

Chemical Engineering Communications

ISSN: 0098-6445 (Print) 1563-5201 (Online) Journal homepage: https://www.tandfonline.com/loi/gcec20

# COMPARATIVE STUDY OF $Ag_2O/CO_3O_4$ CATALYSTS PREPARED BY THE SOL-GEL AND CO-PRECIPITATION TECHNIQUES: CHARACTERIZATION AND CO ACTIVITY STUDIES

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**To cite this article:** Filiz Balikçi , Saba Buket Yüceer & Çiğdem Güldür (2008) COMPARATIVE STUDY OF $Ag_2O/CO_3O_4$ CATALYSTS PREPARED BY THE SOL-GEL AND CO-PRECIPITATION TECHNIQUES: CHARACTERIZATION AND CO ACTIVITY STUDIES, Chemical Engineering Communications, 196:1-2, 171-181, DOI: 10.1080/00986440802290169

**To link to this article:** https://doi.org/10.1080/00986440802290169

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Chem. Eng. Comm., 196:171–181, 2009
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ISSN: 0098-6445 print/1563-5201 online
DOI: 10.1080/00986440802290169

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# Comparative Study of $Ag_2O/Co_3O_4$ Catalysts Prepared by the Sol-Gel and Co-precipitation Techniques: Characterization and CO Activity Studies

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*In this study effects of the preparation method on the characteristic properties and CO oxidation activities of $Ag_2O/Co_3O_4$ catalysts were investigated. Catalysts were prepared by two different methods: sol gel and co-precipitation. $N_2$ physisorption measurements, X-ray diffraction, and scanning electron microscopy measurements were used to characterize the catalysts. CO oxidation activity tests were carried out under 1% CO, 21% $O_2$, and the remainder He feed condition between 20° and 200°C. According to the $N_2$ physisorption measurements, catalysts prepared by the co-precipitation method have a higher surface area than the catalysts prepared by the sol-gel method. $Co_3O_4$ and $AgCoO_2$ phases were obtained from catalysts prepared by both techniques. In addition to these phases, metallic silver peaks were obtained by increasing calcination temperature. SEM micrographs of the catalysts showed that catalysts have uniform particles. Increasing the calcination temperature caused the formation of different-sized agglomerates and an increase in the gaps between agglomerates. The best activity was obtained from the $Ag_2O/Co_3O_4$ catalyst calcined at 200°C and prepared by the co-precipitation method. This catalyst gave 50% CO conversion at 106°C. The other two catalysts gave 100% CO conversion at a higher temperature of 200°C.*

**Keywords** Co-precipitation; CO oxidation; Cobalt; Silver; Sol-gel

## Introduction

Catalyst preparation methods have a significant effect on the structural properties and catalytic activities of the final catalyst. Choosing the most suitable preparation method and pretreatment conditions (pH, calcination temperature, etc.) at the beginning of the study is a very important step. Different types of catalysts have been prepared for different reaction systems. For carbon monoxide oxidation reaction, supported Ag, Co, Ce, Cu, Zr... metal oxide catalysts have been used (Güldür and Balıkçı, 2003; Thamachart et al., 2001; Manriquez et al., 2003; Osorio et al., 2006). In addition to CO oxidation reaction, these types of catalysts have also been used for other reactions, like the water-gas shift reaction, Fischer-Tropsch reaction,

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NOx reduction, and selective CO oxidation reaction (Pintar et al., 2007; Okabe et al., 2004; Şeker et al., 1999; Sedmak et al., 2003; Gulari and Manasilp, 2002). In these studies, researchers also studied the effect of the catalyst preparation method and pretreatment condition on the characteristic properties and activities of the final catalyst (Güldür and Balıkçı, 2003; Thamachart et al., 2001; Manriquez et al., 2003; Osorio et al., 2006; Pintar et al., 2007; Okabe et al., 2004; Şeker et al., 1999; Sedmak et al., 2003; Gulari and Manasilp, 2002; Simonot et al., 1997; Wang et al., 2003). Three common preparation methods were used: sol-gel, co-precipitation, and impregnation. The catalysts prepared by the sol-gel and co-precipitation method gave the highest activities for the desired reactions (Güldür and Balikçi, 2003; Pintar et al., 2007; Okabe et al., 2004; Şeker et al., 1999). The sol-gel method has a very important effect on the characteristic properties of the catalysts. It was found that the catalysts prepared by the sol-gel technique had uniform structure and pore size distribution and larger surface area (Şeker et al., 1999; Gulari and Manasilp, 2002; Simonot et al., 1997; Wang et al., 2003).

