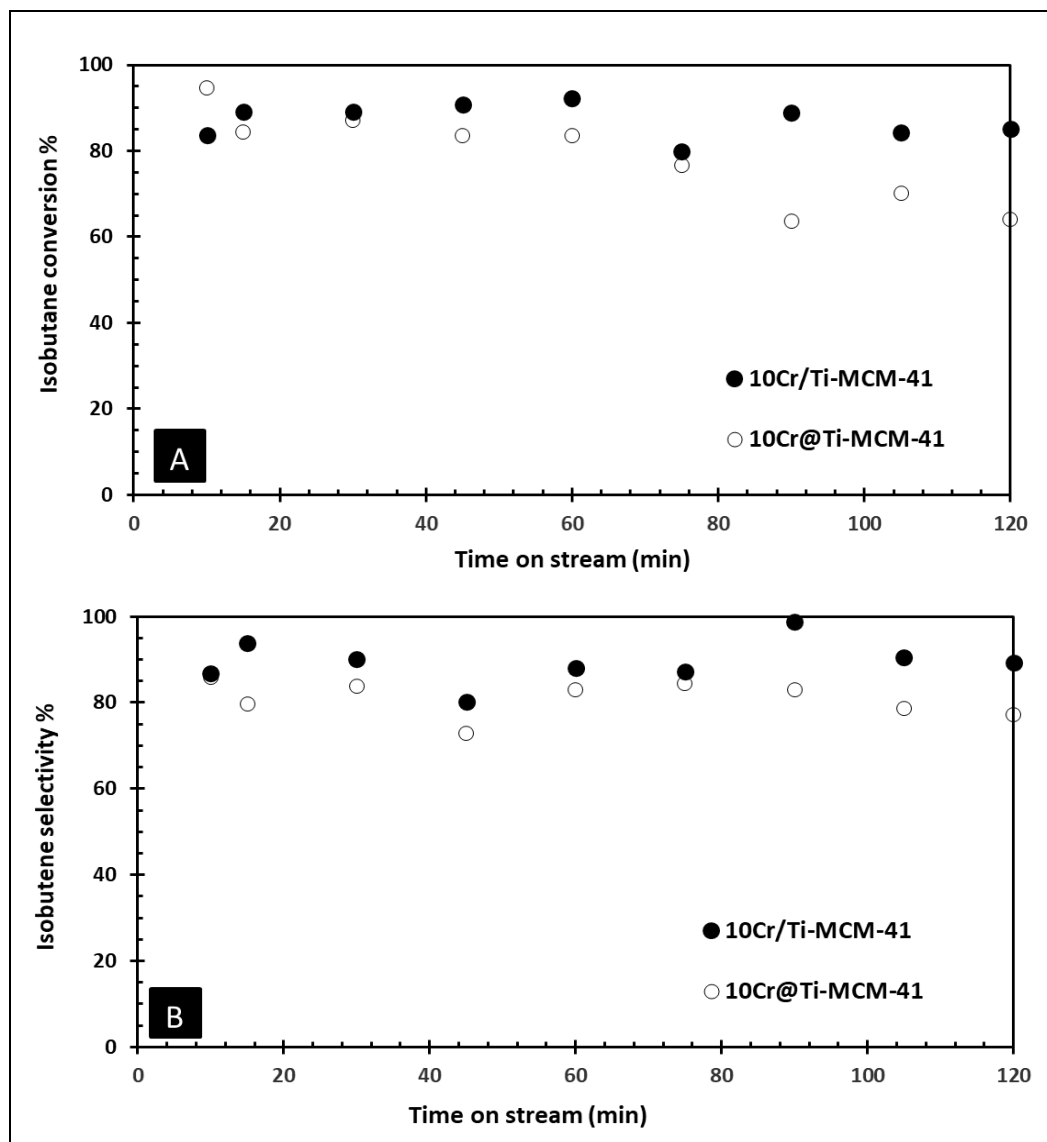


Figure 5.17. Isobutane conversion and isobutene selectivity values over 10Cr/Ti-MCM-41 and 10Cr@Ti-MCM-41 catalysts ($i\text{-C}_4\text{H}_{10}/\text{CO}_2$: 1/5, T: 600°C, P: atmospheric, WHSV: 51 h⁻¹)

The isobutane conversion and isobutene selectivity values for both catalysts were similar, but 10Cr/Ti-MCM-41 catalyst showed a significantly higher values after 75 minutes of reaction. This difference can be explained by the low crystallite size of Cr and Ti based structures (Table 5.6) in 10Cr/Ti-MCM-41.

5.4.2. Effect of ti modification on catalytic activity

A comparative analysis was conducted on the catalytic activity of a chromium-based catalyst supported on titanium-modified MCM-41 (referred to as 10Cr/Ti-MCM-41) and a

chromium-based catalyst supported on MCM-41 (referred to as 10Cr/MCM-41). Figure 5.18 shows the isobutane conversion and isobutene selectivity for both catalysts.

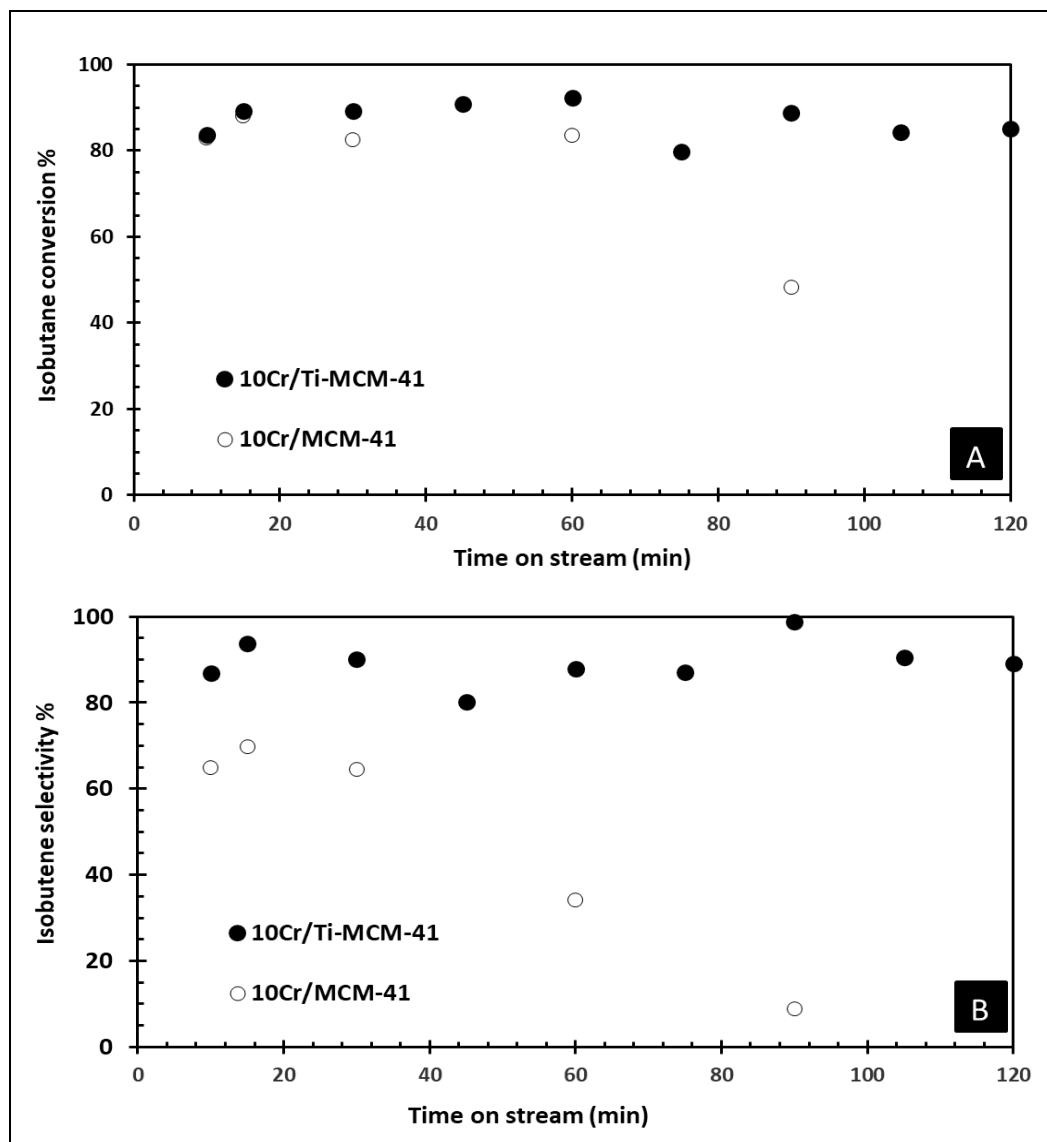


Figure 5.18. Isobutane conversion and isobutene selectivity values over 10Cr/Ti-MCM-41 and 10Cr/MCM-41 catalysts ($i\text{-C}_4\text{H}_{10}/\text{CO}_2$: 1/5, T: 600°C, P: atmospheric, WHSV: 51 h⁻¹)

As can be clearly seen in Figure 5.18 isobutane conversion and isobutene selectivity values decreased significantly for 10Cr/MCM-41, while 10Cr/Ti-MCM-41 catalyst maintain a good conversion and isobutene selectivity values throughout the reaction time.

A recent study published by Wan et al. in 2022 confirms these findings and highlights the increased hydrophilicity and enhanced structural properties that result from the addition of

titanium (Wan et al., 2022). When doping Ti to MCM-41 support a significant modification in the surface characteristics of MCM-41 was noticed. According to the information provided in the literature review there are three possible mechanisms, for the reduction in hydrophobicity upon titanium modification which are surface functionalization, surface charge modification, and structural rearrangement (Gaidau et al., 2017; Wróblewska et al., 2019). Through surface functionalization mechanism Ti species can form bonds with surface silanol groups (Si-OH) on the MCM-41 material. This can result in the formation of new surface functional groups, such as titanium hydroxide (Ti-OH) or titanium oxide (Ti-O), which can have hydrophilic properties. These functional groups can interact with water molecules through hydrogen bonding, enhancing hydrophilic interactions and reducing the overall hydrophobicity of the surface. Surface charge modification mechanism refers to the process by which the electrical charge distribution on the surface of Ti-MCM-41 support. In the surface charge modification mechanism Ti modification can alter the surface charge of MCM-41 by introducing positive or negative charges. This change in surface charge can influence the adsorption behavior of water molecules. For example, if titanium introduces positive charges on the surface, it can attract and interact with the negatively charged oxygen atoms in water molecules, promoting stronger water-surface interactions and reducing hydrophobicity. According to structural rearrangement mechanism the presence of titanium species can induce structural rearrangements within the MCM-41 framework. This may involve the reorientation of silica or titanium species, resulting in the exposure of different surface sites. If these newly exposed surface sites are more hydrophilic in nature, they can enhance the affinity for water molecules and decrease the overall hydrophobicity of the material.

It was believed that the presence of hydrophilic groups facilitated the adsorption of water (produced by R.3) on the catalyst surface.



The presence of monochromates in the structure significantly affects the activity of chromium-based catalysts in dehydrogenation reactions. In the literature, it was reported that the transformation from dichromates (R.9) to monochromates during the reaction occurred in the presence of water in the reaction medium (Erol et al., 2020).



It can be said that, higher hydrophilicity achieved by loading Ti is the reason for the high conversion values over 10Cr/Ti-MCM-41 catalysts.

The selectivity values for propane, propene, and methane over 10Cr/Ti-MCM-41 and 10Cr/MCM-41 catalysts are presented in Figure 5.19.

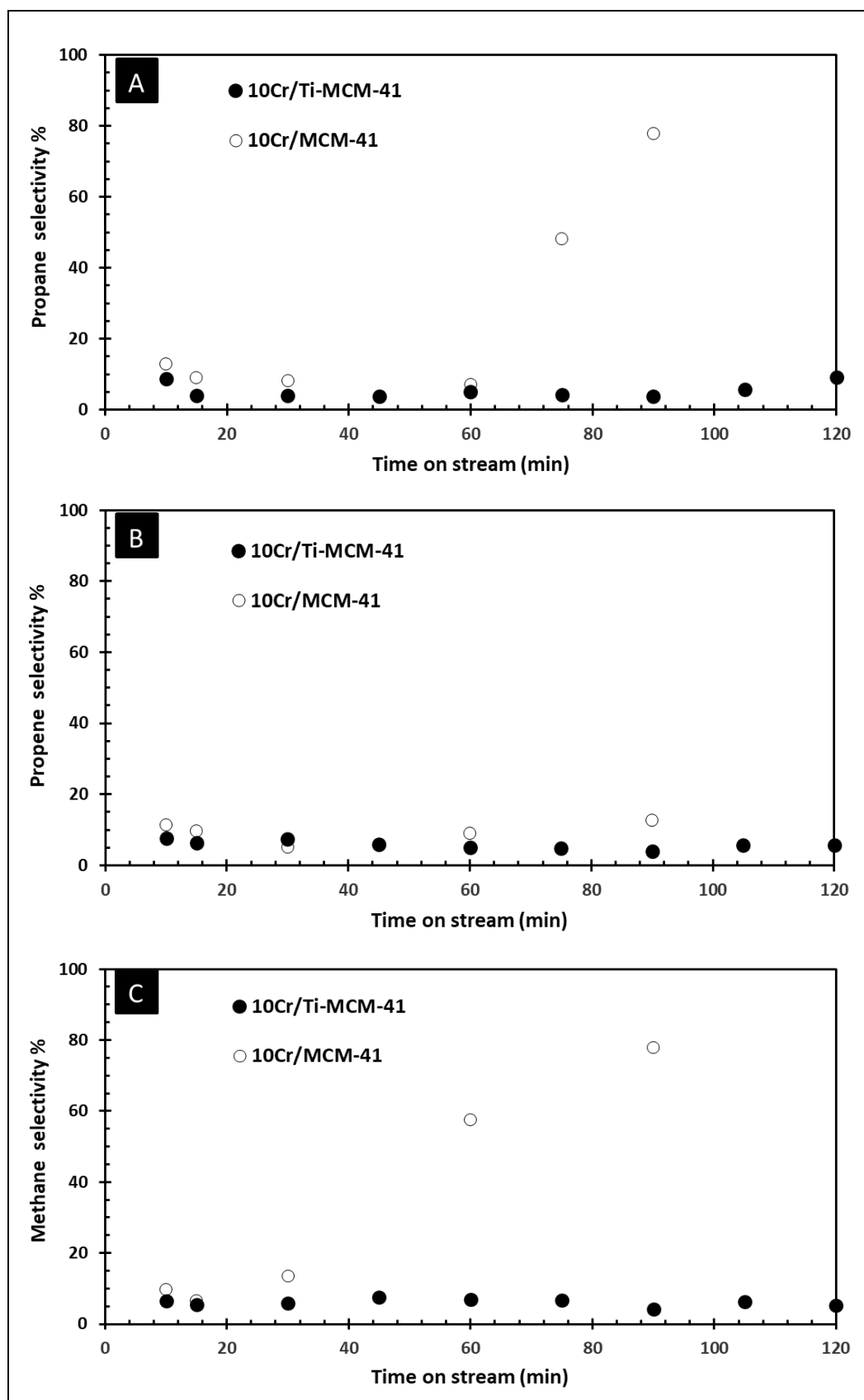


Figure 5.19. Selectivity values of propane, propene, and methane over 10Cr/Ti-MCM-41 and 10Cr/MCM-41 catalysts ($i\text{-C}_4\text{H}_{10}/\text{CO}_2$: 1/5, T: 600°C, P: atmospheric, WHSV: 51 h⁻¹)

From Figure 5.19B it can be clearly seen that isobutane cracking reaction occurred (R.4) for both catalysts.



The results indicate that the propane selectivity (Figure 5.19A) over 10Cr/Ti-MCM-41 and 10Cr/MCM-41 catalysts were similar for the first 60 minutes of the reaction, but after that the selectivity rapidly increased. Also, methane selectivity (Figure 5.19C) over 10Cr/Ti-MCM-41 and 10Cr/MCM-41 catalysts were similar for the first 30 minutes of the reaction, however after that an instant increase in the selectivity was seen. That can be as a result of isobutane hydrogenation reaction (R.5).



This reaction was extensively occurred over 10Cr/MCM-41. On the other hand, propane, propene, and methane selectivity values were remained approximately constant for 10Cr/Ti-MCM-41 throughout the reaction time, this could be due to titanium modification.

5.4.3. Effect of reaction temperature on catalytic activity

Cr-based catalyst supported on titanium-modified MCM-41, synthesized by hydrothermal method, with 10wt.% Cr content and 2.5wt.% Ti loading (10Cr/Ti-MCM-41), was selected for further catalytic activity studies due to its high isobutane conversion and isobutene selectivity. The effect of reaction temperature on catalytic activity was investigated over 10Cr/Ti-MCM-41 catalyst at 500°C and 600°C with a feed flow rate of 50 mL/min (WHSV=51 h⁻¹).

The effect of reaction temperature on isobutane conversion and isobutene selectivity is shown in Figure 5.20. Also, the hydrogen and carbon dioxide selectivity values at two different reactor temperatures are given in Figure 5.21.

