Oxidation of Toluene in Humid Air by Metal Oxides Supported on γ -Alumina

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Abstract

Monometallic and bimetallic supported metal oxides catalysts on γ -alumina were prepared by heterogeneous deposition-precipitation. The γ -alumina used as a support was synthesized by the sol-gel and the co-precipitation methods. Supports and catalysts were characterized by Brunauer–Emmett–Teller (BET) surface area, X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The performance of the prepared catalysts was studied for total oxidation of toluene in air at different relative humidity and oxidation temperatures. Efficiency of bimetallic catalysts for deep oxidation of toluene was higher than copper oxide supported on γ -alumina. Although increasing the lanthanum, cobalt, and nickel loading on the support led to a modified catalyst surface and morphology, the catalytic activity of bimetallic catalysts decreased with increasing lanthanum, cobalt, and nickel content due to the reduced amount of copper oxide which has a higher activity for oxidation of volatile organic compounds. The γ -alumina prepared by the sol-gel method using ethanol as a solvent (AlSE) was the best support and La-Cu/AlSE had the best performance (toluene removal efficiency > 90%). In addition, the presence of water vapor in the feed had a negative effect on toluene conversion.

Key Words: *Toluene, Oxidation, γ -alumina, Sol-gel, Co-precipitation, Heterogeneous deposition-precipitation, Bimetallic catalyst.*

1. Introduction

Numerous studies have reported that catalytic oxidation is an efficient and feasible technique for removal of volatile organic compounds (VOCs) from air and the complete oxidation of toluene as a model VOC in air has been widely reported in the literature [1]. Only a few studies have reported the influence of water vapor in the feed on the catalytic oxidation of VOCs [2-3]. The effects of water vapor on the performance of supported catalysts depend on the nature and morphology of the catalysts. Studies reported in the open literature suggest the negative effect of feed humidity on the catalyst activity. Water vapor is an end product in the oxidation of VOCs and could also be present in a humid feed [4]. It has been reported that the conversion of toluene decreased with increasing relative humidity in the feed due to the competition between water vapor, carbon dioxide, and toluene for adsorption on the metal oxides [5-7]. There are a number of investigations on the oxidation of toluene over supported monometallic and bimetallic metal oxides catalysts with transition and noble metals using a variety of supports including alumina [8-9], carbonaceous materials such as activated carbon [1] and carbon nano tubes [10], halloysite [11], and CeO₂[12]. Nano structural alumina with high surface area and high stability is an appropriate low cost support for deep oxidation of toluene [13-14]. Sol-gel and co-precipitation are the most common methods to prepare different forms of alumina including γ and α -alumina powders [15-16]. Alumina particles were synthesized with various shapes and sizes depending on the preparation method. Hexagonal and spherical alumina particles were prepared by the co-precipitation method while spherical alumina particles were formed by the sol-gel method [17]. In a study where γ -alumina was synthesized by the controlled precipitation method using different precipitating agents, it was found that γ -alumina made from ammonium bicarbonate had higher surface area and adsorption capacity [18]. Although there are extensive studies reported in the literature on the deep oxidation of hydrocarbons by supported bimetallic catalysts [1], no studies were detected in the open literature which had examined the effects of the alumina support

preparation method on the catalyst performance or the performance supported metal oxides catalyst prepared by heterogeneous deposition-precipitation over γ -alumina.

The main scope of this investigation was to prepare nano dispersed supported monometallic and bimetallic catalysts on γ -alumina synthesized by sol-gel and co-precipitation methods and examine the effect of the support preparation method on the catalyst performance. Heterogeneous deposition-precipitation was employed for preparing bimetallic catalysts with copper, lanthanum, cobalt, and nickel oxides. The influence of the relative humidity of the feed and the oxidation temperature was also studied in the oxidation of toluene in contaminated air over the prepared catalysts.