Taking the recent studies into account, $50/50\,Ag_2O/Co_3O_4$ catalyst was prepared by two different preparation methods: sol-gel and co-precipitation. These methods were chosen because catalysts prepared by these methods gave the highest activity for the desired reactions and also gave the highest surface area value and uniform pore size distribution. To study the effect of the pretreatment conditions, the calcination temperature of the catalyst was changed from 200° to 450°C. After preparation of the catalyst, $N_2$ physisorption measurement, X-ray diffraction (XRD), and scanning electron microscopy (SEM) studies were made to characterize the catalysts. Effects of the preparation and pretreatment on the CO oxidation activity were also investigated.

## Experimental Section

### *Catalyst Preparation*

*Co-precipitation Method*

The catalysts were prepared by the co-precipitation method at different metal/metal oxide (molar ratios) and as single oxide catalysts. $AgNO_3$ (Aldrich, 99.8%) and $Co(NO_3)_2 \cdot 6H_2O$ (Fluka, 99.0%) were dissolved in distilled water at desired molar ratios. The total concentration of the metals in the combined aqueous solutions was 0.1 M. The metal salt solution was put in a vessel on a stirrer, and the $Na_2CO_3$ (1 M) solution was added dropwise to the metal salt solution to adjust the pH of the solution to 8. The precipitates were aged for 3 h at pH 8 and filtered and washed with hot distilled water several times in order to remove excess ions. They were air-dried overnight at 110°C. Catalysts were calcined in air at 200°C for 3 h and at 450°C for 3 h.

*Sol-Gel Method*

The desired amount of the $AgNO_3$ (Aldrich, 99.8%) was dissolved in deionized water. The (29% $NH_4OH + H_2O$) solution was prepared by 10/1 volume ratio and added to the metal salt solution until pH 10 was achieved. After the pH reached 10, the solution was aged overnight at room temperature. In order to obtain precipitate the solution was filtered and washed with hot distilled water several times.

A solution having 20–25 wt.% was prepared by using the precipitate. Then this solution was mixed under reflux at 95°C. $HNO_3$ was added to adjust the $HNO_3$/metal ratio to 0.27 (this solution was called solution I). The desired amount of the $Co(NO_3)_2 \cdot 6H_2O$ (Fluka, 99.0%) was dissolved in 1,2-propandiol and added to solution I. The final solution was mixed under reflux at 95°C until gel formation. The gel was air-dried at 110°C for 24 h, and then the catalysts were calcined in air for 3 h at 450°C (Yüceer, 2005).

### *Catalyst Characterization*

*X-Ray Diffraction Measurements (XRD)*
X-ray diffraction (XRD) was used for identifying the phases present in the synthesized samples as well as measuring the average crystallite sizes from observed line broadening through the use of the Debye-Schrrer equation. A Rigaku rotating anode X-ray diffractometer system generating CuK$\alpha$ radiation was used to obtain the XRD patterns.

*Surface Areas and Pore Volumes*
Surface areas and pore volumes of the catalysts were determined by nitrogen adsorption on a Quantochrome Autosorp 1 C system. The samples were kept at the desired temperature under vacuum before starting $N_2$ adsorption at liquid temperature. Calculation of pore sizes followed the method of Barret-Joyner-Halenda (BJH) according to implemented software routines using the Halsey thickness equation to relate the thickness of the adsorbed layer to the relative pressure. All calculations are based on the desorption model.

*Scanning Electron Microscopy (SEM)*
Catalyst morphology was examined using a JEOL/JSM-6335F scanning electron microscope. The electron gun was operating at an accelerating voltage of 12 kV for the collection of all images.

### *Catalytic Activity Studies*

Catalytic activity measurement was carried out in a fixed-bed quartz tube reactor using 25–35 mg catalyst. The flow rate of the feed gas was 25 mL/min. The reactant gas, consisting of 1 vol. % CO, 21 vol. % $O_2$, and the remaining amount He was passed through the catalyst bed. Activity measurements were carried out at different temperatures in the range of 20°–200°C. The analysis of the reactor effluent was performed with an on-line PerkinElmer CLARUS 500 gas chromatograph with a thermal conductivity detector (TCD). The column packing was Carbosphere and the column temperature was maintained at 50°C. The schematic diagram of the reactor system is shown in Figure 1.