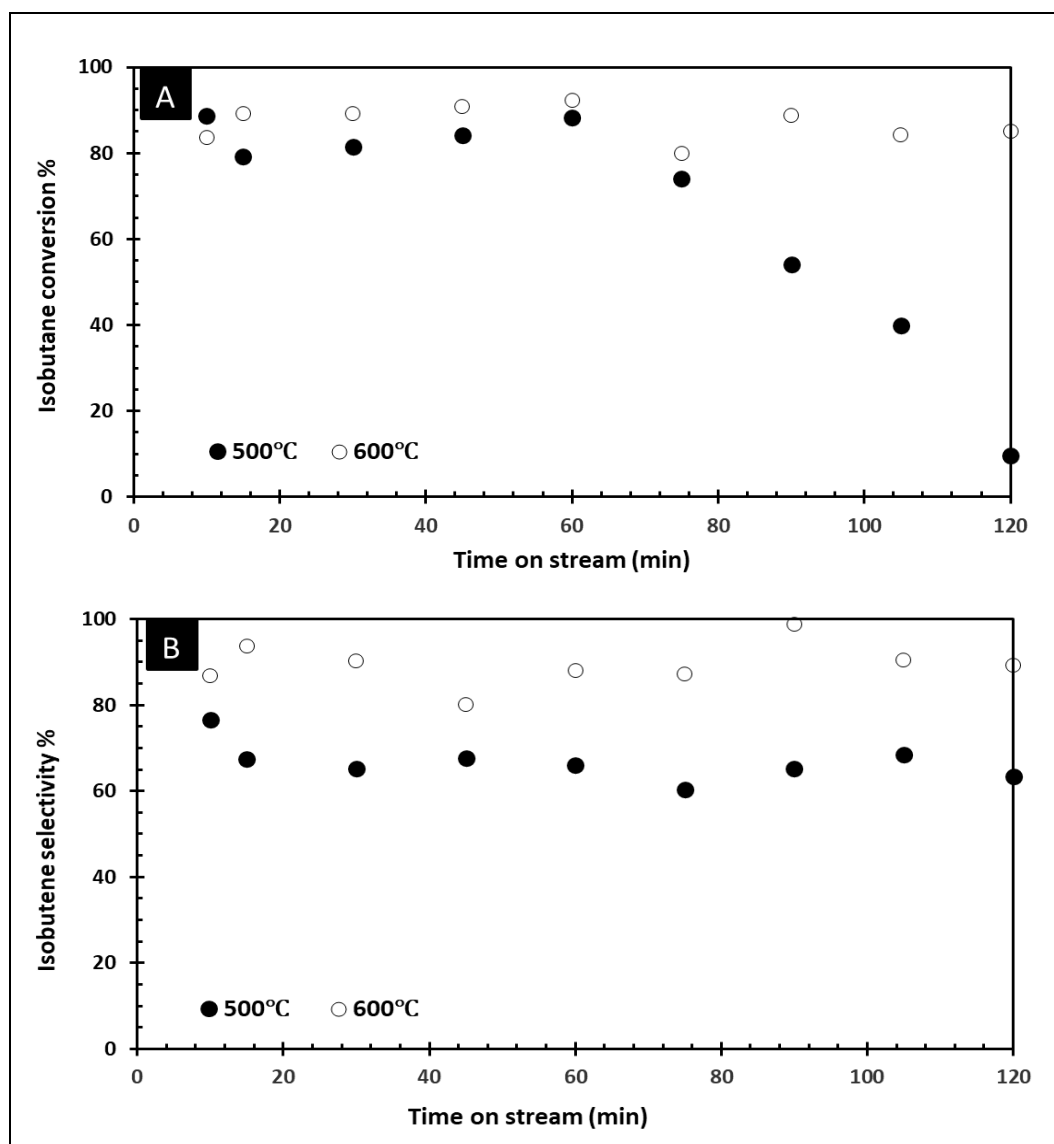


Figure 5.20. Isobutane conversion and isobutene selectivity values at different reaction temperatures (catalyst: 10Cr/Ti-MCM-41, $i\text{-C}_4\text{H}_{10}/\text{CO}_2$: 1/5, P: atmospheric, WHSV: 51 h^{-1})

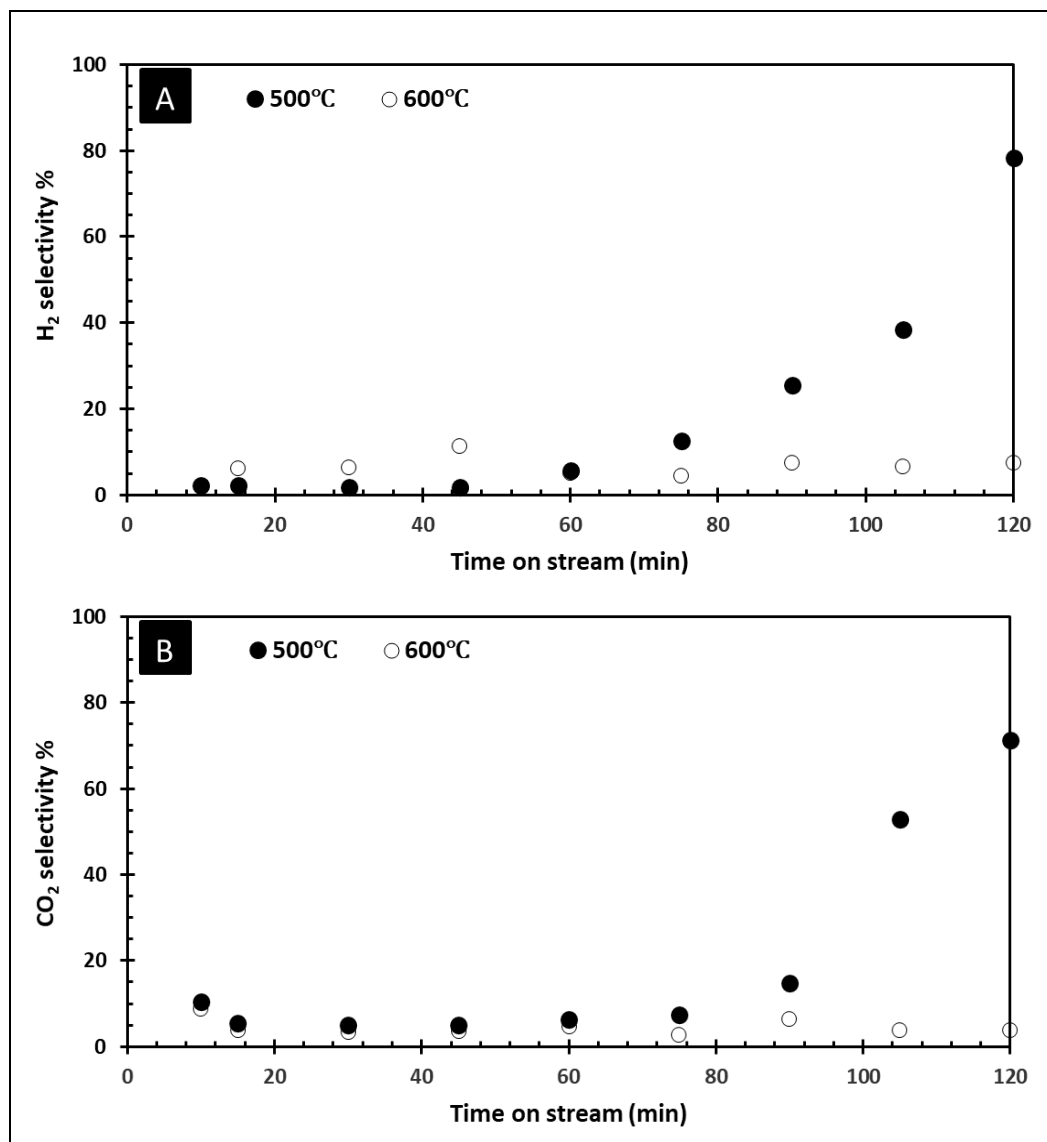


Figure 5.21. Selectivity values of hydrogen and carbon dioxide at different reaction temperatures (catalyst: 10Cr/Ti-MCM-41, $i\text{-C}_4\text{H}_{10}/\text{CO}_2$: 1/5, P: atmospheric, WHSV: 51 h^{-1})

The results presented in Figure 5.20 indicate that the isobutane conversion at 600°C and 500°C remained almost constant for the first hour of the reaction. However, after 75 minutes, the conversion values at 500°C decreased sharply, unlike the conversion at 600°C.

During dehydrogenation reactions, the activity of chromium-based catalysts is significantly impacted by the number of monochromates in their structure. In the presence of water, dichromates transform into monochromates (R.9). By analyzing the gaseous components present in the reaction medium, it was observed that the reverse water gas shift reaction (hydrogenation of carbon dioxide) is highly probable for the formation of water; this reaction

(R.2) takes place with the heterogeneous reaction between CO₂ and H₂ adsorbed to the catalyst structure (Fang et al., 2015).



When examining the selectivities of H₂ and CO₂ at the reactor exit as seen in Figure 5.21, it was found that the hydrogen selectivity is constantly low throughout the reaction at 600°C (~6%); however, when the reaction conducted at 500°C exhibited high amount of CO₂ and H₂ after 75 minutes of reaction. It was thought that reverse water shift reaction could not occur over 10Cr/Ti-MCM-41 catalyst at 500°C.

Therefore, it can be said that the reasons led to the decrease of the isobutane conversion at 500°C after 75 minutes of reaction are as follows: the thermodynamic analysis of the oxidative dehydrogenation reaction (ODH) via CO₂ shows that it is preferred to shift the equilibrium forward by the removal of hydrogen as in reaction (R.1), however the present of the H₂ in the reaction medium shifted the equilibrium to the reactant's direction. This outcome was confirmed by the study published by Zangeneh at the group research (Zangeneh et al., 2015). Another reason is the monochromates that provided high activity and selectivity were not able to be preserved due to the absence of water in the reaction medium (R.2), this observation agreed with the literature (Erdali et al., 2022). Also, the high concentration of CO₂ in the reaction medium had negative impact on the conversion, although CO₂ is a good source of oxygen, but unfortunately when CO₂ is adsorbed to the catalyst surface, the adsorption of the alkanes becomes difficult. That why the present of CO₂ in the reaction medium is preferred to be limited to some extent (Mukherjee et al., 2016). In the studies carried out at different reactor temperatures, the stability of the catalyst at 600 °C was higher than that of the low temperature (500°C).

The propane, propene, and methane selectivity values obtained at different temperatures are given in Figure 5.22.

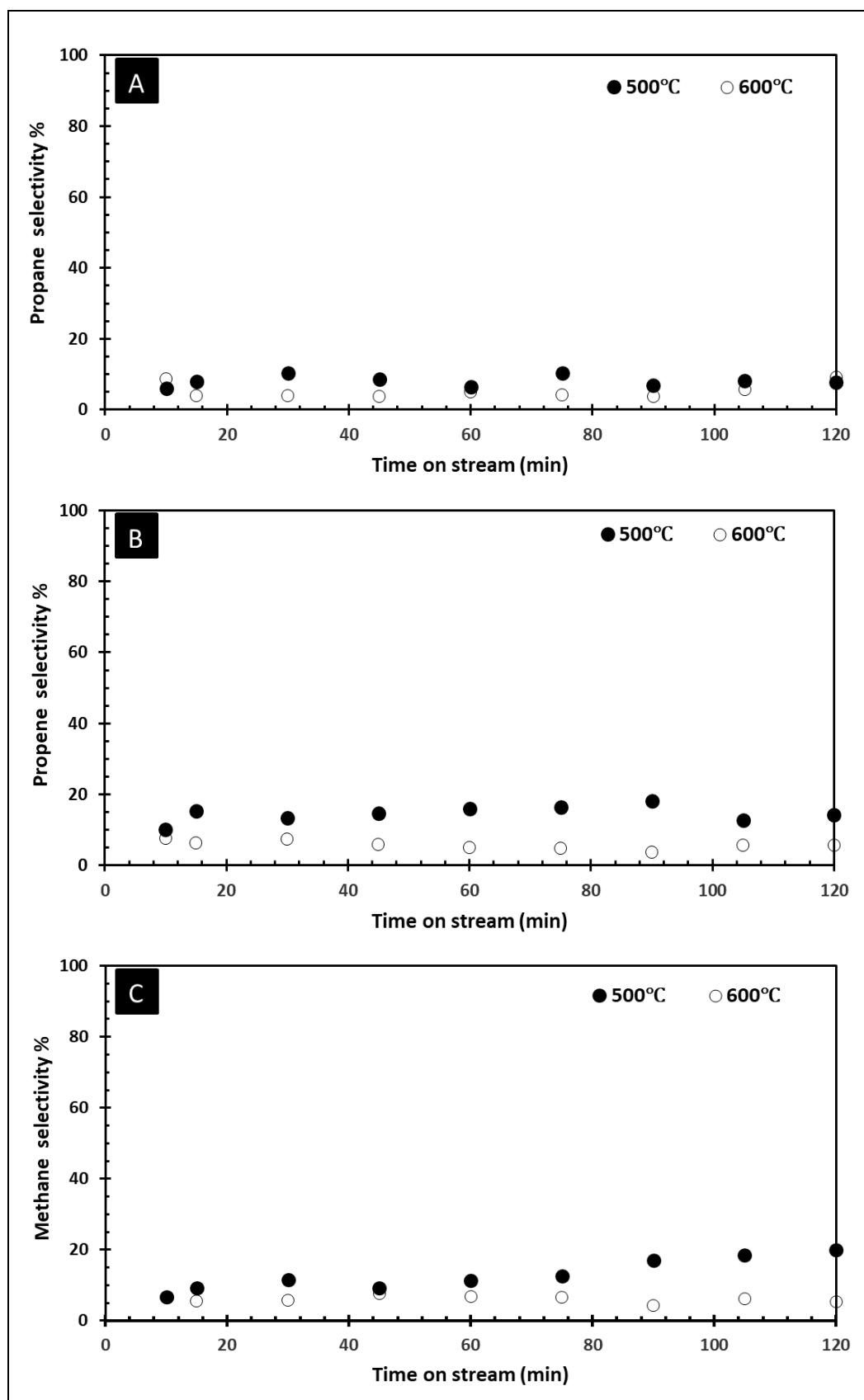


Figure 5.22. Propane, propene, and methane selectivity values at different reaction temperatures (catalyst: 10Cr/Ti-MCM-41, $i\text{-C}_4\text{H}_{10}/\text{CO}_2$: 1/5, P: atmospheric, WHSV: 51 h^{-1})

The propane is produced by reaction R.4.



At 500°C, propane selectivity is expected to be higher due to the exothermic nature of the reaction. However, the values at 600°C and 500°C are similar and did not change significantly with time. It was thought that the chemical decomposition reaction for propane (R.6) has taken place at higher temperature (Hus et al., 2021).



Selectivity values for propene at 500°C are higher than at 600 °C. The formation reaction of propene is represented in equation R.5. Due to the endothermic nature of the reaction, at 600 °C propene selectivity is expected to be higher.



It is thought that at higher reaction temperatures, there could be an increased occurrence of side reactions that consume propene (R.7)(Monai et al., 2021).



In addition, the selectivity values for methane increased throughout the reaction time at 500°C. Methane is produced by the side reactions (R.4, R.5), but it was believed that at 600°C that chemical decomposition reaction for methane (R.8) were more likely to occur.



5.4.4. Effect of weigh hourly space velocity (WHSV) on catalytic activity

10Cr/Ti-MCM-41 catalyst demonstrated high isobutane conversion and isobutene selectivity values at different reactor temperatures. To investigate the effect of weight hourly space velocity (WHSV) on conversion and selectivity values over the 10Cr/Ti-MCM-41 experimental studies were performed at two different WHSV values (51 h⁻¹ and 72 h⁻¹). The effect of weight hourly space velocities (WHSV) on isobutane conversion and isobutene

selectivity values is shown in Figure 5.23, while the selectivity values of hydrogen, CO₂ and CO at different WHSV values is shown in Figure 5.24.

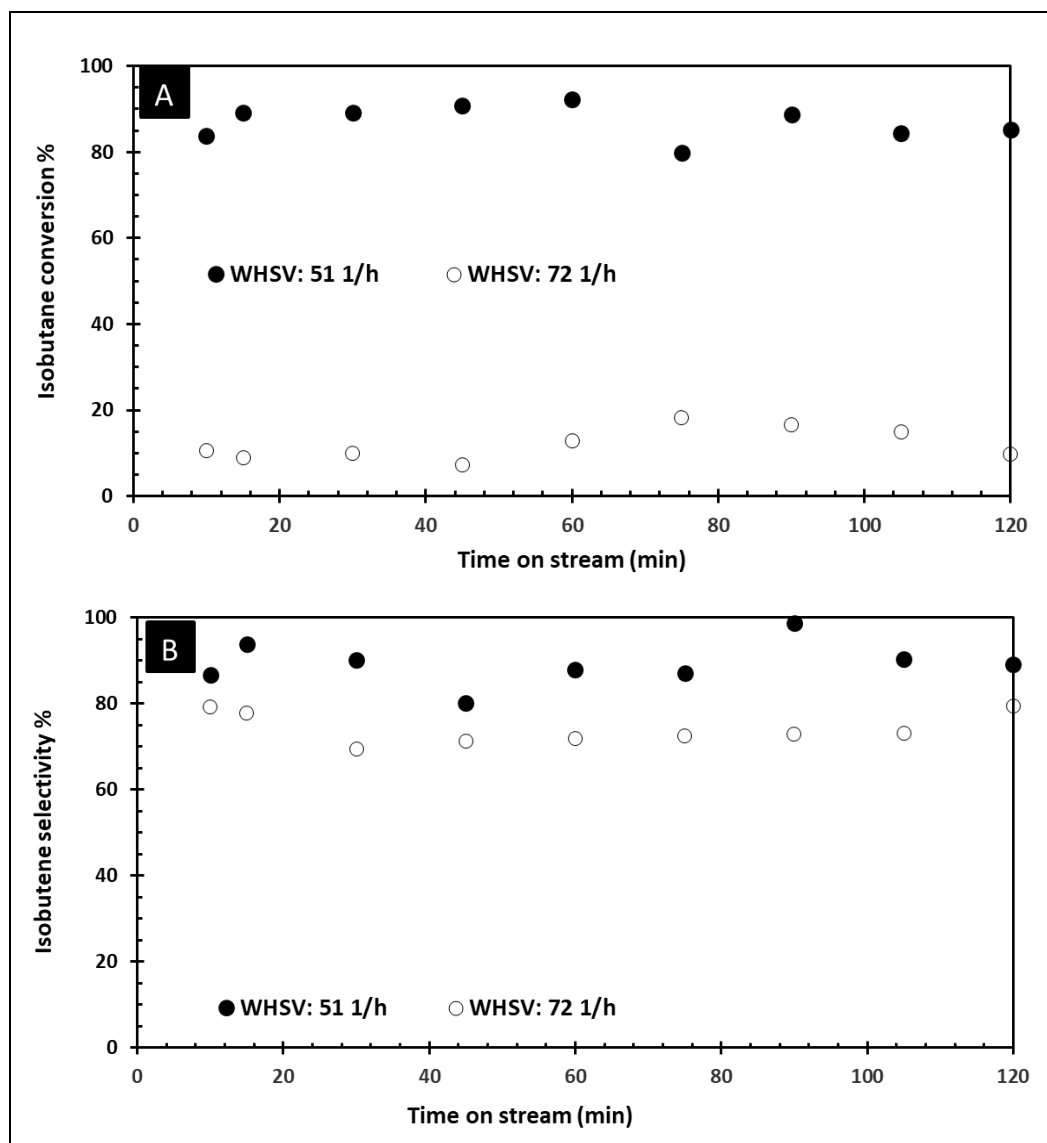


Figure 5.23. Isobutane conversion and isobutene selectivity values at different WHSV values (catalyst: 10Cr/Ti-MCM-41, i-C₄H₁₀/CO₂: 1/5, T: 600°C, P: atmospheric)

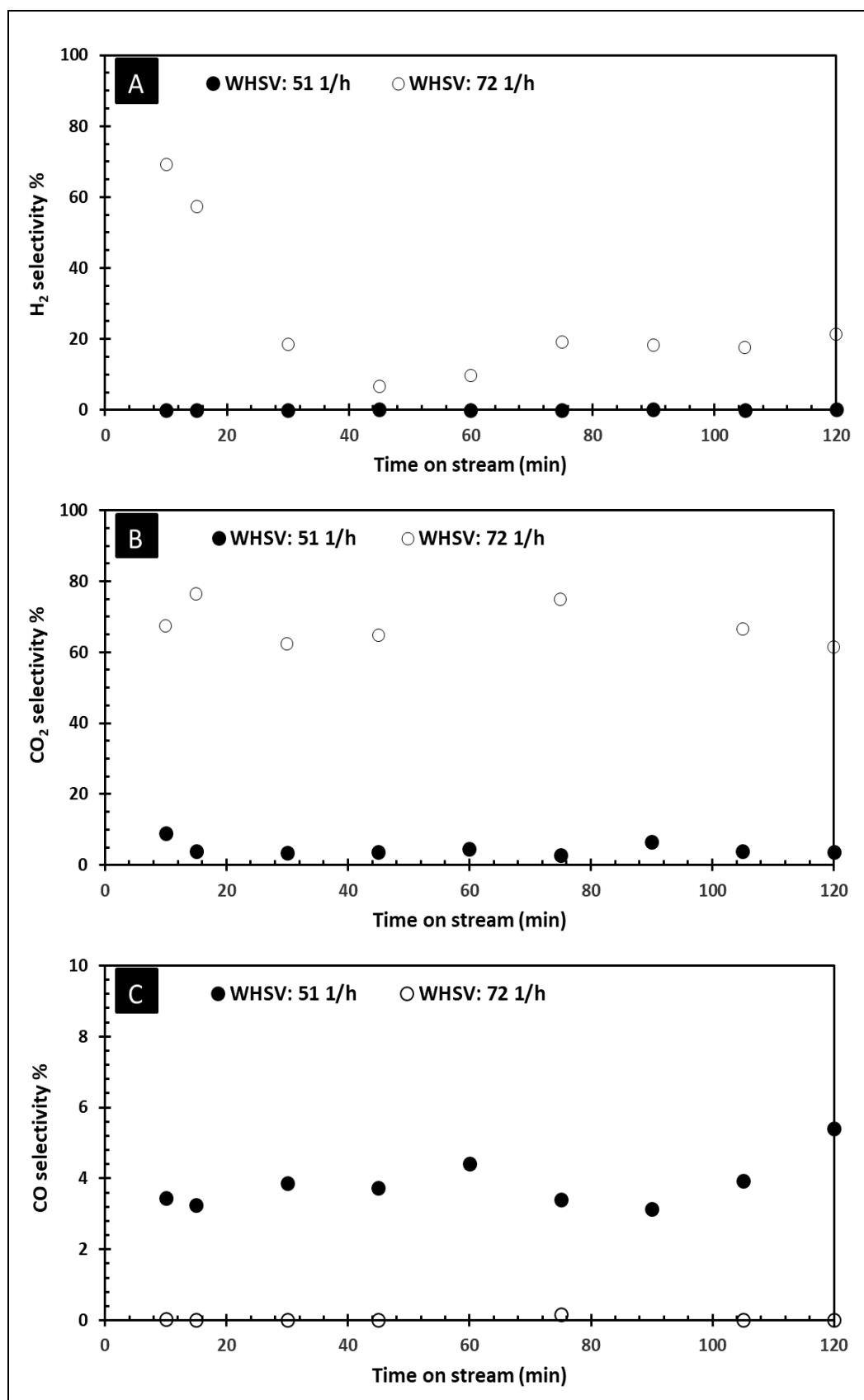


Figure 5.24. Selectivity values of hydrogen, CO₂ and CO at different WHSV values (Catalyst: 10Cr/Ti-MCM-41, i-C₄H₁₀/CO₂: 1/5, T: 600 °C, P: atmospheric)

Based on Figure 5.23, it is evident that increasing WHSV from 51 h⁻¹ to 72 h⁻¹ resulted in a decrease in the average isobutane conversion from 87% to 12%. Recent research states that the isobutane oxidative dehydrogenation reaction over Cr-based catalyst occurs by the adsorption of isobutane and CO₂ on the surface of the catalyst, the adsorption step is critical because it involves the binding of reactant molecules to the active sites on the catalyst (Otroshchenko et al., 2021). It was thought that decreasing the contact time (WHSV: 72 h⁻¹) affected the adsorption process. When increasing WHSV, there may not be sufficient time for reactants to be adsorb on the catalyst surface effectively. Also, it was noticed that the isobutene selectivity for WHSV: 72 h⁻¹ is lower compared to that of 51 h⁻¹ WHSV.