2. Experimental section

2.1 Support Preparation

All chemicals and reagents were obtained from Merck. The following starting materials were used in the co-precipitation method for preparation of nano-alumina: aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 1.1 M), ammonium nitrate (NH_4NO_3 , 1.4 M), sodium bicarbonate (NaHCO_3), and ethanol ($\text{C}_2\text{H}_6\text{OH}$, 75 wt.%). Co-precipitation was carried out at in a batch system at constant pH using a mixture containing specified amounts of aluminumnitrate and ammonium nitrate. Sodium bicarbonate was added dropwise to mixture which was kept at 70°C to maintain the pH at 8. Precipitation was continued for 3 hours. The precipitate was filtrated, washed by ethanol, and subsequently dried at ambient temperature overnight. The dried sample was then calcined under nitrogen flow at 550°C for 5 hours. In the sol-gel method, a 0.1M $(\text{C}_4\text{H}_9)_3\text{AlO}_3$ solution was prepared with ethanol and heated at 90°C . An ammonia solution (28 wt.%) was then added until the gel appeared in the solution. Aging was conducted at room temperature for one day and the gel was subsequently dried at 100°C for 24 hours. Calcination was carried out by heating the sample under nitrogen flow to 1000°C at a rate of $20^\circ\text{C}/\text{min}$ and maintaining it at 1000°C for 2 hours. The sol-gel method was repeated using methanol (100 wt. %) as a solvent. The three alumina samples were named

AlSE (sol-gel with ethanol), AlSM (sol-gel with methanol), AlCP (co-precipitation with ethanol).

2.2 Catalyst Preparation

Supported monometallic and bimetallic catalysts on nano-alumina were prepared by the deposition-precipitation method. Nitrate solutions of metals (copper, cobalt, lanthanum, and nickel) were prepared by addition of a specified volume of deionized water to the metal salts. Deposition-precipitation was conducted for 9 hours with mixing and heating at 70–80°C and metal ions were precipitated on the sieved nano-alumina (below mesh 60) by adding NaOH solution (6 wt.%) in 30 minute intervals until reaching a basic solution of pH=10–11 to obtain an 8 wt.% metal loading. The solution was filtered and the catalyst sample was washed by heated deionized water several times. The sample was then dried in an oven at 110°C overnight. The dried catalyst was subsequently calcined in a tubular furnace under nitrogen flow for 3 hours at 550°C. Preparation of bimetallic catalysts with a total of 8 wt. % metal loading with various ratios (Metal: Cu= 1:1, 1:3 and 3:1) were carried out by co-deposition-precipitation with the nitrate solutions of metals being added simultaneously to the sieved nano-alumina support. Prepared catalysts were denoted by types of support and metal content, Metal (x(wt. %))Cu(y(wt. %))/Support, (x=2,4 and 6, y=8-x). For example, the bimetallic catalyst with 2 wt. % Cu and 6 wt. % La supported on nano-alumina prepared by the sol-gel method with ethanol was named La6-Cu2/AlSE.

2.3 Catalyst Activity

The schematic of the experimental apparatus to carry out the oxidation of toluene in air in the presence of water vapor is presented in Fig. 1. The performance of the prepared catalysts was evaluated in a tubular fixed bed reactor operating at atmospheric pressure. Inlet concentration of toluene and relative humidity were controlled by allowing an air stream to

pass at a specified flow rate set with a rotameter over isolated bubbling saturators each filled with toluene and water. Thermocouples placed in each saturator were used to monitor the liquid temperature in each saturator to control the liquid temperature to provide the desired concentration of toluene and water vapor in the feed to the reactor. A digital thermocouple located at the center inside the reactor and a PID temperature controller was used to monitor and maintain the reactor temperature at the desired level. 1 g of catalyst was packed in the center of the horizontal quartz reactor that was 10 cm in length with an internal diameter of 12 mm. Glass beads and glass wool were used to pack the reactor to prevent flow channeling. The oxidation temperature and relative humidity were adjusted in the range of 250-450°C and 0-94%, respectively. Outlet concentrations from the reactor were determined by gas chromatography-mass spectroscopy (GC-Mass, Agilent) equipped with a 5975C mass detector and 30 m long HP-5MS stainless steel column. The relative humidity of the feed was measured by an electrical thermometer and humidity meter (humidifier, ST-625) at regular time intervals. There were no intermediate oxidation products at the outlet of the reactor indicating the complete oxidation of toluene. All experiments were performed at a constant feed flow rate of 166 ml/min with inlet toluene concentration of 10000 ppmv.

2.4 Catalyst Characterization

Surface area and pore sizes of catalysts were determined by nitrogen adsorption/desorption at 77 K using a BEL (Japan) physical-adsorption apparatus. Catalyst surface area and average pore size was measured by Brunauer–Emmett–Teller (BET) theory. X-ray Diffraction (XRD) patterns obtained at 30kV, 20mA, and copper K α radiation at scanning rate of 3°/min using a STOE model D-64295 equipment were used for identification and determination of the size of catalyst crystallites. The surface morphologies of supported monometallic and bimetallic catalysts were examined using a field-emission electron microscope (FESEM) at 15kV using a model S-4160 Hitachi equipment from Japan. Micro

images of supported catalysts were obtained by transmission electron microscopy (TEM) to investigate the morphology and size distribution of the prepared catalyst samples using an EM208-Philips instrument equipped with a Schottky field emission gun operated at 100 keV and magnification range of 180000x. XPS analysis was carried out on AXIS Ultra DLD (Kratos Analytical, UK).