## Results and Discussion

### *Characterization Results*

The specific surface areas of all samples determined by BET are summarized in Table I. Surface area values of the catalysts changed according to the preparation

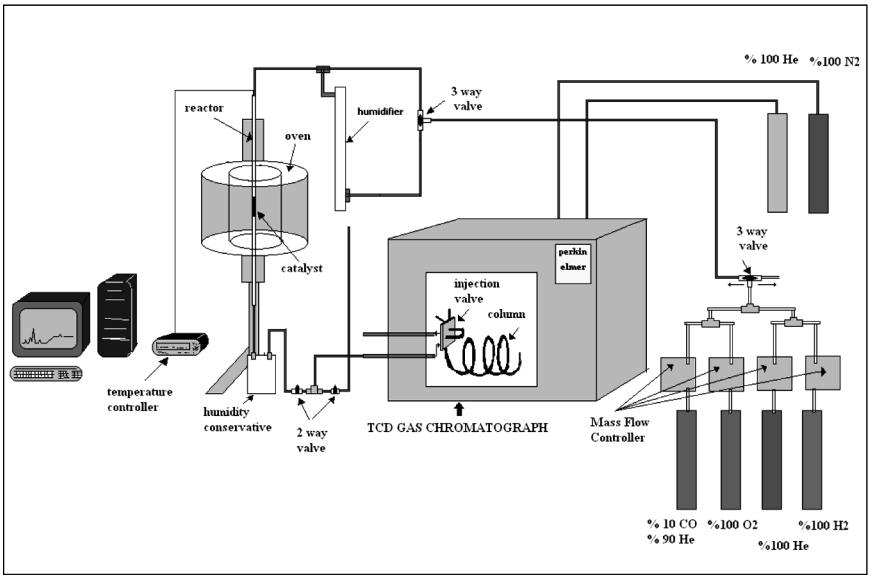



**Figure 1.** Schematic diagram of the catalytic activity system.

method. The effect of the calcination temperature on the surface area values is enormous. The decrease in the surface area may be due to the thermal reduction of silver oxide to metallic silver. The catalyst prepared by the sol-gel method has a lower surface area value than the other catalyst. This result may be due to the small pore sizes of the catalysts. Also, a separate $Co_3O_4$ phase was not formed in the catalyst prepared by the sol-gel method. The structure of the catalysts prepared by the co-precipitation method included a $Co_3O_4$ phase besides metallic Ag and $AgCoO_2$ phases, which were obtained from X-ray analysis. Due to the $Co_3O_4$ phase the catalysts prepared by the co-precipitation gave a higher surface area than the catalyst prepared by the sol-gel method. Although both of the catalysts prepared by sol-gel and co-precipitation were calcined at 450°C, the catalysts prepared by the co-precipitation method have larger surface areas.

XRD patterns of the catalyst prepared by the sol-gel method and the catalyst prepared by the co-precipitation method calcined at 450°C are shown in Figure 2. Table I also shows the phases present in the catalysts, which were obtained from the XRD patterns. Catalysts prepared by the sol-gel method had two phases, which were due to the Ag and $AgCoO_2$. Metallic Ag peaks were observed at $2\theta = 38.29^\circ$, $44.42^\circ$, and $59.41^\circ$; $AgCoO_2$ peaks were observed at $2\theta = 37.06^\circ$, $59.61^\circ$, and $65.04^\circ$. Catalysts prepared by the co-precipitation and calcined at 200°C had two phases, which were due to the $Co_3O_4$ and $AgCoO_2$ (shown in our previous study (Güldür and Balikçi, 2002)). The catalyst prepared by co-precipitation and calcined at 450°C has two identifiable peaks, which were due to the metallic Ag and $Co_3O_4$ phases. $Co_3O_4$ peaks were observed at $2\theta = 31.6^\circ$, $37.2^\circ$, $59.3^\circ$, and $65.5^\circ$; metallic Ag peaks were observed at $2\theta = 37.5^\circ$ and $66.5^\circ$. By increasing calcination temperature of the catalyst prepared by the co-precipitation method from 200° to 450°C, the $AgCoO_2$ phases were decomposed to metallic silver. However, the $Co_3O_4$ phase remained unchanged. Even though the catalysts prepared by the sol-gel were