To understand the reason behind the significant decreases in isobutane conversion, the selectivity values for H₂, CO and CO₂ were analyzed (Figure 5.24). When comparing the selectivity values for H₂ and CO₂ at the two different WHSV values (51 h⁻¹ and 72 h⁻¹) it was observed that increasing the WHSV resulted in an increase in selectivity for both H₂ and CO₂. It is also noticed that, at WHSV: 72 h⁻¹, H₂ selectivity is about 70% at the beginning of the reaction, and it decreases dramatically throughout the first 30 minutes of the reaction. High H₂ selectivity indicates that the reverse water gas shift reaction (RWGS) did not occur at the beginning of the reaction; however, the decrease indicates that the reaction, takes place after. It is interesting that even with the reduction of H₂ selectivity, CO₂ selectivity is still high.

In the literature, it was stated that the main role of CO₂ in the oxidative dehydrogenation reaction is to prevent coke formation via the Boudouard reaction (R.9), which significantly enhances the stability of the catalyst (Ansari and Park, 2012).



Figure 5.24C shows that for lower WHSV, the CO selectivity values were high. At WHSV: 51 h⁻¹, high CO selectivity indicates that reactions R.3 and R.9 occurred, and the CO₂ had played its role as a soft oxidant. Therefore, it was thought that CO generation during the reaction is due to the strong effect of Boudouard reaction.



As seen from Figure 5.24B, at WHSV: 72 h⁻¹, CO₂ selectivity was higher. A higher WHSV results in shorter contact time, potentially reducing the extent of adsorption, especially for slower-adsorbing species. Isobutane has higher adsorption energy than CO₂ and H₂ due to its larger molecular size and stronger interactions with catalyst surfaces via van der Waals interaction (Corma, 1995). It was thought that, at low contact time, it becomes difficult to adsorb CO₂ and H₂ to the catalyst surface, which results in a lack of reverse water gas shift reaction (R.2).



This eventually leads to the absence of water in the reaction medium. Consequently, the monochromates that provide high activity and selectivity cannot be preserved. The literature proved that when CO₂ is adsorbed onto the catalyst surface, it increases the surface acidity, which could lead to undesirable side reactions (the adsorption of alkenes into the catalyst surface occurs in an acidic site). Also, when CO₂ is adsorbed onto the catalyst surface, the number of active sites available for alkanes' adsorption may decrease (Ansari and Park, 2012; Asghari et al., 2016; Mukherjee et al., 2016).

In summary, the lower conversion of isobutane at high WHSV was thought to be due to the excessive presence of CO₂ in the reaction environment. As previously discussed, this has a negative impact on isobutane conversion. In addition, the lack of Boudouard reaction and reverse water gas shift reaction decrease the catalyst's activity.

The propane, propene, and methane selectivity values obtained at different WHSV are given in Figure 5.25.

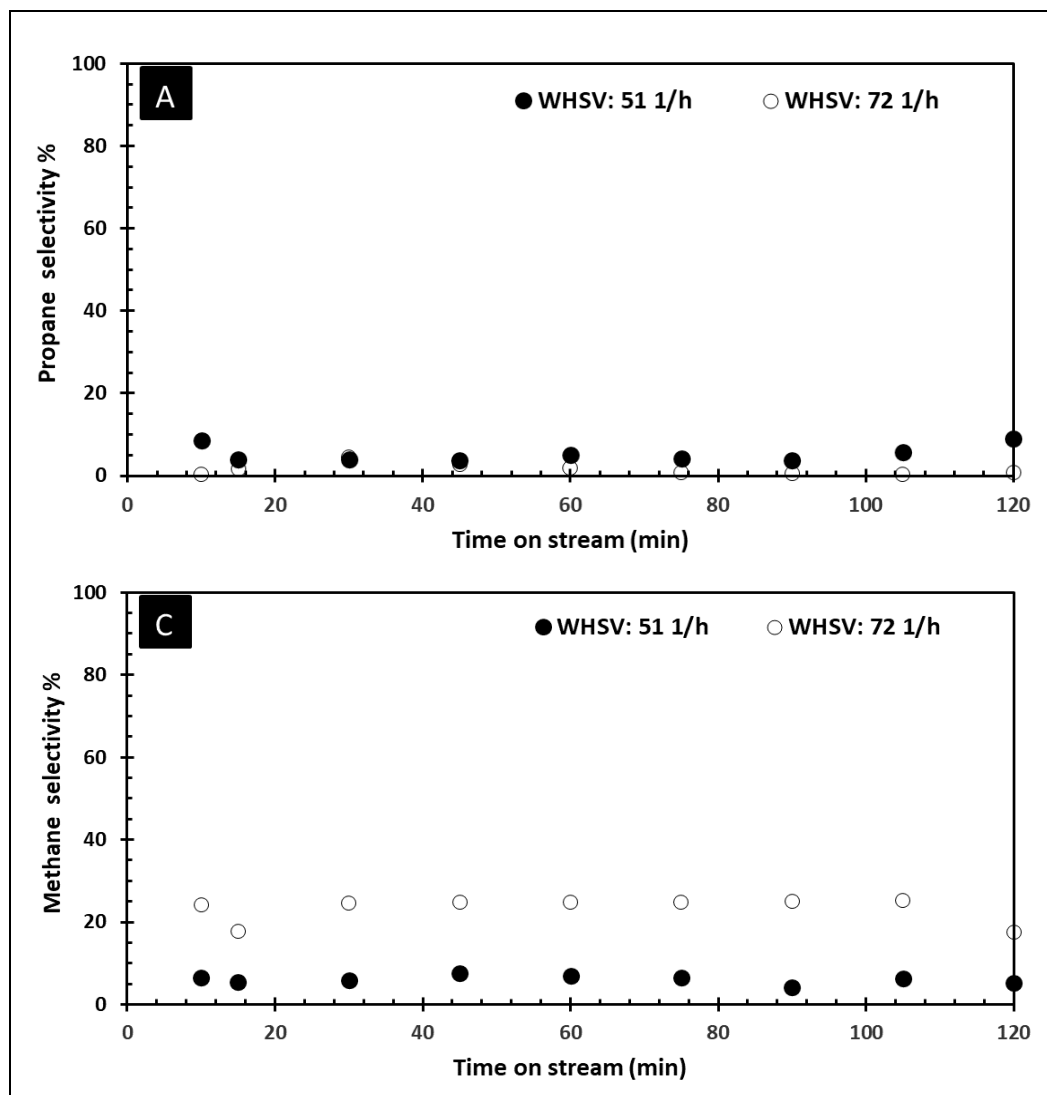


Figure 5.25. Propane, propene, and methane selectivity values at different WHSV values (Catalyst: 10Cr/Ti-MCM-41, $i\text{-C}_4\text{H}_{10}/\text{CO}_2$: 1/5, T: 600 °C, P: atmospheric)

Selectivity values for propane, propene, and methane show that side reactions were occurred (R.4 and R.5).

Selectivity values of propane and propene at both WHSV were similar (Figure 5.25A and B). When analyzing the gaseous medium for WHSV: 72 h^{-1} , higher H_2 concentration was observed, this should result in an increased propane concentration in the reaction medium (R.5).



The propane selectivity values (Figure 5.25A) did not match the expected outcomes. At 600°C, it was thought that the occurrence of propane decomposition reaction (R.6) would contribute to a reduction in the observed propane selectivity.



The endothermic nature of propene formation (R.4) ensures its occurrence at the elevated reaction temperature of 600°C.



However, despite the expected presence of propene, the observed selectivity remains relatively low; it was thought that there is a possibility of increased occurrence of propene decomposition reaction (R.7) that consume propene, consequently reducing the observed selectivity values.



As propane and propene were consistently selective across different weigh hourly space velocity (WHSV) values at 600°C. This suggests that the reaction is likely operating close to thermodynamic equilibrium conditions at this temperature. When this is the case, changes in WHSV may have limited effects on the overall product composition. The system stabilizes, and variations in WHSV do not significantly change the observed selectivity values for propane and propene.

In addition, the selectivity values for methane (Figure 5.25C) were higher at WHSV: 72 h⁻¹. It is observed that the formed methane does not decompose (R.8), especially when WHSV is 72h⁻¹.



5.5. Development of Reaction Rate Expression for Oxidative Dehydrogenation of Isobutane

Cr-based catalyst supported on titanium-modified MCM-41, synthesized by hydrothermal method, with 10wt.% Cr content and 2.5wt.% Ti loading (10Cr/Ti-MCM-41), showed high isobutane conversion and isobutene selectivity. Therefore, this catalyst was selected for the development of reaction rate expression for isobutane oxidative dehydrogenation.

The kinetic measurements for oxidative dehydrogenation of isobutane with CO₂ were obtained from the catalytic tests. The reaction was carried out in a quartz reactor with a diameter of 0.65cm and a length of 100cm at different reactor temperatures under atmospheric pressure. A 0.05 g catalyst was utilized. The reactant mixture consists of isobutane, carbon dioxide, and helium. The partial pressure of isobutane and CO₂ in the reactant mixture ranged from 5 kPa to 20 kPa. The gas samples were taken at the 15th minute of the experiment. Two sets of reaction conditions were designed to obtain the reaction rate expression. In the first set of reactions, catalytic tests were carried out at different isobutane partial pressures (5, 10, 15, 20 kPa), while CO₂ partial pressure was kept constant at 5 kPa. In the second set of reactions, catalytic tests were performed at different CO₂ partial pressures (5, 10, 15, 20 kPa), while isobutane partial pressure was kept constant at 5 kPa.

Catalytic test conditions for the first set of reactions:

- Catalyst amount (0.05g)
- The feed composition consists of isobutane, carbon dioxide, and helium.
- Various isobutane partial pressure (5, 10, 15, and 20 kPa) and constant CO₂ partial pressure at 5 kPa.
- Temperatures: 500°C, 550°C, and 600°C.
- Reaction time :15 minutes.

The catalytic test conditions for the second set of reactions were similar to those in the first set, with the only difference being the variation of the gas feed condition.

Differential reactor assumptions were considered during the development of the reaction rate expression. Due to the relatively low conversion values in differential reactors, the reaction

rate is assumed to remain constant. For a packed bed flow reactor, the reaction rate ($-R_A^*$) is expressed in terms of the catalyst amount (w) as

$$-R_A^* = \frac{X_A \cdot F_{A0}}{w} \quad (5.4)$$

The unit of the observed reaction rate is mol/g_{cat.} s.

The conversion values (X_A) determined from the experimental studies were used in the calculations of the observed reaction rate ($-R_A^*$), and the results at various temperatures were provided in Appendix-6.

In a multi-reaction system, determining the reaction orders for each reaction is not as straightforward as in a single-reaction case. Experimental data cannot provide direct access to reaction order for each reactant. Instead, the kinetic orders for the different reactants can be determined by analyzing the overall reactions and expressing it in terms of a power law kinetic model. The observed rate of reaction ($-R_A^*$) is expressed by "Eq. (5.5)(5.5)".

$$-R_A^* = k P_{i-C_4H_{10}}^\alpha P_{CO_2}^\beta \quad (5.5)$$

The kinetic orders for isobutane and carbon dioxide were α and β respectively. The reaction order of isobutane was calculated from experiment data obtained from set 1 (varying partial pressure of isobutane). Similarly, the reaction order of carbon dioxide was calculated from experiment data obtained from set 2 (varying partial pressure of CO₂).

$$-R_A^* = B P_{i-C_4H_{10}}^\alpha \quad (5.6)$$

When taking the natural logarithm of both sides of the rate equation (for set 1),

$$\ln(-R_A^*) = \ln B + \alpha \ln P_{i-C_4H_{10}} \quad (5.7)$$

$\ln(-R_A^*)$ was plotted against $\ln P_{i-C_4H_{10}}$, the slope gives the α . Similar steps were applied set 2 and β was determined. Then, the reaction rate constant k value was calculated from the rate equation. After finding k value at different temperatures, activity energy (E_A) was calculated.

The reaction order for isobutane was estimated by plotting the observed reaction rate versus the isobutane partial pressures, as shown in Figure 5.26.

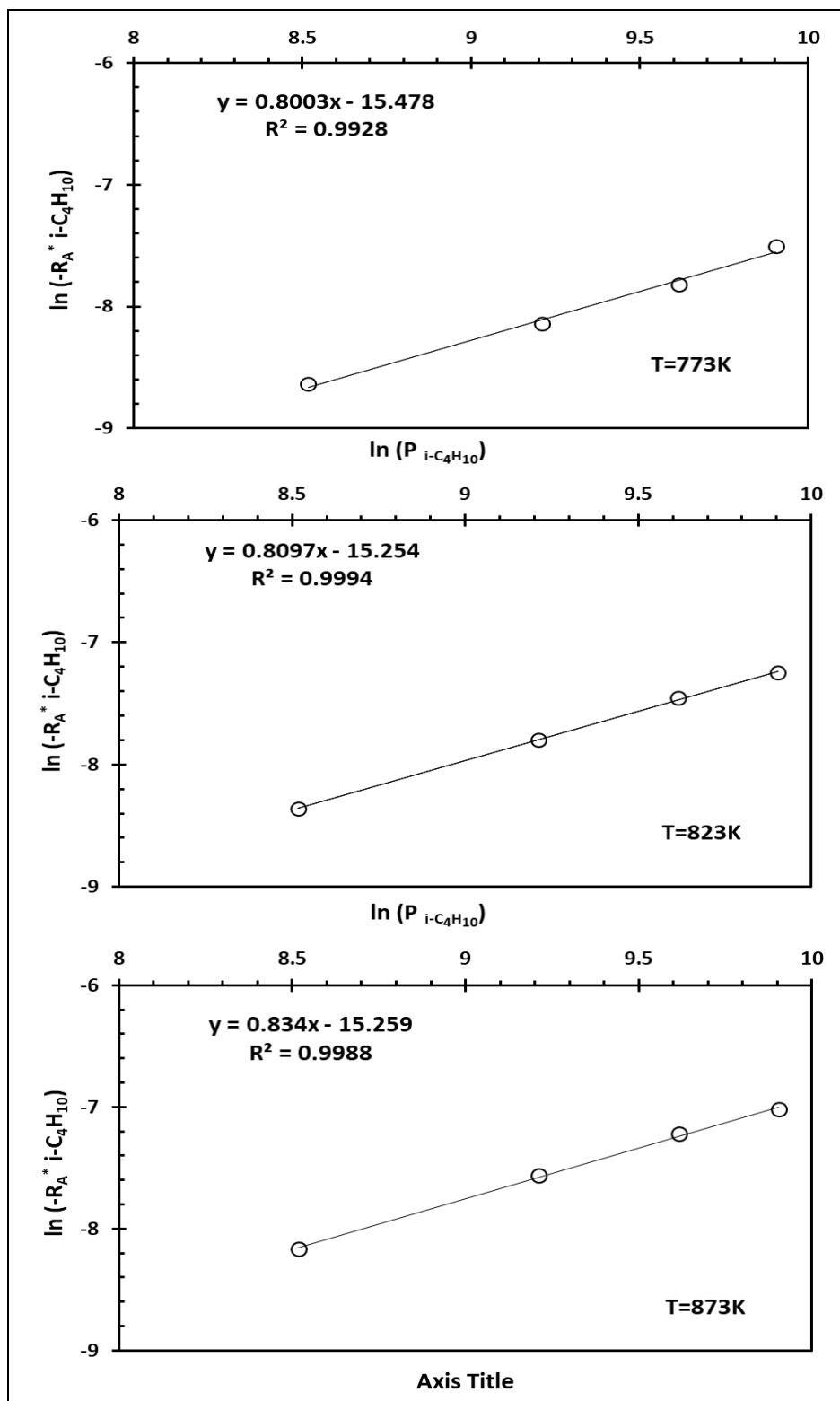


Figure 5.26. Observed reaction rate values versus partial pressure of i-C₄H₁₀ (catalyst: 10Cr/Ti-MCM-41, P_{CO₂}: 5 kPa, P_T: atmospheric)

According to the data obtained from first set of reactions, the reaction order in respect to isobutane is 0.82. Figure 5.27 displays plots of $\ln(-R_A^*)$ versus $\ln P_{\text{CO}_2}$ values to obtain reaction order for CO_2 over 10Cr/Ti-MCM-41 catalyst.

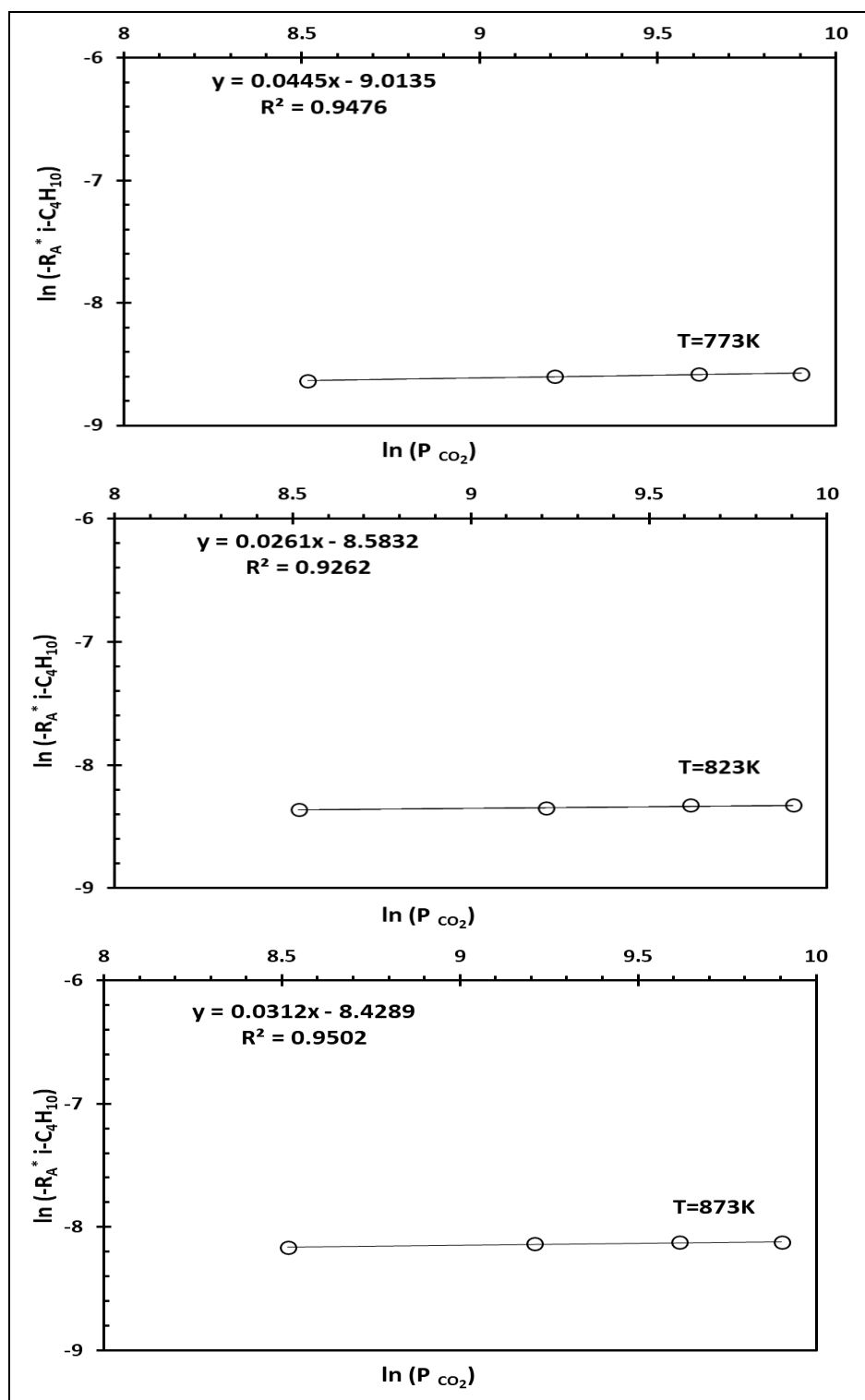


Figure 5.27. Observed reaction rate versus partial pressure of CO_2 (catalyst: 10Cr/Ti-MCM-41, $P_{i\text{-C}_4\text{H}_{10}}$: 5kPa, P_T : atmospheric).