3. Results and Discussion

3.1 Support Characterization

XRD patterns of different supports prepared by co-precipitation and sol-gel methods are presented in Fig. 2. Different alumina phases might be formed during the preparation steps depending on the growth temperatures. Boehmite phase can be observed at low temperatures. γ -Alumina with a high surface area and a high thermal stability would appear with increasing growth temperature. The α -alumina phase with tetragonal morphology and having a higher thermal stability and lower surface area than γ -alumina requires high growth temperatures ($\sim 1000^\circ\text{C}$). Consequently, γ -alumina with high surface area can be a very suitable catalyst support. As indicated in Fig. 2, the sol-gel method is an appropriate method for synthesis of γ -alumina with smaller crystallite sizes. The size of the crystallites was obtained using Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

Where D is the mean crystallite diameter (nm), K is the dimensionless shape factor (spheres = 0.89), λ is the X-ray wavelength (X-ray tube: Cu, $\lambda = 0.154$ nm), β is the line broadening at half the maximum intensity and θ is the Bragg angle. The crystallite sizes for different alumina supports are reported in Table 1 indicating that the sol-gel method with ethanol as solvent is an efficient and the feasible preparation technique to generate well dispersed nano alumina as compared with the co-precipitation method.

FESEM images of the prepared supports are presented in Fig. 3. Alumina showed homogenous sphere structure with light color in all images. The images indicate that alumina prepared by the sol-gel method using ethanol **as a solvent** has a more homogenous structure with higher dispersion of particles. These results are in agreement with the XRD patterns. The observed particle sizes from FESEM images also confirm the results obtained from Scherrer equation.

Architectural porosity of three types of gamma-alumina (AlCP, AlSE and AlSM) was studied by N₂ adsorption-desorption test, which showed type-IV isotherm that is typical for mesoporous adsorbents shown in Fig. 4 based on the IUPAC classification. Important feature of type IV isotherms is the presence of micropores associated with mesopores. It can provide an appropriate porous media for metal ions during catalyst preparation method. The surface area for the AlCP, AlSE and AlSE is calculated 305, 284 and 97 m²/g by BET theory, respectively. It is shown the surface area decreased by forming alumina by sol-gel method with methanol as a solvent which is confirming the XRD and FESEM Results.

The surface area and total pore volume AlSE, AlSM and AlCP obtained by BET, BJH and t-plot analyses are summarized in Table 2.

3.2 Characterization of Monometallic Catalysts

The XRD patterns of monometallic catalysts Cu8/AlSE, Cu8/AlCP, and Cu8/AlSM are presented in Fig.5. Broad peaks with high intensity corresponding to crystallites of CuO were detected at $2\theta=33-40^\circ$ (ICDD: 00-001-1117). Cu (OH)₂ that was formed during catalyst preparation by heterogeneous deposition-precipitation, resulted in the formation copper oxide during the calcinations step that was carried out at high temperatures [1]. XRD patterns did not indicate the formation of Cu₂O and Cu₃O₄ over γ -alumina as was checked by (00-033-0480) and (00-001-1142) ICDD codes representative of Cu₃O₄ and Cu₂O, respectively. The sizes of crystallites were calculated to be below 9 nm according to Scherrer equation and are

reported in Table 3. Results demonstrated that well dispersed nano-structural supported copper oxide catalysts were synthesized when the γ -alumina was prepared by the sol-gel method with ethanol as a solvent.

FESEM images were obtained for Cu8/AlSE, Cu8/AlCP, and Cu8/AlSM catalysts and are presented in Fig. 6 all indicating the bright spherical morphology of nano-particles with high dispersion over γ -alumina. The best results were obtained for Cu8/AlSE with smallest dispersed particles in agreement with XRD results.

Fig. 7 illustrates the TEM images of Cu8/AlSE which was a highly dispersed supported copper oxide over γ -alumina in accordance with XRD and FESEM results. The darker and spherical dots represent CuO crystallites over γ -alumina. Fig. 7 also indicates that size of the uniform CuO crystallites were smaller than 9 nm. The size distributions of the crystallites were obtained by Clemex vision software.