**Table I.** Physical properties of the catalysts

| 50/50 $Ag_2O/Co_3O_4$ Preparation method | Calcination temperature, °C | BET surface area, $m_2/g$ | Pore size, nm | Pore volume, $cm^3/g$ | | Average crystal size, Å | XRD phases |
|---|---|---|---|---|---|---|---|
| | | | | $V_{micro+meso}$ | $V_{total}$ | | |
| Sol-gel | 450 | 9.5 | 2.2, 3.1 | 18.75 | 27.5 | 62.55 | Ag, $AgCoO_2$ |
| Co-precipitation | 200 | 149 | 2.2, 12.3 | 303 | 331 | 26.85 | $Co_3O_4$, $AgCoO_2$ |
| | 450 | 28.7 | 2.4, 3.3, 5.7, 33 | 129 | 200 | 103.6 | Ag, $Co_3O_4$ |

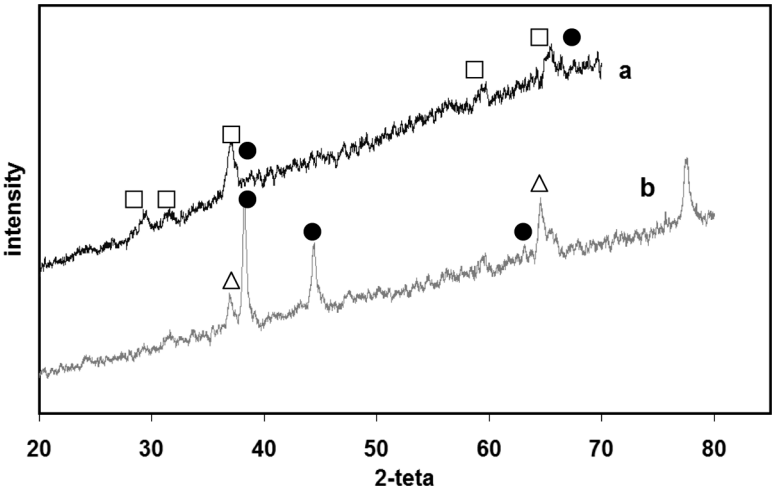



**Figure 2.** XRD patterns of the catalysts: (a) co-precipitation; (b) sol-gel, which were calcined at 450°C, □: $Co_3O_4$, ●: metallic Ag, Δ: $AgCoO_2$).

calcined at 450°C, the $AgCoO_2$ phase remained unchanged, and in addition to the $AgCoO_2$ phase, metallic silver peaks were obtained. Average crystal sizes of the catalysts changed with the preparation method and calcination temperature. The catalyst prepared by the co-precipitation method calcined at 450°C has the largest crystallite size. The average crystallite size of the catalysts increased with an increase in the calcination temperature. Although both of the catalysts were calcined at 450°C, the crystal size of the catalyst prepared by the sol-gel method was 50% of the average crystal size of the catalysts prepared by the co-precipitation method. The difference between these two catalysts is the $AgCoO_2$ phase. This phase may have been the reason for the formation of the small crystal size. The second reason for the smallest crystal size of the catalyst prepared by the sol-gel method was due to the $Co_3O_4$ phase. Since the structure of the catalyst prepared by the sol-gel method did not consist of the $Co_3O_4$ phase, the crystal size of this catalyst is smaller than that of the other catalysts. Also, the activity was affected by these results: the catalysts composed of $AgCoO_2$ phase gave the best activity results.