According to the data obtained from the second set of reactions, the reaction order with respect to CO₂ is 0.03.

Based on the given orders of reaction, the rate equation for the oxidative dehydrogenation of isobutane with CO₂ can be expressed as:

$$-R_A^* = k P_{i-C_4H_{10}}^{0.82} P_{CO_2}^{0.03} \quad (5.8)$$

All the parameters in the above-mentioned equation are known except for the reaction rate constant (k) value. Therefore, this equation was used to calculate the k values at different temperatures and pressures. Then, for each temperature, the average values of k were taken. Reaction rate constant (k) values estimated for each temperature from the reaction rate equation are given in Table 5.9.

Table 5.9. Reaction rate constant (k) values calculated at different temperatures.

Temperature (K)	k ($\frac{\text{mol}}{\text{Pa}^{(0.82+0.03)} \text{ g}_{\text{cat}} \cdot \text{s}}$)
773	1.26×10^{-7}
823	1.67×10^{-7}
873	2.06×10^{-7}

The pre-exponential factor k_0 and activation energy (E_A) were calculated using the reaction rate constant (k) values. The Arrhenius equation was used for this calculation.

$$k = k_0 e^{\frac{-E_A}{RT}} \quad (5.9)$$

$$\ln k = \ln k_0 - \frac{E_A}{RT} \quad (5.10)$$

The plot in

Figure 5.28 displays the values of $\ln(k)$ versus the inverse of temperature ($1/T$) in order to obtain the activation energy and k_0 .

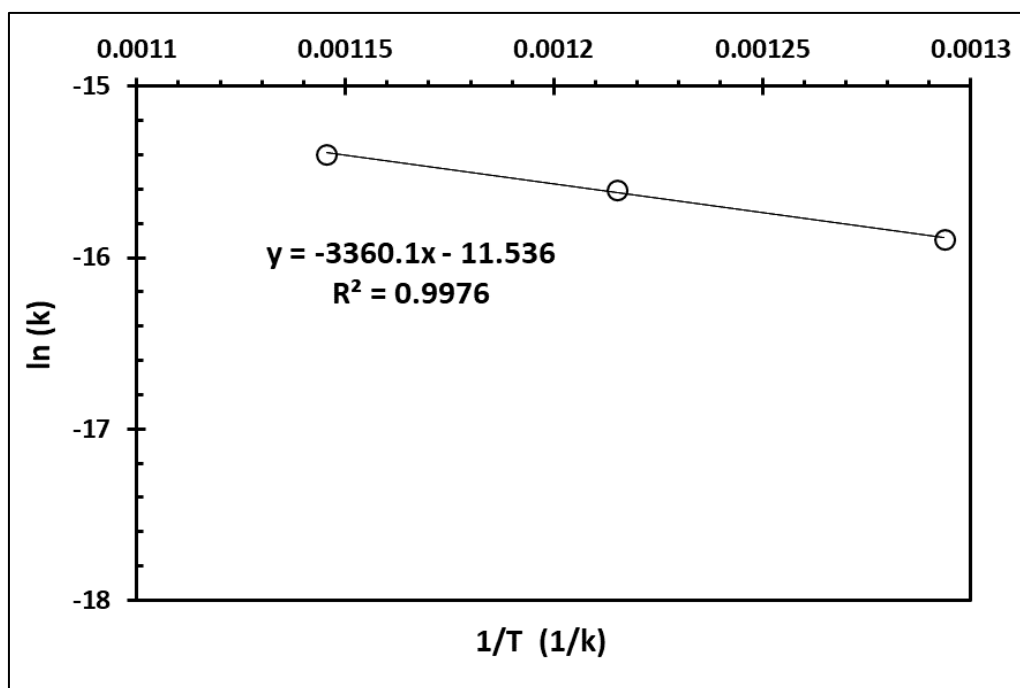


Figure 5.28. $\ln k$ values versus $1/T$ (catalyst: 10Cr/Ti-MCM-41, P_T : atmospheric)

The value of E_A is 27.9 kJ/mol and k_0 is $9.77 \times 10^{-6} \frac{\text{mol}}{\text{Pa}^{(0.82+0.03)} \text{g}_{\text{cat}} \cdot \text{s}}$.

Reaction rate expression obtained as a result of experimental studies is given below:

$$-R_A^* = 9.77 \times 10^{-6} e^{\frac{-27.9}{RT}} P_{i\text{-C}_4\text{H}_{10}}^{0.82} P_{\text{CO}_2}^{0.03} \quad (5.11)$$

When reviewing the literature, one study was conducted to investigate the activation energy of oxidative dehydrogenation of isobutane using CO_2 as soft oxidant. The results of reaction order in respect to isobutane and CO_2 was compared with studies carried for oxidative dehydrogenation of n-butane and propane with various oxidant (O_2 , N_2O , and CO_2).

In a study by Ogonowski and Skrzynska, the isobutane dehydrogenation over VMgOx was carried out in the presence of CO_2 at temperatures between 823 and 760 K, the apparent activation energy was found to be 29 kJ/mol. According to their research, the isobutane dehydrogenation over VMgOx occurs in two different areas as shown in Figure 5.29.

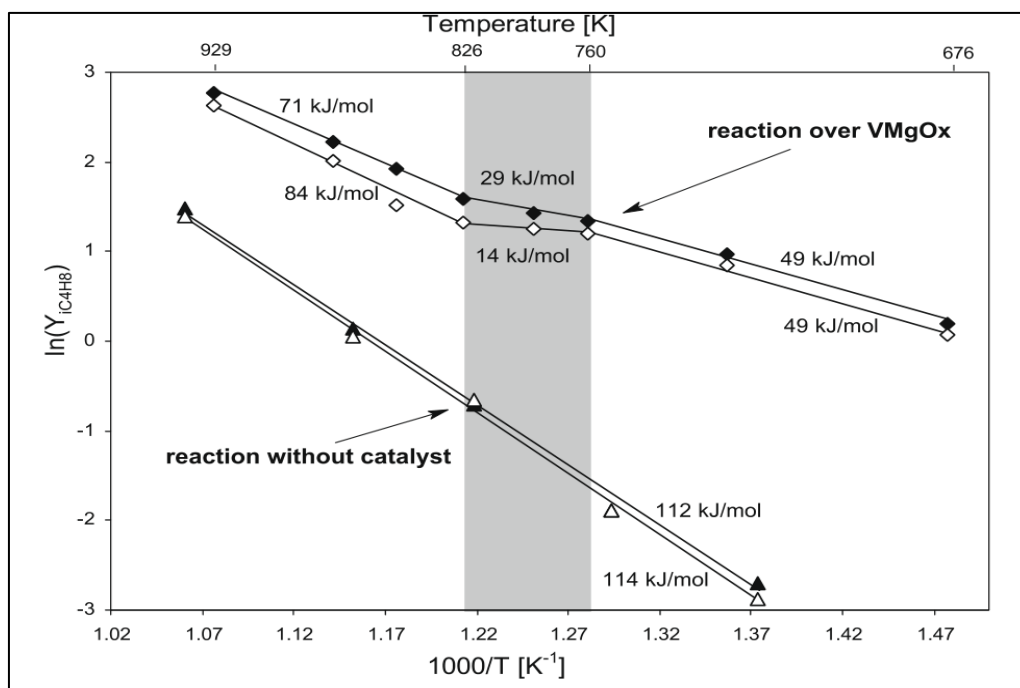


Figure 5.29. Arrhenius plot for the dehydrogenation of isobutane in the presence (full symbols) or absence (open symbols) of carbon dioxide in the feed (Ogonowski and Skrzynska, 2009)

At temperatures below 760 K, the apparent activation energy remains constant at 49 kJ/mol, whether CO_2 is present or not. This implies that both processes occur in a similar manner, by direct dehydrogenation (as in R.1). However, at temperatures above 826 K, the apparent activation energy of the reaction in the presence of carbon dioxide is lower than that under a helium atmosphere (71 and 84 kJ/mol, respectively). Therefore, the presence of carbon dioxide significantly enhances the conversion of isobutane over VMgOx catalyst (Ogonowski and Skrzynska, 2009).

Chaar et al. conducted a study on n-butane ODH using V-Mg-O catalyst, they applied a power law model to describe the reaction and they concluded that the reaction rate was zero order in oxygen and 0.85 order in n-butane (Chaar et al., 1987).

Hoang et al. studied the oxidative dehydrogenation of isobutane to isobutene over chromium oxide supported on lanthanum carbonate, they found the reaction to be first order in isobutane and zero order in oxygen and apparent activation energy for the formation of isobutene of 76 kJ/mol based on a redox (Mars–van Krevelen) mechanism (Hoang et al., 2010).

The study performed by Dasireddy et al. aimed at determining the activation energies (E_A) for the oxidative dehydrogenation of n-butane on Ni-Mo/ Al_2O_3 catalyst. The temperature ranges between 523K and 823K. The results showed that the activation energy varied depending on the oxidant used. When O_2 was used as the oxidant, the E_A was found to be 75 kJ/mol. On the other hand, when CO_2 and N_2O were used, the E_A was found to be 161 kJ/mol and 112 kJ/mol, respectively (Dasireddy et al., 2017).

In a study carried out by Wang et al., oxidative dehydrogenation of propane in the presence of CO_2 over GaN/ SiO_2 catalysts, the reaction is first order in respect to propane and zero order with respect to CO_2 , the apparent activation energy (E_A) over 5GaN/Silicalite-1 catalyst was 55.7 kJ/mol (Wang et al., 2022).

After the derivation of the reaction rate expression for isobutane oxidative dehydrogenation, the data obtained from the experimental studies were analyzed using the SPSS program. Statistical analyses were performed to establish a correlation between the rate of reaction ($-R_A^*$) and the reaction constant (k). During the analysis, the rate of reaction is considered the dependent parameter, while the reaction constant is taken as the independent parameter. The values of the reaction rates were predicted according to the non-linear regression, and it was found that the predicted rate of reaction (R_p) values matched the observed rate of reaction ($-R_A^*$) values obtained from the experimental results.

The reaction rate values predicted (R_p) using the determined reaction rate constant and reaction orders are shown in Table 5.10. together with the experimentally determined ones.

Table 5.10. Comparison of experimental vs predicted reaction rate values (P: atmospheric)

T [°C]	$-R_A^*$	R_p
500	2.7×10^{-4}	2.69×10^{-4}
550	3.61×10^{-4}	3.62×10^{-4}
600	4.50×10^{-4}	4.49×10^{-4}

Based on the data presented in Table 5.10, it can be seen that the experimental reaction rate values ($-R_A^*$) closely match the predicted reaction rate values (R_p).

5.6. Mars–van Krevelen Mechanism for Isobutane Oxidative Dehydrogenation

The Mars-Van Krevelen mechanism involves two main steps. Firstly, a reactant is adsorbed on the catalyst surface. Secondly, a redox reaction occurs between the adsorbed species and lattice oxygen in the catalyst. Depending on the case, the mechanism may be simplified into a two-stage process or a more detailed three-stage mechanism may be proposed (Sharma et al., 2015).

The analysis of initial rate data provides an initial approximation for understanding the dependency of the reaction rate on individual parameters. The data were analyzed using the least squares method through the SPSS computer program. In this study, the aim was to analyze both two-stage and three-stage redox mechanisms for the reaction. Derivation of model-1 and model-2 were given in Appendix-7. Rate equations for model-1 and model-2 are presented in Table 5.11.

Table 5.11. Rate equation for Mars-Van Krevelen mechanism

Model	Mechanism	Rate equation
1	Two stage mechanism $A_g + CrO_x \xrightarrow{k_1} C_g + D_g + CrO_{x-1}$ $CrO_{x-1} + B \xrightarrow{k_2} CrO_x + E$	$-R_A^* = \frac{k_1 P_A k_2 P_B}{k_1 P_A + k_2 P_B}$
2	Three stage mechanism $A_g + CrO_x \xrightarrow{k_1} C_g + D_g + CrO_{x-1}$ $C - CrO_{x-1} \xrightarrow{k_2} C_g + CrO_{x-1}$ $CrO_{x-1} + B \xrightarrow{k_3} CrO_x + E$	$-R_A^* = \frac{k_1 k_2 k_3 P_A P_B}{(k_3 k_2 P_B + k_1 k_2 P_B P_A + k_1 k_3 P_A)}$

The given equations in Table 5.11 were solved to find constants k_1 , k_2 or k_3 , using the SPSS program by applying non-linear regression.

For model-1 and model-2, the reaction rate constant (k) values were determined by using observed rate of reaction. The negative k values found in model-2 indicated model incompatibility. For this reason, it was assumed that the reaction did not occur as predicted by model-2. In literature studies it was seen that elimination was done by this way (Sharma et al., 2015).

Figure 5.30 displays the variations of $-R_A^*$ with $i\text{-C}_4\text{H}_{10}$ partial pressure at different reaction temperatures (500-600°C) and carbon dioxide partial pressure of 5kPa. The experimental

values are represented by points, while the calculated reaction rates for model-1 are shown by solid lines.

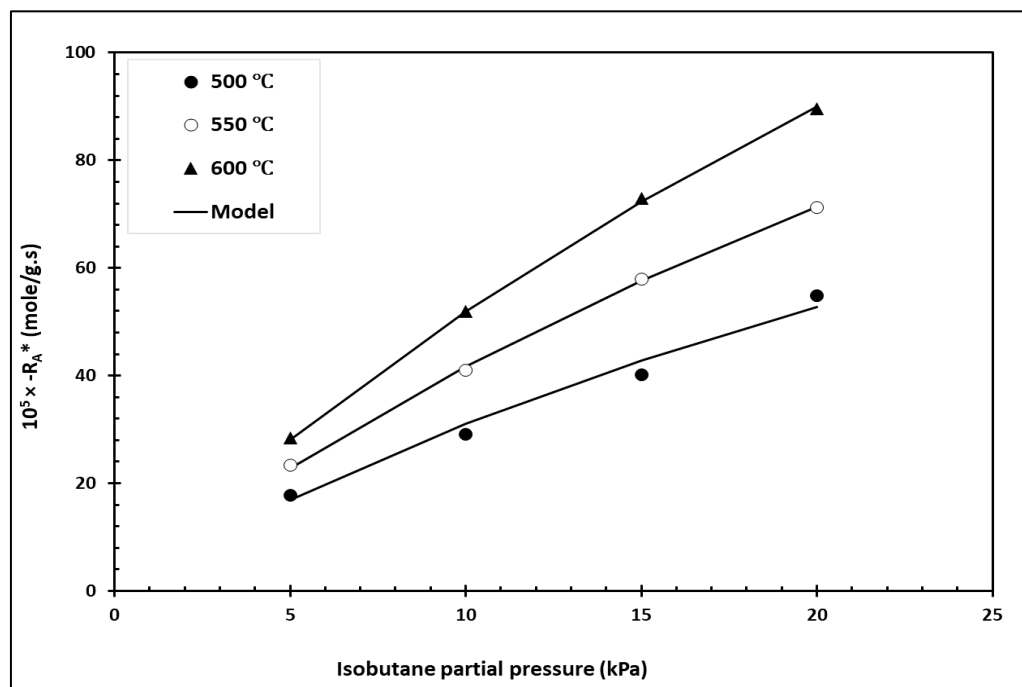


Figure 5.30. Variation of $-R_A^*$ with isobutane partial pressure (catalyst: 10Cr/Ti-MCM-41, CO_2 partial pressure: 5 kPa, model-1)

In Figure 5.30, it can be observed that the behavior of isobutane follows a first-order relation at low partial pressure. However, at higher partial pressure, the relationship becomes non-linear, which means it follows a Langmuir-type rate expression. This pattern is typical for oxidative dehydrogenation reactions on redox catalysts, where one of the adsorbed reactants is in equilibrium with the gas phase (Otroshchenko et al., 2021). The lattice oxygen on the redox catalyst was observed to participate in the reaction (Chen et al., 2023; Hossain, 2017). It is believed that the reaction rate primarily depends on the partial pressure of isobutane. This assumption is based on the premise that the lattice oxygen is replenished at a rate that is equal to or higher than that of its removal.

Figure 5.31 illustrates how the rates of isobutane change in response to different carbon dioxide partial pressures at varying reaction temperatures (500-600 °C), with a constant $i\text{-C}_4\text{H}_{10}$ partial pressure of 5 kPa. The experimental data is represented by points, and the calculated reaction rates for model-1 are shown by solid lines.

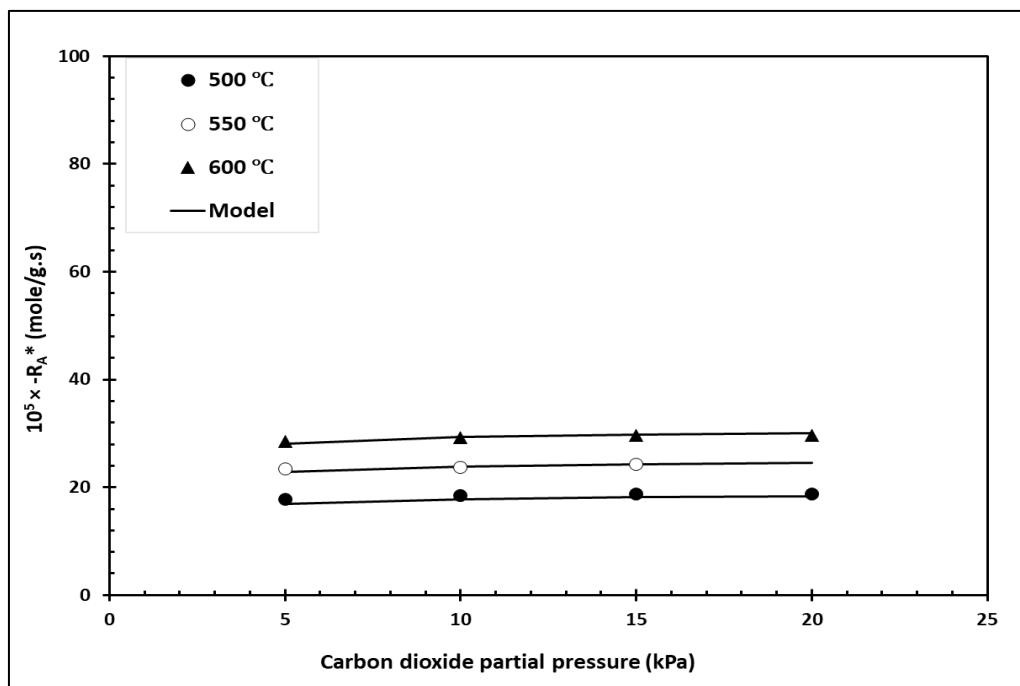


Figure 5.31. Variation of $-R_A^*$ with carbon dioxide partial pressure (catalyst: 10Cr/Ti-MCM-41, $i\text{-C}_4\text{H}_{10}$ partial pressure: 5 kPa, model-1).