Nitrogen adsorption/desorption isotherms for Cu8/AlSE, Cu8/AlCP, and Cu8/AlSM are presented in Fig. 8 indicating a type IV isotherm with hysteresis loops for adsorption on the mesoporous γ -alumina support synthesized by the sol-gel method. Fig. 8 demonstrates the high capacity of Cu8/AlSE for adsorption of nitrogen. Porosity, average pore diameter, and the specific surface area of the catalysts are reported in Table 4. Crystallites with larger size and lower surface area were generated for Cu8/AlSM due to the longer nucleation time in the sol-gel method with methanol as a solvent.

3.3 Characterization of Bimetallic Catalysts

XRD patterns for three types of copper, nickel, cobalt, and lanthanum bimetallic catalysts supported over γ -alumina by heterogeneous deposition-precipitation are presented in Fig. 9. XRD patterns of La6-Cu2/AlSE, La4-Cu4/AlSE and La2-Cu6/AlSE in Fig. 9a indicate two types of crystallites generated over alumina. XRD patterns were compared with those for

CuO, LaO, LaCu₆, La₂O₃, Al₂La, CuLaO₂, and CuLa₂O₄ from ICDD: 00-080-1917, 00-018-0680, 00-037-1448, 01-083-1345, 00-003-0699, 00-022-0238, and 00-022-0239, respectively.

The patterns indicated that the strong and narrow peaks at $2\theta = 35, 53$, and 38° corresponded to CuO, LaO, and LaCu₆, respectively. There were no detected crystallite phases for La₂O₃, Al₂La, CuLaO₂ and CuLa₂O₄ from the XRD patterns. The broad peaks with low intensity disappeared with increasing La loading on the support due to its high adsorption tendency compared with copper ions suggesting that La is initially adsorbed on the support and the available surface would provide for a higher dispersion of copper over the alumina support.

The XRD patterns for Co₂-Cu₆/AlSE, Co₄-Cu₄/AlSE, and Co₆-Cu₂/AlSE are presented in Fig. 9b. Similar results were obtained by loading cobalt and copper ions over alumina simultaneously. As the adsorption tendency for cobalt ions is higher than copper ions on alumina, cobalt ions are dominant in contrast with copper ions for adsorption on alumina. The broad and narrow peaks appeared with increasing cobalt content and CoO crystallites were generated instead of Co₂O₃ crystallites. Strong peaks at $2\theta = 46-61^\circ, 31^\circ$, and $35-38^\circ$ represent CoO, Co₂O₃, and Co₂O₃ crystallites, respectively. No peaks were detected for Co₂O₃CuO, Co and Al₆₂Cu₂₀Co₁₅ over alumina. The XRD patterns for three different catalysts synthesized by copper and nickel deposition are presented in Fig. 9c. The results illustrate that better dispersed supported bimetallic catalysts were generated with increasing nickel and decreasing copper loading over the nano-alumina support. Detectable crystallites for this type of catalysts consisted of NiO, NiAl₂O₄, Ni₂O₃ and CuO at $2\theta = 43-63^\circ, 37^\circ, 31-33^\circ$, and $35-38^\circ$ in the agreement with ICDD codes 00-001-1239, 00010-0339, 00-010-0339, and 01-080-1917, respectively. XRD peaks were examined for the presence of Cu_{0.8}Ni according to ICDD code (00-009-0205) which was undetectable. With increasing nickel content peaks with lower intensity and broader width were observed implying that nickel was more readily deposited on the alumina surface compared with copper. The crystallite sizes for these three groups of bimetallic catalysts were calculated by Scherrer equation and are reported in Table 5 with the

smallest size belonging to La-Cu/AlSE catalysts. There were no significant differences between the crystallite sizes of Ni-Cu/AlSE and Co-Cu/AlSE catalysts.

TEM images of some of the bimetallic supported catalysts with different copper, cobalt, nickel, and lanthanum contents are presented in Fig. 10 indicating three different colors including white, lighter black, and dark black corresponding to conventional bright field, alumina, and metal oxide crystallites, respectively. Images indicated a uniform and narrow size distribution of dispersed metal oxide crystallites over alumina which confirmed the XRD results. TEM images display uniform size below 10 nm for metal oxide crystallites on the support. Statistical analysis was carried out to determine the size distribution of metal oxides reported in Table 5 using the Clemex vision software confirming that La-Cu/AlSE catalyst had the smallest crystallites among the bimetallic catalysts.