Figure 3 shows the adsorption-desorption isotherms of the catalysts and Figure 4 shows the pore size distribution patterns of the catalyst. The adsorption-desorption isotherms of the composite oxide catalysts fit the Type IV isotherm in the BDDT classification. The characteristic feature of isotherms in the BDDT classification is the hysteresis loop. The separation place of the adsorption-desorption isotherm of the catalysts changed with the preparation method and calcination temperature. The separation place of the catalyst prepared by the co-precipitation method and calcined at 200°C and 450°C are $P/P_0 = 0.5$ and $P/P_0 = 0.1$ respectively. The separation place of the catalyst prepared by the sol-gel method is $P/P_0 < 0.1$. The area with a bottle-gourd shape decreased when increasing the calcination temperature, indicating that part of the mesopores changed, therefore leading to a decrease in the pore volume and surface area. The pore size distributions were obtained according to the BJH method. Pore size distribution patterns of the catalysts changed with an increase in the calcination temperature and a change of the catalyst preparation method. All of the catalysts have pore size in the mesopore scale. The catalyst

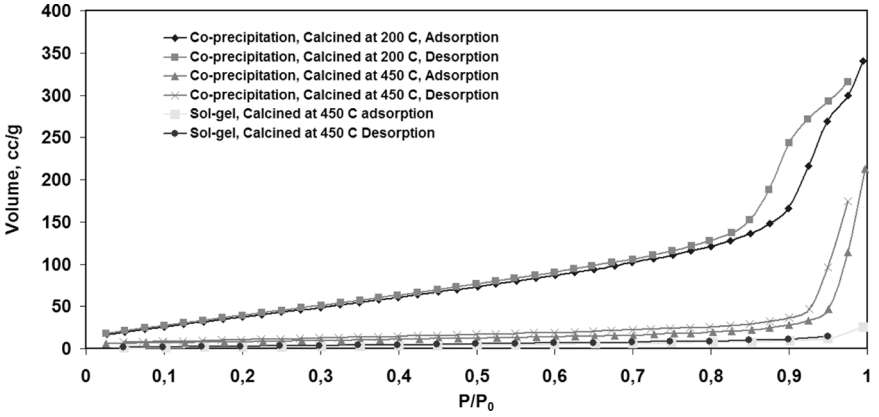
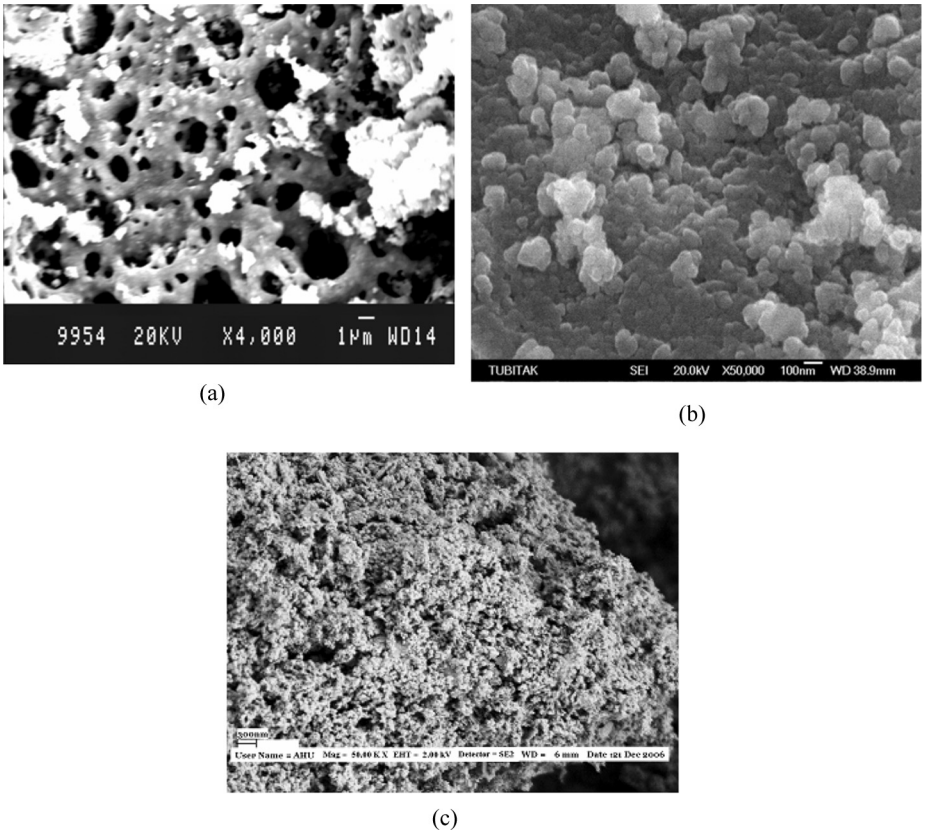