Figure 5.31 shows zero-order with respect to carbon dioxide partial pressure. Assuming no mass transfer limitations, the oxidation of hydrocarbon on redox metal oxide catalyst is expected to occur. The reaction takes place between the adsorbed isobutane and lattice oxygen, leading to the reduction of the catalyst. It's important to note that if the rate of re-oxidation of the catalyst is fast compared with the rate of removal of lattice oxygen, the rate of isobutane reaction would be independent of carbon dioxide partial pressure. This figure clearly shows this fact.

Oxidative dehydrogenation of isobutane is described by a Mars-van Krevelen given by model-1. The agreement between the calculated and observed rates is good, indicating that the kinetic models are consistent with the experimental data in the conditions studied. Table 5.12 provides the values of k_1 and k_2 in the model-1 equation.

Table 5.12. Rate constants determined using model-1

Rate constant (mol/gcat. s. Pa)	Reaction temperature °C		
	500	550	600
$k_1 \times 10^{-8}$	3.76	5.02	6.14
$k_2 \times 10^{-7}$	3.56	4.93	6.64

Data given in Table 5.12 were used to calculate the reaction rates for isobutane oxidative dehydrogenation based on Mars-van Krevelen mechanism. The results showed good agreement between the calculated and observed reaction rates, indicating that the kinetic model is consistent with the experimental data.

5.7. Reactor Modelling

Model equations for the fixed bed reactor were derived. The assumptions in modeling studies are listed below:

- Ideal gas conditions.
- The reactor is operating at steady state conditions.
- Plug flow conditions are available in the catalyst bed.
- There is no pressure drop through the catalyst bed.
- The temperature variation in the radial and axial directions in the catalyst bed is negligible (Isothermal conditions).
- Negligible mass and heat transfer limitation
- No deactivation of the catalyst
- Only catalytic conversion was assumed.

The mass balance was derived for the system. The reaction rate expression was combined with the mass balance equation to obtain the reactor model equation. The reactor model was analyzed for two different temperatures, 600°C and 500°C, under atmospheric pressure, with a gas feed rate of 50 ml/min (WHSV: 51h⁻¹). The differential volume element for the mass balance can be seen in Figure 5.32.

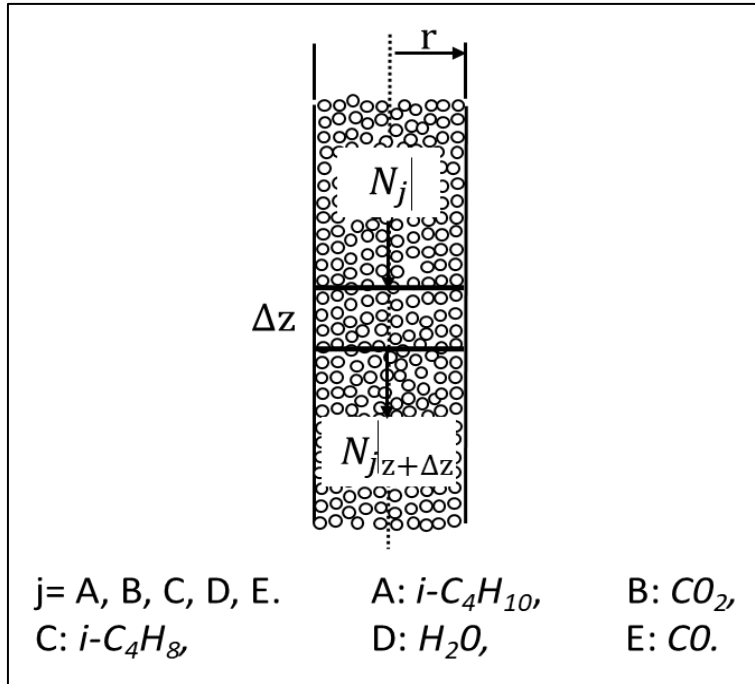


Figure 5.32. Differential volume element for which model equations are derived.

Mole balance for isobutane (A);

$$-v_0 \frac{dC_A}{dz} + R_A^* \rho (1 - \varepsilon) = 0 \quad (5.12)$$

Mole balance for CO₂ (B);

$$-v_0 \frac{dC_B}{dz} + R_B^* \rho (1 - \varepsilon) = 0 \quad (5.13)$$

Mole balance for isobutene (C);

$$-v_0 \frac{dC_C}{dz} + R_C^* \rho (1 - \varepsilon) = 0 \quad (5.14)$$

Mole balance for H₂O (D);

$$-v_0 \frac{dC_D}{dz} + R_D^* \rho (1 - \varepsilon) = 0 \quad (5.15)$$

Mole balance for CO (E);

$$-v_0 \frac{dC_E}{dz} + R_E^* \rho (1 - \varepsilon) = 0 \quad (5.16)$$

Equations from (5.12) to (5.16) are the obtained expressions for the reactor modeling. In the modeling studies, reaction rate expression developed for 10Cr/Ti-MCM-41 catalyst was used.

MATLAB R2011a/ODE45 program was used to solve the obtained ordinary differential equations. ODE45 is the solution program primarily used in solving ordinary differential equations with initial-value problems. All the calculations are given in Appendix-8.

After the solution of the model equations, the conversion value when the catalyst bed length (z) was equal to 2 cm matched the conversion value obtained from the experimental result. Table 5.13 displays the comparison between the results of the experimental study and those of the reactor modeling study.

Table 5.13. Isobutane conversion values determined from reactor modeling and experimental studies

Studies	Isobutane conversion (%)
Experimental (T: 873 K, P: atmospheric, WHSV:51 h ⁻¹)	92
Modeling (T= 873 K, P: atmospheric, WHSV:51 h ⁻¹)	98
Experimental (T= 773 K, P: atmospheric, WHSV:51 h ⁻¹)	89
Modeling (T= 773 K, P: atmospheric, WHSV:51 h ⁻¹)	87

Table 5.13 showed consistency between isobutane conversion values obtained from the experimental and modeling results. However, at 873 K, there was a 6% difference between the experimental and the modeling results. This difference is attributed to the fact that the model did not account for side reactions. It was confirmed that these side reactions do occur in the fixed-bed reactor at 873 K and WHSV 51h⁻¹ (Section 0). It is believed that these side reactions had an impact on the experimental findings, which explains the discrepancy observed at this temperature.

According to the model results, isobutane conversion values at different catalyst bed lengths at 873 and 773 K are given in Figure 5.33.

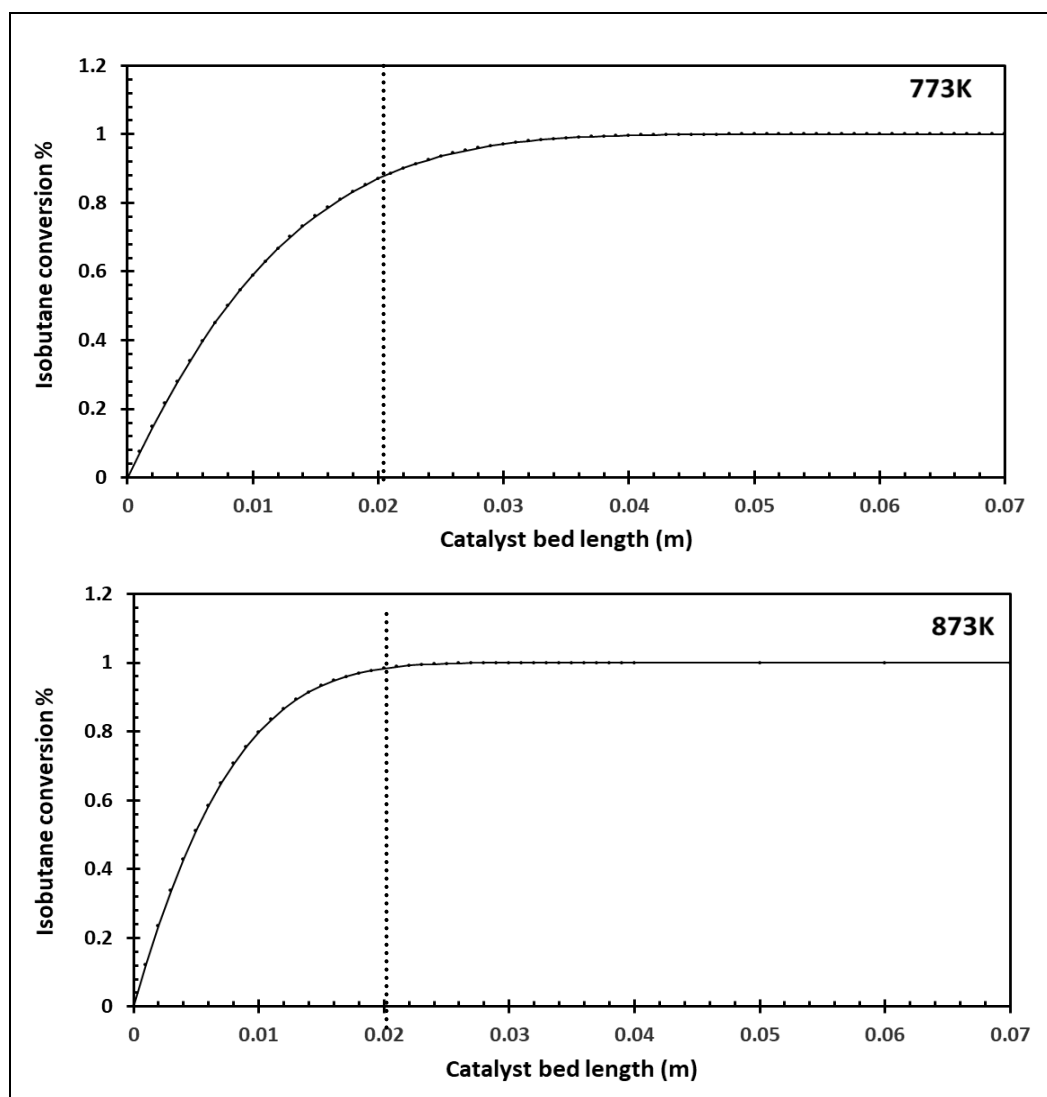


Figure 5.33. Change of isobutane conversion values along the catalyst bed as determined by the modeling studies (catalyst: 10Cr/Ti-MCM-41, P: atmospheric, WHSV: 51h⁻¹)

When comparing the isobutane conversion values at a bed length of 0.02 m, it was higher at 873 K than at 773 K. This difference reflected the temperature dependence of the reaction rate. It was thought that higher temperatures enhance the reaction kinetics, resulting in a faster and more complete conversion. It was also seen that near-complete conversion was achieved at a bed length of approximately 0.05 m for 773 K and 0.03 m for 873 K.

5.8. Studies on the Limitations of Heat and Mass Transfer

In heterogeneous catalytic reactions, the rate of the reaction is influenced by both heat and mass transfer. This study described the oxidative dehydrogenation of isobutane over a Cr/Ti-

MCM-41 catalyst using CO_2 as an oxidant in a fixed-bed reactor. The reaction is assumed to follow first-order kinetics. To understand the influence of mass transfer on the reaction rate, internal and external diffusion were examined using Weisz-Prater and Mears criteria. These criteria help determine whether mass transfer limitations are significant and need to be addressed in the analysis of the reaction kinetics. Furthermore, the study analyzes heat transfer limitations by calculating the temperature difference within the catalyst particle.

By examining both mass and heat transfer limitations, the study aims to provide a comprehensive understanding of the factors that control the rate of the oxidative dehydrogenation reaction. This understanding is crucial for optimizing reactor design and operating conditions, thereby enhancing the overall performance of the process.

5.8.1. Diffusion effects

In heterogeneous catalytic reactions, the movement of reactants and products into and out of the catalyst material can be hindered by mass transfer limitations caused by both internal and external diffusion. Internal diffusion occurs within the catalyst particle, while external diffusion occurs between the bulk fluid and the catalyst surface. These diffusion mechanisms act as resistances, which affect the rate of reaction, and they should not be neglected. Figure 5.34 shows the heterogeneous catalytic reactions steps taking place in a porous catalytic particle.

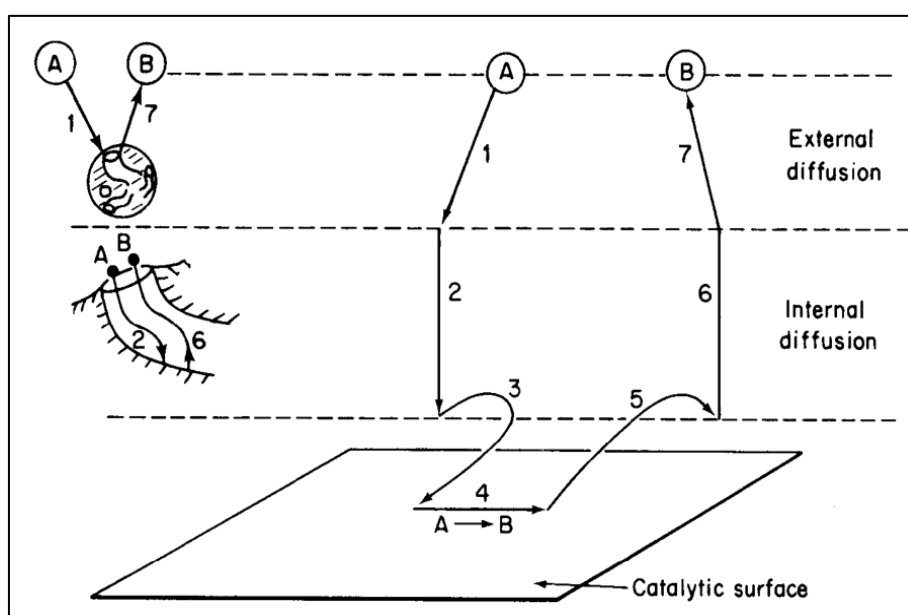


Figure 5.34. Steps in a heterogeneous catalytic reaction (Scott Fogler, 1987)

- 1) Mass transfer (diffusion) of the reactants from the bulk fluid to the external surface of the catalyst pellet.
- 2) Diffusion of the reactant from the pore mouth through the catalyst pores to the immediate vicinity of the internal catalytic surface.
- 3) Adsorption of reactant A onto the catalyst surface.
- 4) Reaction on the surface of the catalyst.
- 5) Desorption of the products from the surface.
- 6) Diffusion of the products from the interior of the pellet to the pore mouth at the external surface.
- 7) Mass transfer of the products from the external pellet surface to the bulk fluid.

For a spherical catalyst particle of radius r in which first-order reaction takes place at a steady state, the mass balance for A is given in Figure 5.35.

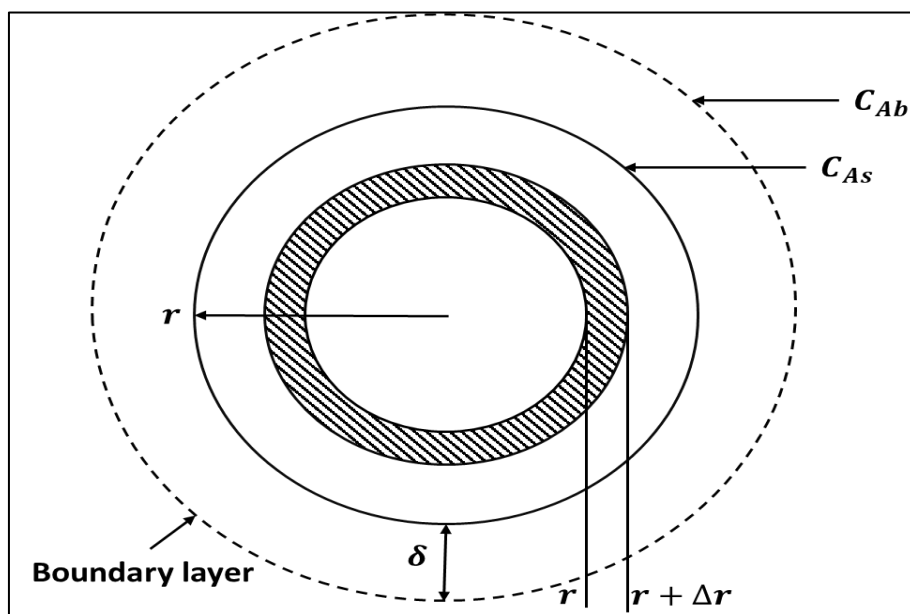


Figure 5.35. Shell Balance on a catalyst particle

Shell Balance on a catalyst particle:

[Rate of mass A in]-[Rate of mass A out]+ [Rate of disappearance of A within the element Δr]= 0

$$[4\pi r^2 N_A]_r - [4\pi r^2 N_A]_{r+\Delta r} + [-R_A^* \rho_C 4\pi r^2 \Delta r] = 0$$

$$\frac{d(N_A r^2)}{dr} - R_A^* \rho_c r^2 = 0 \quad (5.17)$$

The molar flux of A is given by,

$$N_A = -D_e \frac{dC_A}{dr} \quad (5.18)$$

where D_e is effective diffusivity given by;

$$D_e = \frac{D_{AB} \varepsilon}{\tau} \quad (5.19)$$

Where:

D_{AB} is diffusion coefficient in gas filling the pores,

ε is the pellet porosity,

The tortuosity (τ) (Abbas, 2011) of catalyst is calculated from porosity by;

$$\tau = 1 - 0.5 \ln \varepsilon \quad (5.20)$$

Thiele modulus Φ_1 of first reaction order is given by;

$$\Phi_1 = \frac{\text{Surface reaction rate}}{\text{Diffusion rate}} = r \sqrt{\frac{k_1'' S_a \rho_c}{D_e}} \quad (5.21)$$

Where:

r is the radius of catalyst particle,

k_1'' is the rate constant per unit surface area of catalyst,

S_a is the surface area of catalyst,

ρ_c is the catalyst density.

If the Thiele modulus is very high, the mass transfer controls the reaction, and if it is low, then the surface reaction is the rate-limiting step.

The internal effectiveness factor (η) is a parameter that can also be used to determine if the rate of a chemical reaction is limited by internal diffusion. The value of η depends on the order of the reaction and the shape of the catalyst used. In the case of a first-order reaction on a spherical catalyst (Scott Fogler, 1987), the internal effectiveness factor can be expressed as follows:

$$\eta = \frac{3}{\Phi_1^2} (\Phi_1 \coth \Phi_1 - 1) \quad (5.22)$$

The internal effectiveness factor (η) is nearly equal to 1 when internal diffusion in the catalyst is negligible.

The Weisz–Prater Criterion utilizes the observed reaction rate ($-R_A^*$), obtained from experimental measurements to determine if internal diffusion limits the reaction.

$$C_{WP} = \frac{\text{Observed reaction rate}}{\text{Diffusion rate}} = \frac{-R_A^* \rho_C r^2}{D_e C_{As}} \quad (5.23)$$

The Weisz–Prater criterion dictates that:

If $C_{WP} \ll 1$ no internal diffusion limitations

If $C_{WP} \gg 1$ internal diffusion limitations

C_{WP} can be calculated to determine if there are any diffusion limitations, as all the terms in Equation (7) are either measured or known. The parameter values required for calculating the Weisz-Prater criteria are given in Appendix-9.

When substituting the given values in Appendix-9, the C_{WP} value was equal to 0.01.

$$C_{WP} = 0.01 \rightarrow C_{WP} \ll 1$$

Which means internal diffusion is negligible in the reaction.