The nature of surface species and composition of the copper, cobalt, lanthanum and nickel were investigated by XPS measurements. XPS graph of fresh calcined Cu8/AlSE with three sharp peaks is shown in Fig. 11. Comparing the values of the binding energy with those in the open literature, the two main peaks situated at 933.5 and 953.7 eV belong to Cu^{2+} in CuO. The presence of the satellite peak for Cu $2\text{P}_{3/2}$ core level spectra illustrates vaguely the presence of Cu^{2+} on the surface of support. Furthermore, no satellite peaks were detected in studying Cu^{2+} and Cu^0 which is in a good agreement with previous reports [19-21]. The XPS pattern of La2-Cu6/AlSE is also seen in Fig. 12. The peak at binding energy of 933.4 eV ($\text{Cu}2\text{P}_{3/2}$) indicates that copper exists on La2-Cu6/AlSE Only as a copper oxide (CuO). The binding energy for $\text{La}3\text{d}_{5/2}$ level at 835eV originates from La^{3+} is present as La_2O_3 , which could be identified by XRD results [22-23]. Fig.13 shows the XPS of fresh Co2-Cu6/AlSE with the main peak situated at 780 eV belong to Co^{2+} in CoO. The $\text{Co}2\text{P}_{1/2}$ binding energy of the catalyst is 795 eV, it suggests the presence of Co_2O_3 in the surface layer of the alumina as a support [24]. The XPS result of Ni2-Cu6/AlSE is shown in Fig. 14. The binding energy for $\text{Ni}2\text{P}_{3/2}$ level at 855.8 eV originates from Ni^{2+} is present as Ni_2O_3 . The peak at the binding

energy of 873.8 eV ($\text{Ni}2\text{P}_{1/2}$) suggests the presence of NiO on the surface of the catalyst [25] which can confirm XRD findings.

4. Catalytic Performance

4.1 Screening experiments for selection of the support

To investigate the effect of support preparation method on catalyst performance in the conversion of toluene in humid air, experiments were carried out over 1 g of catalyst at a reaction temperature of 350°C using a feed with flow rate of 166 ml/min, toluene concentration of 10000 ppmv, and relative humidity of 0-94%. Toluene conversions as a function of time-on-stream are presented in Fig.15 for Cu8/AlSE, Cu8/AlCP, and Cu8/AlSM catalysts indicating that after an initial drop in catalyst activity, toluene conversions reached steady values. For all three catalysts toluene conversion decreased with increasing relative humidity from 0 to 94% during contact time. Fig. 15 also indicates that the maximum conversion of toluene was achieved by Cu8/AlSE for both levels of feed relative humidity. Oxidation products including water vapor and carbon dioxide as well as the water vapor present in the humid feed can cover the hydrophilic active sites of alumina thus reducing the catalyst activity. Results illustrated that toluene conversions were 60.9, 43.7 and 30.2% over Cu8/AlSE, Cu8/AlCP, and Cu8/AlSM, respectively using a feed with relative humidity of 94%. The higher catalytic activity for Cu8/AlSE could be due to higher dispersion of smaller size of metal oxides over the γ -alumina support.

4.2 Effect of oxidation temperature on the performance of Cu8/AlSE

Fig.16 presents the toluene conversion data obtained for Cu8/AlSE using a feed with relative humidity in the range of 0-94% and reaction temperatures in the range of 250-400°C while keeping other operating conditions the same as reported above. As indicated in Fig.16, toluene conversions were higher for dry feed at all reaction temperatures. Results also

indicated that after a sharp decrease over the initial stage of the reaction (up to 20 minutes from the start of a run), toluene conversions reached steady values at about 60 min from the start of a run. The catalyst is highly active at the start of a run and as the reaction proceeds, oxidation products such as carbon dioxide compete with toluene to occupy the active metal sites thus lowering the toluene conversions. The highest toluene conversions were 93.6, 91.8, and 82.8% over Cu₈/AlSE at 400°C with relative humidity of 0, 40 and 94%, respectively. The present study demonstrated that relative humidity did not have a significant effect on toluene conversions at either low reaction temperatures (250°C) where the catalyst activity is very low or at high reaction temperatures (400°C) where the catalyst activity is high and the competitive adsorption of water vapor is less likely.