**Figure 3.** $N_2$ adsorption/desorption isotherms of the catalysts.

prepared by the sol-gel method has a narrow pore size but the other two catalysts have rather broad pore size distributions. The $Co_3O_4$ phase in the catalyst structure affected the pore size distribution of the catalysts. The catalyst prepared by the




(a)

(b)

(c)

**Figure 4.** SEM micrographs of the catalysts: (a) prepared by sol gel and calcined at 450°C; (b) prepared by co-precipitation and calcined at 200°C; (c) prepared by the co-precipitation and calcined at 450°C.

sol-gel method has uniform and smaller pore size, because the catalyst structure did not include the $Co_3O_4$ phase. The uniform pore size of the catalyst prepared by the sol-gel method affects the activity of the catalyst.

Scanning electron microscopy (SEM) studies were made to see the homogeneity and shapes of the particles. Figures 4(a) shows the SEM micrographs of the catalyst prepared by the sol-gel method calcined at 450°C, and Figures 4(b) and 4(c) shows the SEM micrographs of the catalyst prepared by the co-precipitation method and calcined at 200° and 450°C. The catalyst calcined at 200°C has spherical particles, and gaps between the particles are almost the same size on the catalyst surface. Significant changes occurred due to increasing the calcination temperature from 200° to 450°C. SEM micrographs of the catalyst calcined at 450°C showed that the size of the gaps between agglomerates increased. The shape and homogeneity of the particles changed. The sizes of the agglomerates became smaller. These changes were due to the sintering process at high temperature.

### *Catalytic Activity Results*

Recent studies showed that preparation technique and pretreatment conditions have a great effect on the catalytic activity of the final catalysts (Güldür and Balıkçı, 2003). Deciding the preparation method at the beginning is very important. In this study two common preparation methods were chosen. The activity test showed that catalyst preparation has a very important effect. Figure 5 shows the % CO conversion as a function of temperature, and Table II shows the 50% CO conversion and 100% CO conversion temperature of the catalysts. The three catalysts gave different catalytic activity behavior for CO oxidation. The best activity was obtained from the catalyst prepared by the co-precipitation method and calcined at 200°C. Although the catalyst prepared by the sol-gel and the catalyst prepared the co-precipitation were calcined at 450°C, these catalysts showed different catalytic activity behavior. The main reason for this result may be due to the uniform pore size distribution

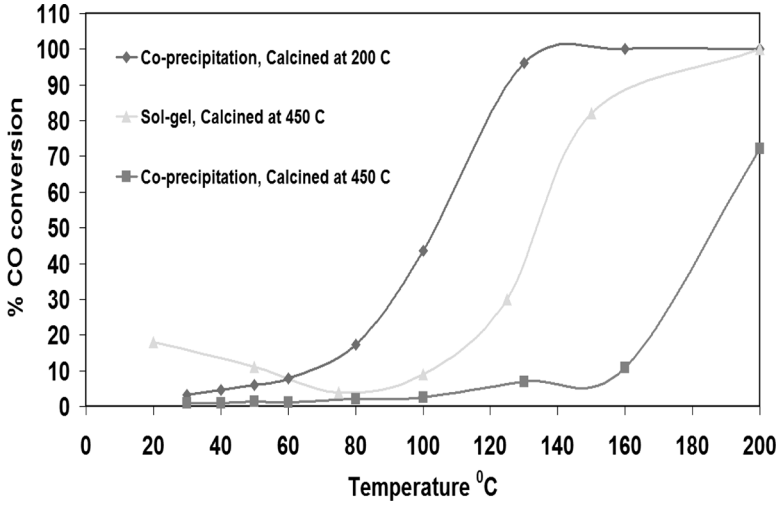



**Figure 5.** CO oxidation activity of catalysts as a function of temperature (SV: 45000 $h^{-1}$, 25–35 mg catalyst, 1 vol.% CO, 21 vol.% $O_2$ , and the remainder He).