The Mears Criterion, like the Weisz–Prater criterion, uses the observed reaction rate ($-R_A^*$), to determine whether external mass transfer from the bulk gas phase to the catalyst surface can be neglected.

$$C_m = \frac{-R_A^* \rho_b r n}{K_c C_{Ab}} \quad (5.24)$$

Where:

ρ_b is the catalyst bulk density,

n is the reaction order (taken as 1),

C_{Ab} is the bulk concentration of A,

K_c : is the mass transfer coefficient.

Mears criteria proposed that:

If $C_m < 0.15$ no external diffusion limitations present, and no concentration gradient exists between the bulk gas and the external surface of the catalyst pellet.

The mass transfer coefficient (K_c) is calculated using the following equation

$$K_c = \frac{D_{AB} Sh(1-\varepsilon)}{d_p \varepsilon} \quad (5.25)$$

Sherwood number (Sh)(McCabe et al., 1993) when mass transfer occurs in a sphere pellet is given by

$$Sh = 2 + 0.6 Re^{1/2} Sc^{1/3} \quad (5.26)$$

The Sherwood, Reynolds, and Schmidt numbers are used in forced convection mass transfer correlations. For calculations of Re and Sc, various properties of gases are obtained from references (Doble, 2007; Lide, 2004). The values needed for calculating the Mears criteria are listed in Appendix-9.

$$C_m = 0.004 \rightarrow C_m < 0.15$$

Which means that the external diffusion is negligible.

5.8.2. Heat transfer effects in the catalyst

The study focuses on the oxidative dehydrogenation reaction of isobutane using CO₂, which is endothermic in nature. Unlike exothermic reactions, this reaction causes only minor non-isothermal effects within the catalyst, due to heat absorption by the reaction, the catalyst particle tends to be cooler than the surrounding fluid.

Radial heat flux in a spherical pellet is represented by

$$q_r = -4\pi R^2 K_{eff} \frac{dT}{dr} \quad (5.27)$$

Where:

q_r is the rate of heat transfer in the radial direction and K_{eff} is the effective thermal conductivity.

The effective thermal conductivity of a porous catalyst is an important factor that affects the temperature gradients within the catalyst pellet. One useful way to predict thermal conductivities is the geometric average value by Woodside and Messmer (Hill and Root, 1977).

$$K_{eff} = K_s^{1-\varepsilon} K_f^\varepsilon = K_s \left(\frac{K_f}{K_s} \right)^\varepsilon \quad (5.28)$$

Where:

K_s is the thermal conductivity of solid.

K_f is the thermal conductivity of fluid.

The value of K_{eff} was 0.2 W/m.K.

The temperature difference (ΔT) within the catalyst particle, is determined by Prater's equation for any particle geometry and kinetics.

$$\Delta T_{partical} = \frac{D_e(C_{As}-C_{A,centre})}{K_{eff}} \quad (5.29)$$

$\Delta T_{partical}$ is nearly equal to zero, this indicates that the temperature gradient inside the catalyst particle is negligible. It is confirmed that the catalytic reaction is isothermal. All calculations were provided in Appendix-9.

6. CONCLUSION AND RECOMMENDATIONS

The conclusions of the conducted studies are provided below.

Evaluation of the Equilibrium Calculations

- The equilibrium calculations were carried out for the isobutane oxidative dehydrogenation reaction. The results reveal that, at a temperature of 900 K, for $i\text{-C}_4\text{H}_{10}/\text{CO}_2$ molar ratios of 1/5, 1/9, and 1/15, isobutane conversion values were 53.25%, 97.90 %, and 99.99%, respectively. This indicates that increasing the number of moles of CO_2 shifts the equilibrium of the isobutane oxidative dehydrogenation reaction into completion.

Evaluations of the Characterization Studies of Pure MCM-41 and titanium-modified MCM-41

- After the loading of titanium onto the MCM-41, the hexagonal structure of MCM-41 was preserved. titanium-modified MCM-41 isotherms exhibited Type IV isotherm with Hysteresis I.
- TiW-MCM-41 had BET surface area of $554 \text{ m}^2/\text{g}$ and pore volume $0.59 \text{ cm}^3/\text{g}$. TiA-MCM-41 showed BET multi-point surface area of $473 \text{ m}^2/\text{g}$, and the mean pore volume of $0.57 \text{ cm}^3/\text{g}$. Both materials had an average mesopore diameter of $22 \text{ \AA}$.
- The addition of titanium led to the formation of strong bonds like Ti-OH, Si-O-Ti, and Ti-O metal oxides. The presence of these bonds led to significant improvements in the hydrothermal stability of the MCM-41, improved the resistance to collapse, and helped maintain the ordered mesoporous structure of MCM-41.

Evaluations of the Characterization Studies for Cr-Based Catalysts

- The wide-angle XRD patterns of 3Cr/Ti-MCM-41 and 3Cr@Ti-MCM-41 did not show peaks corresponding to $\alpha\text{-Cr}_2\text{O}_3$.
- The formation of the anatase phase of TiO_2 and $\alpha\text{-Cr}_2\text{O}_3$ were observed for 10Cr@Ti-MCM4 and 10Cr/Ti-MCM41 catalysts.

- Smaller CrO_x and TiO₂ crystals were formed using hydrothermal synthesis method. Also, the prepared catalysts showed a homogeneous structure.
- The ordered structure of the MCM-41 support was retained even after the loading of Ti and Cr.

Evaluations of the Catalytic Activity Tests

- The catalytic activity was studied under two different i-C₄H₁₀/CO₂ molar ratios (1/9 and 1/5). The highest isobutene selectivity values were achieved when the i-C₄H₁₀/CO₂ molar ratio was 1/5. That is why it was chosen to be utilized for the following catalytic test.
- Among the catalysts prepared using the hydrothermal synthesis method, 10Cr/Ti-MCM-41 showed the best stability. Similarly, among the catalysts synthesized using the impregnation method, 10Cr@Ti-MCM-41 demonstrated the highest stability.
- The 10Cr/Ti-MCM-41 catalyst showed higher isobutane conversion and isobutene selectivity after 75 minutes of reaction compared to 10Cr@Ti-MCM-41. This improved stability is probably due to the smaller Cr and Ti crystallite sizes in 10Cr/Ti-MCM-41. Because of this, 10Cr/Ti-MCM-41 was chosen for further investigations.
- Isobutane conversion and isobutene selectivity decreased significantly for 10Cr/MCM-41, while 10Cr/Ti-MCM-41 maintained high values throughout the reaction time. High catalytic activity observed for 10Cr/Ti-MCM-41 was explained by the improved hydrophilic properties.

The reaction rate expression for 10Cr/Ti-MCM-41 catalyst was identified as

$$-R_A^* = 9.77 \times 10^{-6} e^{\frac{-27.9}{RT}} P_{i\text{-C}_4\text{H}_{10}}^{0.82} P_{\text{CO}_2}^{0.03}$$

Evaluations of the Mars–van Krevelen Mechanism

- The oxidative dehydrogenation of isobutane follows the Mars-van Krevelen mechanism, described by a two-stage process (model-1). Good agreement between the calculated and observed reaction rates was observed.

Evaluations of the Reactor Modelling

- Model equations for the fixed bed reactor were derived. In the modeling studies, reaction rate expression developed for 10Cr/Ti-MCM-41 catalyst was used.
- The difference between the model and experimental results (at 873 K) is explained by the fact that side reactions are not included in the model equations.

Evaluations of the Heat and Mass Transfer Effects

- It was shown that internal and external diffusion are negligible, and the temperature gradient limitations inside the catalyst particle is negligible.

Based on the obtained results, here are some recommendations for future work to further enhance the performance of the catalysts used for isobutane oxidative dehydrogenation (ODH).

Investigation of Catalyst Stability and Deactivation Mechanisms

- Since stability and deactivation are critical for catalyst performance. For the selected catalyst (10Cr/Ti-MCM-41), it is important to conduct a long-term stability test to study the potential deactivation mechanisms of the catalysts, focusing on coke deposition and structural changes over time, which may impact the catalytic performance.

Exploration of Operating Conditions

- Evaluation of catalytic performance under mild conditions (lower temperatures and pressures) to understand and determine the flexibility of the catalysts and identify operating conditions that minimize energy consumption.

Catalyst Supports modifications

- Further modifications of MCM-41 support with serum oxides is recommended. Incorporating CeO₂ provides redox functionality and oxygen storage capacity, which might improve catalytic activity. Testing other modifications, such as zirconium oxide

(ZrO₂) or lanthanum oxide (La₂O₃), could also enhance hydrothermal stability and catalytic activity.

- Investigating the effect of using alternative support like alumina oxides (Al₂O₃) is essential. Alumina (Al₂O₃) is a strong choice due to its availability, but it is worth emphasizing the importance of controlling its acidity to avoid undesired side reactions. Testing dual-function materials like magnesium aluminate (MgAl₂O₄) could provide both structural stability and tunable acidity. Also, it is thought that the addition of magnesium (Mg) and potassium (K) to the alumina structure might affect the surface acidity and help control the side reactions.

Reaction Mechanism Elucidation

- Advanced reaction models, such as the Langmuir-Hinshelwood and Eley-Rideal models, can be tested to gain a deeper understanding of the reaction mechanism and surface interactions.

The results obtained in this study are presented in Table 6.1. together with the dehydrogenation reaction results conducted in the literature.

Table 6.1. Comparison of the obtained results with the literature

Alkane	Oxidant	Catalyst	Condition	Catalytic activity	Ref.
Ethane	-	Ga ₂ O ₃ /Al ₂ O ₃	T: 650°C, P: atmospheric, WHSV: 22 h ⁻¹ .	conversion 28% selectivity 93%	(Nakagawa et al., 2000)
isobutane	-	Pt-Sn-K/γ-Al ₂ O ₃	T: 580°C, P: atmospheric, WHSV: 2 h ⁻¹ .	conversion 57% selectivity 94%	(Luo et al., 2013)
isobutane	-	Cr/MCM-41	T: 600°C, P: atmospheric, WHSV: 26 h ⁻¹ .	conversion 60 % selectivity 80%	(Erol et al., 2020)
Ethane	CO ₂	Ga ₂ O ₃ /Al ₂ O ₃	T: 650°C, P: atmospheric, WHSV: 22 h ⁻¹ .	conversion 29% selectivity 87%	(Nakagawa et al., 2000)
isobutane	CO ₂	3Cr-3Ce/SBA-15	T: 570°C, P: atmospheric, Flow rate: 19.3 mL/min ⁻¹ .	conversion 35% selectivity 90%	(Wei et al., 2017).
isobutane	O ₂	Cr/ZnAlLaOx	T: 580, P: atmospheric, Space velocity: 200 mL/g•h.	conversion 52% selectivity 84%	(He et al., 2015)
isobutane	CO ₂	Cr/Ti-MCM-41	T: 600°C P: atmospheric WHSV: 51 h ⁻¹	conversion 89% selectivity 94%	This study
isobutane	CO ₂	Cr@Ti-MCM-41	T: 600°C P: atmospheric WHSV: 51 h ⁻¹	conversion 87% selectivity 91%	This study

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APPENDICES

APPENDIX-1. Calculations related to MCM-41 synthesis

Calculation of the amount of surfactant required.

Composition of sodium silicate solution:

Composition	% by mass	Molecular mass (M_A) g/mol
SiO ₂	27	60.084
Na ₂ O	8	61.979
H ₂ O	65	18.015

The density of Sodium Silicate solution = 1.391 g/mL.

The molecular weight of surfactant (N-cetyl N, N, N trimethyl ammonium bromide; C₁₉H₄₂BrN) = 364.46 g/mol .

Since the volume of sodium silicate solution used in the synthesis solution was taken as 11.3 ml.

To calculate the amount of SiO₂ in the solution:

$$density \rho = \frac{m}{V}$$

Where: ρ is density, m is mas and V is volume.

$$1.391 \frac{g}{ml} = \frac{m}{11.3 ml}$$

$$m = 15.72 g$$

Each 11.3 ml Sodium Silicate Solution contains 15.7183 g of SiO₂. The solution contains 27% SiO₂ therefore the amount of SiO₂ will be:

$$m_{SiO_2} = 15.72 \times 0.27 = 4.245 g$$

The number of moles can be calculated by:

$$n = \frac{m}{M_A}$$

Where: n is the number of moles, m is mass, and M_A is Molecular mass.

$$n_{SiO_2} = \frac{4.245 g}{60.084 g/mol} = 0.07065 mol$$

The surfactant/Si (mol/mol) ratio was chosen as 0.5.

$$\frac{n_{surfactant}}{n_{Silica source}} = 0.5$$

The number of moles for the silica source was calculated earlier. Therefore, the number of moles of the surfactant C₁₉H₄₂BrN can be determined by

$$n_{C_{19}H_{42}BrN} = 0.5 \times n_{SiO_2} = 0.5 \times 0.07 = 0.035 mol$$

Consequently, the mass of the surfactant C₁₉H₄₂BrN can be calculated by

$$cm_{C_{19}H_{42}BrN} = n \times M_A = 0.035 \times 364.46 = 12.87 g$$

That means 12.87 g of the surfactant C₁₉H₄₂BrN must be added to 11.3 ml of the sodium silicate solution for the ratio to be kept at 0.5.

APPENDIX-1. (continued) Calculations for Ti-doped MCM-41 material synthesis by the hydrothermal methods

Is an attempt to add 2.5 wt.% of titanium to the mesoporous metal-supported MCM-41.

$$\frac{x}{x + M_A} = \frac{a}{100}$$

Where: x is the mass of titanium, which is calculated based on 1 mole SiO_2 , M_A is the Molecular mass (g/mol) of the SiO_2 , and a is the titanium weight.

$$\frac{x}{x + 60.084} = \frac{2.5}{100}$$

$$(x * 100) - 2.5 * (x + 60.084) = 0$$

$$x = 1.54 \text{ g}$$

That means to keep the ratio of 2.5 wt.% titanium; for one mole of SiO_2 , an amount of 1.4771 grams of Titanium must be added. However, according to the calculation n of the amount of surfactant required, only 0.07 mole of SiO_2 is used. Based on that, the mass of titanium to be added is $m_{Ti} = 1.54 \times 0.07 = 0.109 \text{ g}$.

The titanium source is K_2TiF_6 (Dipotassium titanium hexafluoride), and its molecular mass is 240.051 g/mol . While the titanium molecular mass is 47.867 g/mol . How many grams must be used from K_2TiF_6 to get 0.1076 g of titanium?

$$m_{\text{K}_2\text{TiF}_6} = \frac{M_{\text{K}_2\text{TiF}_6} \times m_{Ti}}{M_{Ti}}$$

$$m_{\text{K}_2\text{TiF}_6} = \frac{240.051 \times 0.109}{47.867} = 0.546 \text{ g}$$

That means 0.546 g of the dipotassium titanium hexafluoride K_2TiF_6 must be used in the preparation of titanium doped MCM-41 material to get the titanium metal to be 2.5% by mass as planned.

APPENDIX-2. Calculations for Cr-based catalyst supported on Ti-modified MCM-41

using the hydrothermal methods synthesis (Cr/Ti-MCM-41)

It is an attempt to synthesize a catalyst containing 3 wt.% Cr and 2.5 wt.% Ti (3Cr/Ti-MCM-41)

$$\frac{x}{x + y + M_A} = \frac{a}{100}$$

Where: x is the mass of chromium and y is the mass of titanium, which is calculated based on 1 mole SiO_2 , M_A is the Molecular mass (g/mol) of the SiO_2 , and a is the chromium weight.

$$\frac{x}{y + x + 60.084} = \frac{3}{100}$$

$$\frac{Cr}{Ti} = \frac{x}{y} = \frac{3}{2.5} = 1.2$$

$$x = 1.2 y \text{ and } y = 0.833x$$

$$\frac{x}{0.833x + x + 60.084} = \frac{3}{100}$$

$$(100x) = 3 \times (0.833x + x + 60.084) = 2.5x + 3x + 180.25$$

$$x = \frac{180}{94.5} = 1.91g$$

That means to keep the loading ratio of 3 wt.% chromium; for one mole of SiO_2 , an amount of 1.9 grams of chromium must be added. However, according to the calculation made in Appendix-1 (Calculation of the amount of surfactant required), only 0.07 mole of SiO_2 is used. Based on that, the mass of chromium to be added will be $m_{Ti} = 1.91 \times 0.0706 = 0.135 g$.

The chromium source is chromium nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), its molecular mass is $400.15 g/mol$. The chromium molecular mass is $51.996 g/mol$. How many grams must be used from $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to get 0.135 g of chromium?

$$m_{\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}} = \frac{M_{\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}} \times m_{Cr}}{M_{Cr}}$$

$$m_{\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}} = \frac{400.15 \times 0.135}{51.996} = 1.036 g$$

That means 1.036 g of the chromium nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$)₆ must be used in the preparation of MCM-41 supported chromium catalysts to get the chromium metal to be 3% by mass as planned. From the calculations above $x = 1.9g$ the value of y can be derived as $y = 0.833x = 0.112$. That means the number of titanium grams must be used to get 2.5 wt.% Ti loading is 0.112 grams.

The titanium source is K_2TiF_6 (Dipotassium titanium hexafluoride), and its molecular mass is $240.051 g/mol$. The titanium molecular mass is $47.867 g/mol$. How many grams must be used from K_2TiF_6 to get 0.112 g of titanium?

$$m_{\text{K}_2\text{TiF}_6} = \frac{M_{\text{K}_2\text{TiF}_6} \times m_{Ti}}{M_{Ti}}$$

APPENDIX-2. (continued) Calculations for Cr-based catalyst supported on Ti-modified MCM-41

$$m_{K_2TiF_6} = \frac{240.051 \times 0.112}{47.867} = 0.56 \text{ g}$$

That means 0.556 g of the dipotassium titanium hexafluoride K_2TiF_6 must be used in the preparation of MCM-41 supported titanium catalysts to get the titanium metal to be is 2.5% by mass as planned.

$$n_{Cr} = \frac{m_{Cr}}{M_{Cr}} = \frac{0.135}{51.996} = 2.59 \times 10^{-3} \text{ mole.}$$

The number of moles of chromium existing in the used amount of the chromium nitrate is 0.00156 mole. Taking into consideration $n_{Si} = n_{SiO_2}$ the ratio between Si and Cr can be calculated as:

$$Cr/Si = 2.59 \times 10^{-3} / 0.07065 = 0.037$$

For loading of 6 wt.% Cr, an amount of 0.28 grams of chromium is needed. Therefore, 2.14 grams of chromium nitrate must be used in the synthesis of the catalyst. In addition to that, 2.5 wt.% Ti loading is planned to be added to the catalyst, to keep the Cr/Ti ratio at 2.4, an amount of 0.115 gram of Ti must be used in the catalyst synthesis, which means 0.58 gram of the dipotassium titanium hexafluoride.

The same calculation has been done for 10 wt.% chromium loading, an amount of 0.49 grams of chromium is needed, and 3.7 grams of chromium nitrate must be used in the synthesis of the catalyst. Additionally, 2.5 wt.% Ti loading is planned to be added to the catalyst and to keep the Cr/Ti ratio at 4, an amount of 0.12 gram of Ti must be used in the catalyst synthesis, which means 0.61 gram of the dipotassium titanium hexafluoride.

The Si/Cr ratios for 6wt.% and 10 wt.% Cr loading on the catalyst were also calculated; the ratios are 0.076 and 0.132, respectively.

Using the impregnation synthesis method (Cr@Ti-MCM-41).

It is an attempt to synthesize a catalyst containing wt.% of Cr using Ti-MCM-41 support

$$\frac{x}{x + M} = \frac{a}{100}$$

Where: x is the mass of chromium, which is calculated based on 1 mole SiO_2 , M_A is the Molecular mass (g/mol) of the SiO_2 , and a is the chromium weight.

$$\frac{x}{x + 60.084} = \frac{3}{100}$$

$$(x * 100) - 3 * (x + 60.084) = 0$$

$$x = 1.858 \text{ g}$$

That means to keep the loading ratio of 3 wt.% Cr; for one mole of SiO_2 , an amount of 1.858 grams of chromium must be used.