**Table II.** The 50% CO conversion and 100% CO conversion temperatures of the catalysts

| 50/50 $Ag_2O/Co_3O_4$ Preparation method | Calcination temperature, °C | 50% CO conversion temperature, °C | 100% CO conversion temperature, °C |
|---|---|---|---|
| Sol-gel | 450 | 133 | 200 |
| Co-precipitation | 200 | 103 | 200 |
| | 450 | 185 | T > 200 |

SV: 45000 $h^{-1}$; 25–35 mg catalyst; 1 vol.% CO, 21 vol.% $O_2$, and remainder He.

of the catalyst prepared by the sol-gel method. The highest activity of the catalyst prepared by the co-precipitation method and calcined at 200°C is due to the highest surface area, biggest crystal size, and highest pore volume of the catalyst.

The $N_2$ adsorption/desorption isotherms of the catalysts provided some information about the catalytic activity of the catalyst. The width of the hysteresis loop on the $N_2$ adsorption/desorption isotherm of the catalyst is related to the activity. The catalyst prepared by the co-precipitation method and calcined at 200°C has largest hysteresis loop and it gave the highest activity. Since the structure of this catalyst includes more cobaltoxide phase, the activity of this catalyst is higher than that of the other catalysts. The CO oxidation activity of the $Ce_{0.9}Cu_{0.1}O_{2-\delta}$ catalyst showed that the higher surface area resulted in better catalytic activity. The reason for this was explained as catalysts with a higher surface area could provide more active species, which could decrease the reaction temperature and enhance the activity (Luo et al., 2007). It is reported that the nanometer $CeO_2$ supported Pd-Cu catalyst gives highest activity for CO oxidation and it can maintain CO complete conversion at about 400°C (Yujin et al., 2007). When the calcination temperature increased from 200° to 450°C, the 50% CO conversion temperature of the catalyst prepared by co-precipitation increased from 103° to 185°C. In this study the decrease in the activity was obtained because of the increase in pore size, decrease in surface area, and decomposition of the silveroxide to metallic silver. Calcination temperature affected the catalytic activities of the catalysts. The catalytic activity of the copper-manganese catalysts, which were prepared by the sol-gel method, decreased with increased calcination temperature, which was due to the sintering processes at a high temperature and a decrease in the surface area (Kramer et al., 2006). As a result, in our study the catalytic activity of the catalysts mostly depends on the calcination temperature. Activity decreased with increasing calcination temperature. It was due to the decomposition of $AgCoO_2$ phase into $Co_3O_4$ and metallic Ag phase. Also, at high temperature the calcination sintering process occurred, which decreased the surface area of the catalyst (observed from SEM studies).

## Conclusion

In this study a 50/50 $Ag_2O/Co_3O_4$ catalyst was prepared by two different methods: co-precipitation and sol-gel. The effect of the preparation method on the physical properties and catalytic activities for CO oxidation was investigated.

Characterization results showed that the highest surface area was obtained from the catalyst prepared by the co-precipitation method and calcined at 200°C. The $Co_3O_4$ phase in the catalyst structure has influence on the surface area, pore volume, and crystal size of the catalysts. The surface areas of the catalysts decreased with increasing calcination temperature because of the decomposition of silveroxide to metallic silver and sintering of the particles during calcination at high temperature. Since the catalysts prepared by the sol-gel method were composed of metallic silver and $AgCoO_2$ phases, the surface area, average crystal size, and pore volume of the catalyst are smaller than those of the catalysts prepared by the co-precipitation method.

CO oxidation activity tests were carried out between 20° and 200°C. The best activity was obtained from the catalyst prepared by the co-precipitation method and calcined at 200°C. The catalyst prepared by the sol-gel method and calcined at 450°C gave the closest activity to the catalyst prepared by the co-precipitation method and calcined at 200°C. It is concluded that the main reason for this is due to the catalyst prepared by sol-gel having a uniform pore size distribution and $AgCoO_2$ phase in addition to the metallic silver and $Co_3O_4$ phases. The catalyst prepared by the co-precipitation method and calcined at 200°C showed the best activity to CO oxidation. Although the catalyst prepared by the sol-gel method and the catalyst prepared by the co-precipitation method were calcined at 450°C, the catalyst prepared by the sol-gel method gave higher activity, which was due to the uniform pore size distribution of catalyst and $AgCoO_2$ phase in the catalyst.

## Acknowledgments

The authors gratefully acknowledge the financial support of the TUBITAK MISAG-229 and Gazi University BAP 06/2006-17 project.

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