However, in the synthesis, only 0.5 g of Ti-MCM-41 will be used.

APPENDIX-2. (continued) Calculations for Cr-based catalyst supported on Ti-modified MCM-41

$$\begin{array}{ll} 60.084 \text{ g SiO}_2 & \longrightarrow 1.858 \text{ g Cr} \\ 0.5 \text{ g SiO}_2 & \longrightarrow \chi \text{ g Cr} \end{array}$$

That means to keep the loading ratio of 3 wt.% chromium; an amount of 0.0155 grams of chromium must be used.

The chromium source is chromium nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), its molecular mass is 400.15 g/mol . The chromium molecular mass is 51.996 g/mol . How many grams must be used from $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to get 0.0155 g of chromium?

$$m_{\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}} = \frac{M_{\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}} \times m_{\text{Cr}}}{M_{\text{Cr}}}$$

$$m_{\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}} = \frac{400.15 \times 0.0155}{51.996} = 0.12 \text{ g}$$

That means 0.12 g of the chromium nitrate must be impregnated to Ti-MCM-41 supported for the synthesis 3Cr@Ti-MCM-41 as planned.

The number of moles of nitrate salt containing 0.0155 Cr is calculated as

$$n_{\text{Cr}} = \frac{m_{\text{Cr}}}{M_{\text{Cr}}} = \frac{0.0155}{51.996} = 2.97 \times 10^{-4} \text{ moles.}$$

$$\begin{array}{ll} 1 \text{ mol SiO}_2 & \longrightarrow 60,086 \text{ g} \\ \chi \text{ mol SiO}_2 & \longrightarrow 0.5 \end{array}$$

$$\chi = 8.32 \times 10^{-3} \text{ mol}$$

Taking into consideration $n_{\text{Si}} = n_{\text{SiO}_2}$, the ratio between Si and Cr can be calculated as:

$$\text{Cr/Si} = 2.97 \times 10^{-4} / 8.32 \times 10^{-3} = 0.036$$

The same calculation was done for 6% and 10% wt.% chromium loading; an amount of 0.032 and 0.056 grams of chromium must be added to the catalyst, respectively. That means to get 6 wt.% Cr 0.246 grams of chromium nitrate must be used. Similarly, to get 10 wt.% Cr 0.43 grams of chromium nitrate must be used as well. For 6 wt.% and 10% wt.% Cr catalysts, the ratios between Si and Cr were also calculated, which were 0.074 and 0.128, respectively.

APPENDIX-3. Thermodynamic equilibrium calculations

Thermodynamic equilibrium calculations were made for the isobutane oxidative dehydrogenation reaction. all the calculations are made taking one-step reaction pathway in to consideration. Isobutane oxidative dehydrogenation occurs according to the following equation.



Table 3.1 states the components enthalpy and Gibbs free energy values at temperature of 298 K, and pressure 1atm.

Table 3.1. Components enthalpy and Gibbs free energy values(Poling et al., 2001)

Component	ΔH° kJ/mol	ΔG° kJ/mol
i-C ₄ H ₁₀	-134.18	-20.76
CO ₂	-393.509	-394.39
i-C ₄ H ₈	-17.1	58.08
CO	-110.525	-137.16
H ₂ O	-241.8	-228.61
H ₂	0	0

Gibbs Free energy change of the reaction will be calculated by using Eq. 3.1.

$$\Delta G^\circ_{\text{rxn}} = (\Delta G_{i\text{-}C_4H_8} + \Delta G_{CO} + \Delta G_{H_2O}) - (\Delta G_{i\text{-}C_4H_{10}} + \Delta G_{CO_2}) \quad (3.1)$$

Enthalpy change of the reaction will be calculated by using Eq. 3.2.

$$\Delta H^\circ_{\text{rxn}} = (\Delta H_{i\text{-}C_4H_8} + \Delta H_{CO} + \Delta H_{H_2O}) - (\Delta H_{i\text{-}C_4H_{10}} + \Delta H_{CO_2}) \quad (3.2)$$

The specific heat capacity can be calculated by using Eq. 3.3.

$$C_p = a + b \times T + c \times T^2 + d \times T^3 \quad (3.3)$$

Table 3.2 display the ideal-gas specific heats of gases appeared in the isobutane oxidative dehydrogenation reaction system, where a,b,c,d are in kJ/kmol.K (Cengel and Boles, 2010).

APPENDIX-3. (continued) Thermodynamic equilibrium calculations

Table 3.2. Ideal-gas specific heats of gases for the reaction system (Cengleand Boles, 2010)

Component	$a \cdot 10^3$	$b \cdot 10^5$	$c \cdot 10^8$	$d \cdot 10^{12}$
i-C ₄ H ₁₀	-7.913	41.6	-23.010	49.91
CO ₂	22.26	5.981	- 3.501	7.469
i-C ₄ H ₈	-1.02	36.19	-21.410	50.5
CO	28.16	0.1675	0.537	-2.222
H ₂ O	32.24	0.192300	1.055	-3.595
H ₂	29.11	-0.191600	0.4003	-0.8704

The specific heats of the reaction system will be calculated by estimating the change (Δ) in ideal-gas specific heats value of a,b, c, and d for the reaction components using data shown in Table 3.2 the specific heat capacity of the reaction (kJ/kmol.K) can be obtained using Eq. 3.4

$$\Delta C_{prxn} = 45.033 \times 10^{-3} - 11.0312 \times 10^{-5} \times T + 6.6932 \times 10^{-8} \times T^2 - 12.696 \times 10^{-12} \times T^3 \quad (3.4)$$

The equilibrium constant of the reaction at 298 K can be calculated as in Eq. 3.5,

$$\Delta G^\circ_{rxn} = -RT \ln K_{298} \quad (3.5)$$

Where $R = 0.00831300$ kJ/mol.K.

The temperature dependence of enthalpy will be determined by the specific heat capacity C_p (at constant pressure) as stated in Eq. 3.6

$$\Delta H_T = \Delta H^\circ_{rxn} + \int_{298}^T \Delta C_{prxn} dT \quad (3.6)$$

The temperature dependence of the equilibrium constant will be calculated by using Eq. 3.7.

$$\ln K_T = \ln K_{298} + \int_{298}^T \frac{\Delta H_T}{RT^2} dT \quad (3.7)$$

The temperature dependence of enthalpy ΔH_T was calculated at different temperatures, then the temperature dependence of the equilibrium constant $\ln K_T$ was calculated, and the results are shown in Table 3.3.

Table 3.3. The Change of the equilibrium constant with temperature

T	K
773	2.4×10^{-2}
823	1.1×10^{-1}
873	4.2×10^{-1}
923	1.37
973	3.96

APPENDIX-3. (continued) Thermodynamic equilibrium calculations

By determining the equilibrium constant values at different temperatures, equilibrium conversion calculations were started. Table 3.4 shows the stoichiometric for isobutane oxidative dehydrogenation reaction.

Table 3.4. The reaction stoichiometry

Substance	Initial value	Change	Final value
i-C ₄ H ₁₀	1	-x	1-x
CO ₂	1	-x	1-x
i-C ₄ H ₈	0	X	x
CO	0	X	x
H ₂ O	0	X	x
H ₂	0	0	0
total	2	X	2+x

The reaction constant is calculated as given

$$K = \frac{P_{i-C_4H_8} P_{CO} P_{H_2O}}{P_{i-C_4H_{10}} P_{CO_2}} = \frac{y_{i-C_4H_8} y_{CO} y_{H_2O}}{y_{i-C_4H_{10}} y_{CO_2}} P_T \quad (3.8)$$

$$P_i = \frac{n_i}{n_T} P_T = y_i P_T \quad (3.9)$$

$$K = \frac{\left(\frac{x}{2+x}\right)\left(\frac{x}{2+x}\right)\left(\frac{x}{2+x}\right)}{\left(\frac{1-x}{2+x}\right)\left(\frac{1-x}{2+x}\right)} \times P_T \quad (3.10)$$

Equation 3.10 shows the mathematical relation between X (stoichiometric conversion) and K (reaction constant). To put the equation into a more straightforward form, the algebra principle was applied, and the relation between x and k was found to be a 3-degree linear equation. This means that to solve equation 3.11, their routes are valuable; 2 of them are imaginary numbers, and one is a real number.

The equilibrium conversion depends mainly on the feed ratio of the reaction substances,

$$X_{Ae} = \frac{F_{A0} - F_A}{F_{A0}} \quad (3.11)$$

Where F_{A0} = initial moles of isobutane and F_A = the number of moles of isobutane at equilibrium and by taking into account that the feed consists of 1:1 isobutane/CO₂.

Since the equilibrium calculations were carried out by the unit of kJ/mol.K for the heat capacity and kJ/mol for enthalpy and Gibbs free energy therefore the units of the total presser were chosen to be 101.325 Kpa.

APPENDIX-3. (continued) Thermodynamic equilibrium calculations

In addition to that, The GASEQ program, which is a chemical equilibrium program for Windows, was also used to calculate equilibrium conversion considering the one-step reaction and two-step reaction pathway.

APPENDIX-4. N₂ adsorption-desorption isotherms DataN₂ adsorption-desorption isotherms Data of TiW-MCM-41 material

P/Po	Volume [cc/g]	P/Po	Volume [cc/g]	P/Po	Volume [cc/g]
0.052941	99.0718	0.70057	216.5299	0.64447	222.3812
0.1025	114.0391	0.75333	221.3487	0.59896	218.5658
0.15336	126.9612	0.80016	226.935	0.55299	214.7863
0.20062	140.9757	0.85095	238.3026	0.49071	210.3367
0.24749	157.2328	0.8967	253.6718	0.44925	204.9111
0.30378	174.6188	0.94684	284.1966	0.39529	197.3367
0.35342	185.2444	0.99209	382.2342	0.3443	189.5214
0.39926	191.6427	0.95404	305.0889	0.29863	178.4274
0.45249	196.4684	0.90177	270.9163	0.254	164.6082
0.50219	201.0992	0.84221	251.2051	0.19913	144.4668
0.55514	204.5761	0.80003	240.2701	0.14337	127.4715
0.60524	207.9436	0.74795	231.4462	0.097483	114.5205
0.65502	211.3761	0.69288	225.1829		

Diameter Å	Pore Vol[cc/g]	Surf Area[m ² /g]	Dv(d) [cc/Å/g]	Ds(d) [m ² /Å/g]	Dv/(log d) [cc/g]	Ds/(log d) [m ² /g]
16.69	0.02781	66.66	0.01209	28.98	0.4637	1112
19.21	0.07578	166.6	0.01747	36.39	0.7715	1607
21.99	0.1435	289.8	0.0241	43.85	1.218	2217
24.61	0.1895	364.4	0.01879	30.53	1.064	1729
27.19	0.2248	416.4	0.01301	19.14	0.8141	1197
30.24	0.2467	445.4	0.006497	8.594	0.4519	597.8
33.97	0.2674	469.7	0.005042	5.936	0.3939	463.8
37.83	0.2818	485	0.003973	4.201	0.3459	365.7
42.9	0.2905	493.1	0.001348	1.257	0.1329	123.9
49.12	0.2982	499.4	0.001291	1.051	0.1458	118.7
55.71	0.3056	504.7	0.001025	0.7362	0.1313	94.3
64.24	0.3094	507	0.000382	0.2377	0.05636	35.09
76.86	0.3211	513.2	0.000764	0.3975	0.1347	70.12
95.5	0.3386	520.5	0.000797	0.3336	0.1744	73.04
120.27	0.3606	527.8	0.000797	0.2649	0.2196	73.04
172.88	0.3984	536.5	0.000487	0.1127	0.1907	44.12
325.19	0.4602	544.1	0.000272	0.03346	0.1951	24
1443.2	0.5853	547.6	6.23E-05	0.001726	0.1676	4.645

APPENDIX-4. (continued) Area-volume-pore size summary

Surface area data		
Multipoint BET is	553.5	m ² /g
BJH Method Cumulative Adsorption Surface Area is	574	m ² /g
BJH Method Cumulative Desorption Surface Area is	547.6	m ² /g
DH Method Cumulative Adsorption Surface Area is	594.6	m ² /g
DH Method Cumulative Desorption Surface Area is	567.2	m ² /g
DR Method Micro Pore Area is	727.6	m ² /g
volume-pore data		
BJH Method Cumulative Adsorption Pore Volume is	0.5993	cc/g
BJH Method Cumulative Desorption Pore Volume is	0.5853	cc/g
DH Method Cumulative Adsorption Pore Volume is	0.5879	cc/g
DH Method Cumulative Desorption Pore Volume is	0.5746	cc/g
DR Method Micro Pore Volume is.	0.2592	cc/g
HK Method Cumulative Pore Volume is	0.1966	cc/g
SF Method Cumulative Pore Volume is	0.2031	cc/g
pore size data		
BJH Method Adsorption Pore Diameter (Mode) is	21.85	Å
BJH Method Desorption Pore Diameter (Mode) is	21.99	Å
DH Method Adsorption Pore Diameter (Mode) is	21.85	Å
DH Method Desorption Pore Diameter (Mode) is	21.99	Å
DR Method Micro Pore Width is	40.14	Å
DA Method Pore Diameter (Mode) is	20	Å
HK Method Pore Width (Mode) is	3.625	Å
SF Method Pore Diameter (Mode) is	4.477	Å

P/Po	Volume [cc/g]	P/Po	Volume [cc/g]	P/Po	Volume [cc/g]
0.051151	73.5314	0.70862	162.6808	0.64611	178.7156
0.10714	86.9311	0.75791	165.2922	0.59418	175.5672
0.1494	95.7041	0.807	168.4516	0.54052	173.2151
0.20502	110.7798	0.84815	176.1956	0.49321	169.9715
0.24868	128.4754	0.89667	185.1942	0.44784	154.3088
0.30893	139.7572	0.95236	217.4482	0.39661	150.5063
0.357	143.4355	0.99122	358.7226	0.34322	147.5586
0.40533	147.61	0.95277	248.7178	0.29437	142.3095
0.45833	150.2798	0.89329	201.7849	0.25168	133.1063
0.50905	152.4762	0.85008	193.7363	0.19411	110.8839
0.55959	154.2866	0.7988	190.0976	0.14238	97.7908
0.6056	158.0251	0.74874	185.7711	0.10003	88.327
0.65874	160.282	0.69792	181.9847		

APPENDIX-4. (continued) BJH desorption pore size distribution Data of TiA-MCM-41 catalyst

Diameter Å	Pore Vol[cc/g]	Surf Area[m ² /g]	Dv(d) [cc/Å/g]	Ds(d) [m ² /Å/g]	Dv/(log d) [cc/g]	Ds/(log d) [m ² /g]
16.73	0.01895	45.32	0.008942	21.38	0.3439	822.5
19.06	0.05548	122	0.01435	30.13	0.629	1320
21.8	0.1366	270.9	0.02763	50.7	1.385	2541
24.43	0.167	320.6	0.01304	21.35	0.733	1200
27.04	0.1803	340.3	0.004608	6.817	0.2866	424
30.25	0.1839	345	0.001016	1.343	0.07069	93.47
33.96	0.1907	353	0.001755	2.067	0.1371	161.5
37.89	0.24	405.1	0.01241	13.1	1.081	1142
42.3	0.2474	412.1	0.001536	1.453	0.1495	141.3
48.07	0.2513	415.4	0.000582	0.4842	0.06431	53.51
55.52	0.2574	419.7	0.000734	0.5287	0.09364	67.47
64.98	0.2633	423.3	0.00055	0.3382	0.08203	50.49
77.59	0.27	426.8	0.000468	0.2412	0.08333	42.96
95.31	0.2775	430	0.000357	0.1497	0.07798	32.73
123.35	0.2823	431.5	0.000137	0.04444	0.03866	12.54
168.21	0.2962	434.8	0.000254	0.06038	0.09748	23.18
311.41	0.3809	445.7	0.000366	0.04695	0.2495	32.05
1317.95	0.5601	451.1	0.000101	0.003052	0.2511	7.622

Surface area data

Multipoint BET is	473	m ² /g
BJH Method Cumulative Adsorption Surface Area is	473.1	m ² /g
BJH Method Cumulative Desorption Surface Area is	451.1	m ² /g
DH Method Cumulative Adsorption Surface Area is	491.6	m ² /g
DH Method Cumulative Desorption Surface Area is	467.3	m ² /g
DR Method Micro Pore Area is	584	m ² /g

volume-pore data

BJH Method Cumulative Adsorption Pore Volume is	0.5729	cc/g
BJH Method Cumulative Desorption Pore Volume is	0.5601	cc/g
DH Method Cumulative Adsorption Pore Volume is	0.5608	cc/g
DH Method Cumulative Desorption Pore Volume is	0.5485	cc/g
DR Method Micro Pore Volume is.	0.2081	cc/g
HK Method Cumulative Pore Volume is	0.1498	cc/g
SF Method Cumulative Pore Volume is	0.1558	cc/g

pore size data

BJH Method Adsorption Pore Diameter (Mode) is	21.99	Å
BJH Method Desorption Pore Diameter (Mode) is	21.8	Å
DH Method Adsorption Pore Diameter (Mode) is	21.99	Å
DH Method Desorption Pore Diameter (Mode) is	21.8	Å
DR Method Micro Pore Width is	42.81	Å
DA Method Pore Diameter (Mode) is	21	Å
HK Method Pore Width (Mode) is	3.525	Å
SF Method Pore Diameter (Mode) is	4.477	Å

APPENDIX-5. Calculation of the distance between layers(d), Lattice parameter (a_o) , wall thickness (δ) and crystal size (L)

For the TiW-MCM-41 material.

Calculations were made using Bragg's law.

$$\lambda n = 2d \sin \theta$$

$$d = \frac{\lambda n}{2 \sin \theta}$$

Where:

λ : expressed as the wavelength of the beam used = 1.5406 Å

n : A constant that depends on the instruments used to obtain X-ray diffraction patterns and the sample being analyzed = 1

d : expressed as the distance between layers of the material Å

θ : reflected angle

$$2\theta = 2.76^\circ$$

$$\theta = 1.38^\circ$$

Distance between layers

$$d = \frac{1.5406 \times 1}{2 \sin 1.38} = \frac{1.5406}{2 \times 0.024} = \frac{1.5406}{0.048}$$

$$d = 31.985 \text{ Å}$$

Lattice parameter

$$a_o = d(2/\sqrt{3})$$

$$a_o = 31.985 \times (2/1.732) = 67.87 \times 1.155$$

$$a_o = 36.93 \text{ Å}$$

Wall thickness

$$\delta = a_o - D_p$$

a_o : Lattice parameter

D_p : mean pore diameter (determined from the N₂ adsorption/desorption data, BJH desorption data used)

D_p Pore diameter calculated by the BJH method (we used the average value of adsorption and desorption pore diameter) = 21.92 Å

$$\delta = 36.93 - 21.92$$

$$\delta = 15.01 \text{ Å}$$

Crystal size

In order to determine the solid particle sizes of the synthesized materials, Scherrer's law was used.

$$L = \frac{n\lambda}{\beta \cos \theta}$$

L : nano-crystallite size by using XRD radiation.

n : dimensionless crystal form factor with a value close to one. The value of the shape factor is about 0.9, but varies with the actual shape of the crystallite.

λ : expressed as the wavelength of the beam used (0.15406 nm)

θ : diffraction angle of the highest peak of nickel.

β : full width (of half maximum of peaks FWHM) (the highest peak in the X-ray pattern) in radians. This amount is sometimes also expressed as $\Delta(2\theta)$.

$$L = \frac{0.9 \times 1.5406}{0.44 \times \frac{\pi}{180} \cos 1.38} = 177.87 \text{ Å}$$

APPENDIX-5. (continued) Calculation of the distance between layers(d), Lattice parameter (a_o) , wall thickness (δ) and crystal size (L)

For the TiA-MCM-41 material.

Calculations were made using Bragg's law.

$$\lambda n = 2d \sin \theta$$

$$d = \frac{\lambda n}{2 \sin \theta}$$

$$2\theta = 2.56^\circ$$

$$\theta = 1.28^\circ$$

$$\lambda = 1540.6 \text{ mm} = 1.5406 \times 10^9 \text{ m} = 1.5406 \times 10^{10} = 1.5406 \text{ \AA}$$

$$n=1$$

Distance between layers

$$d = \frac{1.5406 \times 1}{2 \sin 1.28}$$

$$d = 34.2 \text{ \AA}$$

Lattice parameter

$$a_o = d(2/\sqrt{3})$$

$$a_o = 34.2 \times (2/1.732) = 34.2 \times 1.155$$

$$a_o = 39.82 \text{ \AA}$$

Wall thickness

$$\delta = a_o - D_p$$

$$\delta = 39.52 - 21.895$$

$$\delta = 17.62 \text{ \AA}$$

Crystal size

$$L = \frac{0.9 \times 1.5406}{0.39 \times \frac{\pi}{180} \cos 1.28} = \frac{1.38654}{0.0068 \times 0.9997} = 203.79 \text{ \AA}$$

$$L = 203.79 \text{ \AA}$$

For the 3Cr/Ti-MCM-41 catalyst (hydrothermal method)

$$2\theta = 22.02^\circ \quad \text{and} \quad \theta = 11.01^\circ$$

Distance between layers

$$d = \frac{1.5406 \times 1}{2 \sin 11}$$

$$d = 4 \text{ \AA}$$

Lattice parameter

$$a_o = d(2/\sqrt{3})$$

$$a_o = 4 \times (2/1.732) = 4 \times 1.155$$

$$a_o = 4.66 \text{ \AA}$$

Crystal size

$$L = \frac{0.9 \times 1.5406}{6.3 \times \frac{\pi}{180} \cos 11} = 12.8 \text{ \AA}$$

Table 5.1 Calculation for the 10Cr/Ti-MCM-41 catalyst

Catalyst \ Measurement	Cr				Ti			
	$\theta(deg)$	$\beta(deg)$	d, \AA	L, \AA	$\theta(deg)$	$\beta(deg)$	d, \AA	L, \AA
10 Cr/Ti-MCM-41	18.085	0.7	2.48	116	27.4	0.71	1.67	126.0

APPENDIX-5. (continued) Calculation of the distance between layers(d), Lattice parameter (a_o) , wall thickness (δ) and crystal size (L)

For the 3Cr@Ti-MCM-41 catalyst (impregnation method)

$$2\theta = 22.53^\circ \quad \text{and} \quad \theta = 11.2^\circ$$

Distance between layers

$$d = \frac{1.5406 \times 1}{2 \sin 11.2}$$

$$d = 3.9 \text{ \AA}$$

Lattice parameter

$$a_o = d(2/\sqrt{3})$$

$$a_o = 3.9 \times (2/1.732) = 3.9 \times 1.155$$

$$a_o = 4.55 \text{ \AA}$$

Crystal size

$$L = \frac{0.9 \times 1.5406}{8.63 \times \frac{\pi}{180} \cos 11.2} = 9.4 \text{ \AA}$$

Table 5.2 Calculation for the 10Cr@Ti-MCM-41 catalyst

Measurement Catalyst	Cr				Ti			
	$\theta(deg)$	β (deg)	d, \AA	L, \AA	$\theta(deg)$	β (deg)	d, \AA	L, \AA
10 Cr@Ti-MCM-41	18.09	0.323	2.48	258.8	27.4	0.322	1.67	277.9

APPENDIX-6. Experimentally determined $-R_A^*$ at different temperatures

For the first set of reactions, calculations were performed at different isobutane partial pressures (5,10,15,20 kPa) while carbon dioxide partial pressure was kept constant at 5 kPa.

T=500 °C

P i-C ₄ H ₁₀ (kPa)	$-R_A^*$ (mol/g _{cat} ·s)
5	1.77E-04
10	2.92E-04
15	4.02E-04
20	5.49E-04

T=550 °C

P i-C ₄ H ₁₀ (kPa)	$-R_A^*$ (mol/g _{cat} ·s)
5	2.34E-04
10	4.10E-04
15	5.80E-04
20	7.13E-04

T=600 °C

P i-C ₄ H ₁₀ (kPa)	$-R_A^*$ (mol/g _{cat} ·s)
5	2.84E-04
10	5.19E-04
15	7.30E-04
20	8.95E-04

For the second set of reactions, calculations were performed at different CO₂ partial pressures (5, 10, 15, 20 kPa) isobutane partial pressure was kept constant at 5 kPa.

T=500 °C

PCO ₂ (kPa)	$-R_A^*$ (mol/g _{cat} ·s)
5	1.77E-04
10	1.84E-04
15	1.88E-04
20	1.88E-04

T=550 °C

PCO ₂ (kPa)	$-R_A^*$ (mol/g _{cat} ·s)
5	2.34E-04
10	2.37E-04
15	2.42E-04
20	2.42E-04

T=600 °C

PCO ₂ (kPa)	$-R_A^*$ (mol/g _{cat} ·s)
5	2.84E-04
10	2.92E-04
15	2.96E-04
20	2.96E-04

APPENDIX-7. Derivation of MVK mechanism

In this study, the aim was to analyze both two-stage and three-stage redox mechanisms for the reaction.

Two stage mechanism



If the coverage of the surface by adsorbed B species is given by CrO_X (θ_B) and that of empty sites is given by $1 - CrO_X$ ($\theta_\emptyset$) (where $\theta_B + \theta_\emptyset = 1$), the rates of these two steps are given by:

$$Rate = R_1 = k_1 P_A CrO_X \quad (6.1)$$

$$R_2 = k_2 P_B (1 - CrO_X) = k_2 P_B (1 - \theta_B) \quad (6.2)$$

from which, with $r_1 = r_2$ in a steady state, value of θ_B is obtained

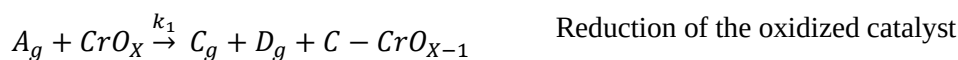
$$CrO_X = \theta_B = \frac{k_2 P_B}{k_1 P_A + k_2 P_B} \quad (6.3)$$

Thereby the rate of reaction is given by

$$r = k_1 P_A CrO_X = \frac{k_1 P_A k_2 P_B}{k_1 P_A + k_2 P_B} \quad (6.4)$$

where k_1 is the rate constant for isobutane consumption and k_2 is the rate constant for catalyst reoxidation.

Three stage mechanism



Applying steady state approximation for $C - CrO_{X-1}$ and CrO_{X-1}

$$k_1 P_A CrO_X = k_2 [C - CrO_{X-1}]$$

$$[C - CrO_{X-1}] = \frac{k_1 P_A CrO_X}{k_2}$$

$$k_2 [C - CrO_{X-1}] = k_3 P_B CrO_{X-1}$$

$$CrO_{X-1} = \frac{k_2 [C - CrO_{X-1}]}{k_3 P_B}$$

$$1 = CrO_X + CrO_{X-1} + C - CrO_{X-1}$$

$$1 = CrO_X + \frac{k_2 [C - CrO_{X-1}]}{k_3 P_B} + \frac{k_1 P_A CrO_X}{k_2}$$

$$1 = CrO_X + \frac{k_2 k_1 P_A CrO_X}{k_2 k_3 P_B} + \frac{k_1 P_A CrO_X}{k_2}$$

$$1 = CrO_X + \frac{k_1 P_A CrO_X}{k_3 P_B} + \frac{k_1 P_A CrO_X}{k_2}$$

$$CrO_X = \frac{1}{\left(\frac{k_1 P_A CrO_X}{k_3 P_B} + \frac{k_1 P_A CrO_X}{k_2} \right)}$$

APPENDIX-7. (continued) Derivation of MVK mechanism

$$\text{Rate} = r_1 = k_1 P_A CrO_X = \frac{k_1 P_A}{\left(\frac{k_1 P_A CrO_X}{k_3 P_B} + \frac{k_1 P_A CrO_X}{k_2} \right)} \quad (6.5)$$

Where k_1 is the rate constant for isobutane consumption, k_2 is the rate constant for desorption of the products and k_3 is the rate constant for catalyst reoxidation.

The analysis of initial rate data provides an initial approximation for understanding the dependency of the reaction rate on individual parameters. The data were analyzed using the least squares method through the SPSS computer program.

APPENDIX-8. Model outputs

 $T=600^{\circ}\text{C}$ and $WHSV=51h^{-1}$

Table 8.1. Variation in concentration along the catalyst bed length

Catalyst bed length (m)	C_A (mol/m ³)	C_B (mol/m ³)	C_C (mol/m ³)	C_D (mol/m ³)	C_E (mol/m ³)
0	2.142	10.458	0	0	0
0.005	0.9645	9.2805	1.1775	1.1775	1.1775
0.01	0.3809	8.6969	1.7611	1.7611	1.7611
0.015	0.1249	8.4409	2.0171	2.0171	2.0171
0.02	0.031	8.347	2.111	2.111	2.111
0.025	0.0048	8.3208	2.1372	2.1372	2.1372
0.03	0.0003	8.3163	2.1417	2.1417	2.1417
0.035	0	8.316	2.142	2.142	2.142
0.04	0	8.316	2.142	2.142	2.142

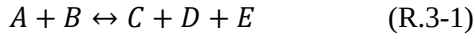
 $T=500^{\circ}\text{C}$ and $WHSV=51h^{-1}$

Table 8.2. Variation in concentration along the catalyst bed length

Catalyst bed length (m)	C_A (mol/m ³)	C_B (mol/m ³)	C_C (mol/m ³)	C_D (mol/m ³)	C_E (mol/m ³)
0	2.37	11.85	0	0	0
0.005	1.4796	10.9596	0.8904	0.8904	0.8904
0.01	0.8851	10.3651	1.4849	1.4849	1.4849
0.015	0.5029	9.9829	1.8671	1.8671	1.8671
0.02	0.2682	9.7482	2.1018	2.1018	2.1018
0.025	0.132	9.612	2.238	2.238	2.238
0.03	0.0586	9.5386	2.3114	2.3114	2.3114
0.035	0.0226	9.5026	2.3474	2.3474	2.3474
0.04	0.0072	9.4872	2.3628	2.3628	2.3628
0.045	0.0017	9.4817	2.3683	2.3683	2.3683
0.05	0.0002	9.4802	2.3698	2.3698	2.3698
0.055	0	9.48	2.37	2.37	2.37
0.06	0	9.48	2.37	2.37	2.37

APPENDIX-9. Calculations for Heat and Mass Transfer Limitations in Oxidative Dehydrogenation of Isobutane over 10Cr/Ti-MCM-41 Catalyst

Diffusion effect on Heterogeneous reaction



For $i\text{-C}_4\text{H}_{10} - \text{CO}_2$ system at T: 600°C=873 K and P: 0.901 atm

Binary diffusivity for system A-B

$$D_{AB} = 0.0018583 \sqrt{T^3 \left(\frac{1}{M_A} + \frac{1}{M_B} \right) \frac{1}{P \sigma_{AB}^2 \Omega_{DAB}}}$$

Where:

T: Temperature,

M: Molecular Weight,

σ_{AB} and ϵ_{AB} : Lennard-Jones potential appearing between one molecule of A and one of B,

Ω_{DAB} : Collisional integral for diffusion, is a function of the dimensionless temperature KT/ϵ_{AB} .

Table 9.1. Lennard-Jones Potential Parameters

Substance	M (g/mol)	σ (Å)	k/ϵ (K)
A	58.12	5.393	295
B	44.01	3.99	195

$$\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B) = 4.695$$

$$\epsilon_{AB}/k = \sqrt{\epsilon_A/k + \epsilon_B/k} = 236.7 \text{ K}$$

$$k/\epsilon_{AB} = 0.004 \text{ 1/K}$$

$$Tk/\epsilon_{AB} = 3.68$$

$$\Omega_{DAB} = 0.9008 \quad \text{and} \quad \Omega_K = 0.9868$$

$$D_{AB} = 0.0018583 \sqrt{T^3 \left(\frac{1}{M_A} + \frac{1}{M_B} \right) \frac{1}{P \sigma_{AB}^2 \Omega_{DAB}}} = 0.35 \text{ cm}^2/\text{s}$$

Effective diffusivity

$$D_e = \frac{D_{AB} \epsilon}{\tau}$$

ϵ : Porosity,

τ : Tortuosity (τ) of catalyst is calculated from porosity (Abbas, 2011) by

APPENDIX-9. (continued) Calculations for Heat and Mass Transfer Limitations in Oxidative Dehydrogenation of Isobutane over 10Cr/Ti-MCM-41 Catalyst

$$\tau = 1 - 0.5 \ln \varepsilon$$

Tortuosity calculation was given in Table 9.2

Table 9.2. Calculation for tortuosity

ρ_c g/cm ³	catalyst amount g	Reactor volume cm ³	(1- ε)	ε	τ
0.4	0.1	0.663	0.38	0.62	1.2

Then effective diffusivity value was calculated

$$D_e = 0.177 \text{ cm}^2/\text{s} = 1.77 \times 10^{-5} \text{ m}^2/\text{s}$$

Weisz–Prater Criterion

The Weisz–Prater Criterion is used to determine if internal diffusion limits the reaction.

$$C_{WP} = \frac{\text{Observed reaction rate}}{\text{Diffusion rate}} = \frac{-R_A^* \rho_c r^2}{D_e C_{As}}$$

Where:

$-R_A^*$: Observed rate of reaction,

ρ_c : Catalyst density,

r : radius of catalyst particle,

C_{As} : Concentration of A at the surface of catalyst.

The values needed for calculating the Weisz-Prater Criteria are listed in Table 9.3.

Table 9.3. Parameters values for calculating Weisz-Prater Criteria

Parameters	Values
$-R_A^*$	4.5×10^{-4} (mol/g _{ca} .s)
ρ_c	0.4×10^6 (g/m ³)
r	110 (μm)
D_e	1.77×10^{-5} (m ² /s)
C_{As}	12.41 (mol/m ³)

When substituting the given values, the C_{WP} value was equal to 0.01. Which means internal diffusion is negligible in the reaction.

APPENDIX-9. (continued) Calculations for Heat and Mass Transfer Limitations in Oxidative Dehydrogenation of Isobutane over 10Cr/Ti-MCM-41 Catalyst

$$C_{WP} = 0.01 \rightarrow C_{WP} \ll 1$$

Mears Criterion

The Mears Criterion is used to determine whether external mass transfer from the bulk gas phase to the catalyst surface can be neglected.

$$C_m = \frac{-R_A^* \rho_b r n}{K_c C_{Ab}}$$

Where:

ρ_b : Catalyst bulk density.

n : Reaction order (taken as 1).

C_{Ab} : Bulk concentration of A.

K_c : Mass transfer coefficient.

The mass transfer coefficient (K_c) is calculated using the following equation

$$K_c = \frac{D_{AB} Sh(1 - \varepsilon)}{d_p \varepsilon}$$

Sherwood number (Sh)(McCabe et al., 1993) when mass transfer occurs in a sphere pellet is given by

$$Sh = 4 + (1.21 Pe^{2/3})^{1/2}$$

The Sherwood, Reynolds, and Schmidt numbers are used in forced convection mass transfer correlations. For calculations of Re and Sc, various properties of gases are obtained from references (Doble, 2007; Lide, 2004).

Pectlet number (Pe)

$$Pe = Re \times Sc$$

Schmidt number (Sc)

$$Sc = \frac{v}{D_{AB}}$$

v : kinematic viscosity (m^2/s).

Reynolds number (Re)

$$Re = \frac{U \rho d_p}{\mu}$$

Where

U : Velocity (m/s),

d_p : Dimeter of the particle (m),

μ : Viscosity (g/m.s).

APPENDIX-9. (continued) Calculations for Heat and Mass Transfer Limitations in Oxidative Dehydrogenation of Isobutane over 10Cr/Ti-MCM-41 Catalyst

Calculated values for Sc, Re, Pe, and Sh were shown it Table 9.4.

Table 9.4. Calculated values for Sc, Re, Pe, and Sh

ρ_b g/m ³	ρ_{mix} g/m ³	μ_{mix} g/m.s	ν m ² /s	U m/s	Sc	Re	Pe	h
1.5×10^5	2.8×10^{-6}	0.04	1.3×10^7	0.03	3.7×10^8	4.3×10^{-10}	0.16	2.1

The values needed for calculating the Mears criteria are listed in Table 9.5.

Table 9.5. Parameters values for calculating Mears Criteria

Parameters	Values
R_A^*	4.5×10^{-4} (mol/g _{ca} .s)
ρ_c	1×10^{-6} (g/m ³)
r	110 (μm)
D_e	1.77×10^{-5} (m ² /s)
C_{Ab}	12.41 (mol/m ³)
K_C	0.16 (m ³ /m ² .s)

$$C_m = 0.004 \rightarrow C_m < 0.15$$

Which means that the external diffusion of gases into the catalyst is negligible.

Thiele modulus Φ_1 of first order reaction

$$\Phi_1 = \frac{\text{Surface reaction rate}}{\text{Diffusion rate}} = r \sqrt{\frac{k_1'' S_a \rho_c}{D_e}}$$

Where:

r : radius of catalyst particle.

k_1'' : rate constant per unit surface area of catalyst

S_a : surface area of catalyst.

ρ_c : catalyst density.

If the Thiele modulus is very high, the mass transfer controls the reaction, and if it is low, then the surface reaction is the rate-limiting step.

To find the rate constant per unit surface area of the catalyst (k_1'') in m/s, the R_A^* was multiplied by the catalyst surface area, $R_A^* / S_a = R_c = 1.28 \times 10^{-6} \text{ mol/m}^2 \cdot \text{s}$, then the obtained value was multiplied by the concentration of the gas, $k_1'' = R_c / C_A = 1 \times 10^{-7}$

APPENDIX-9. (continued) Calculations for Heat and Mass Transfer Limitations in Oxidative Dehydrogenation of Isobutane over 10Cr/Ti-MCM-41 Catalyst

$$\Phi_1 = 0.10$$

The internal effectiveness factor (η)

The internal effectiveness factor (η) is a parameter that can also be used to determine if the rate of a chemical reaction is limited by internal diffusion. The value of η depends on the order of the reaction and the shape of the catalyst used. In the case of a first-order reaction on a spherical catalyst (Scott Fogler, 1987), the internal effectiveness factor can be expressed as follows:

$$\eta = \frac{3}{\Phi_1^2} (\Phi_1 \coth \Phi_1 - 1) = 1$$

The internal effectiveness factor (η) is 1, which confirms that the catalyst's internal diffusion is negligible.

Heat Transfer Effects in the Catalyst

K_{eff} is the effective thermal conductivity.

The effective thermal conductivity of a porous catalyst (K_{eff}) is predicted by Woodside and Messmer geometric average value (Hill and Root, 1977).

$$K_{eff} = K_s^{1-\varepsilon} K_f^\varepsilon = K_s \left(\frac{K_f}{K_s} \right)^\varepsilon$$

Where:

K_{eff} : the effective thermal conductivity.

K_s : the thermal conductivity of solid.

K_f : thermal conductivity of fluid.

Thermal conductivity values of $i\text{-C}_4\text{H}_{10}$ and CO_2 at different temperature were given in Table 9.6.

Table 9.6. Thermal conductivity values of $i\text{-C}_4\text{H}_{10}$ and CO_2

Temperature(K)	Thermal conductivity	
	$i\text{-C}_4\text{H}_{10}$ K_f (mW/mK)	CO_2 K_f (mW/mK)
500	42.1	33.5
600	57.6	41.6

At T: 873 K K_f for $i\text{-C}_4\text{H}_{10}$ is 99.9 mW/mK.

At T: 873 K K_f for CO_2 is 63.7 mW/mK.

Thermal conductivity K_f of the gas mixture when the $i\text{-C}_4\text{H}_{10}/\text{CO}_2$ molar ratio: 1/5 is 0.07 mW/mK.

The thermal conductivity of the amorphous silica (K_s) is taken as 1.3 W/mK

The value of K_{eff} was 0.2 W/m.K.



Gazili olmak ayrıcalıktır