4.3 Catalytic performance over bimetallic catalysts

Fig. 17 presents toluene conversions over La-Cu/AlSE, Co-Cu/AlSE, and Ni-Cu/AlSE bimetallic catalysts at reaction temperature of 350°C and relative humidity of 94% while keeping all other operating conditions the same as previously stated. Fig.17a indicates that addition of lanthanum and copper oxides to the alumina support reduces the catalyst activity for complete oxidation of toluene despite the surface modification caused by simultaneous addition of lanthanum and copper. Activity of copper oxide for total oxidation of toluene is higher than other metal oxides as reported in the literature [4]. Compared with other La-Cu/AlSE bimetallic catalysts, therefore, La₂-Cu₆/AlSE had the highest activity for oxidation of toluene in the humid air. Fig.17b and Fig. 17c also show a similar trend of decreasing catalyst activity with increasing cobalt content of Co-Cu/AlSE catalysts and with increasing nickel content of Ni-Cu/AlSE catalysts, respectively. Maximum toluene conversions of 90.2, 76.4, and 64% were obtained over La₂-Cu₆/AlSE, Co₂-Cu₆/AlSE, and Ni₂-Cu₆/AlSE, respectively. Fig.18 shows the long term performance of La₂-Cu₆/AlSE for toluene

conversion for a feed with relative humidity of 94% indicating that after the initial decrease, catalyst activity remained constant for up to 54 hours.

Toluene might be oxidized over supported metal oxides catalysts at temperatures below those for thermal combustion in the presence of water vapor. Supported noble and transition metal oxides are widely applied for complete oxidation of toluene. Li et al. [3] found that the conversion of toluene in the presence of water vapor was near 100% at 330°C with an inlet feed toluene concentration of 1200 ppmv over Cu-Mn O_x/gamma-Al₂O₃ in the comparison with the supported catalysts over TiO₂ and cordierite. They used commercial alumina for synthesize nano catalysts. Other copper based catalysts supported on commercial alumina, cord and cordierite was also studied for total oxidation of toluene in the presence water vapor, Jiancai et al. [26], who reported a high activity of copper oxide supported on gamma-alumina for reaction at 450°C and inlet feed concentration of 3.5 gm⁻³. Synthesized bimetallic catalysts in this work have been utilized at 350°C as an oxidation temperature.

Plasma catalysis system and photocatalytic oxidation are another approaches for complete oxidation of toluene in the humidified air which has been investigated in many researches [27-28]. Wu et al. [27] found that supported nickel oxide catalysts over gamma-alumina, SBA-15 and TiO₂ can be appropriate catalysts for oxidation of toluene. Nickel oxide catalyst over commercial alumina had a good performance for complete oxidation of toluene in comparison with other supports. To the best of our knowledge, using nano gamma-alumina prepared by sol-gel method for synthesis of dispersed supported nano bimetallic catalysts for oxidation of toluene is addressed for the first time in our investigation.

5. Conclusion

Monometallic and bimetallic catalysts were prepared using γ -alumina as a support for total oxidation of toluene in humid air at atmospheric pressure. Three series of γ -alumina were

synthesized by the sol-gel method with either ethanol or methanol as a solvent and by the co-precipitation method. Catalytic activity of supported copper oxide on the γ -alumina synthesized by the sol-gel method with **ethanol as a solvent** (AlSE) was higher compared with the same catalyst supported on other γ -alumina supports. Heterogeneous deposition-precipitation method was used for preparation of bimetallic catalysts supported on AlSE with different ratios of copper oxide to oxide of other metals including lanthanum, cobalt, and nickel. The type and ratio of the second metal had significant effects on the size of the metal oxide crystallites, the formation of different crystallite phases, the dispersion of active sites, the surface area and the morphology of the prepared catalyst samples, and the catalyst activity. Although the addition of the second metal led to enhanced dispersion of copper and better surface characteristics, the activity of supported bimetallic catalysts (La, Co, or Ni)-Cu/AlSE decreased with increasing lanthanum, cobalt, or nickel loading on the γ -alumina. Among the three series of bimetallic catalysts, those prepared with copper and lanthanum resulted in the best performance for complete oxidation of toluene in air. Antonym effect of water vapor in reactor feed was investigated which had no significant effect on the catalyst activity at either low reaction temperatures (250°C) where the catalyst activity is very low or at high reaction temperatures (400°C) where the catalyst activity is high and the competitive adsorption of water vapor is less likely.

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Table 1. Crystallite size of alumina prepared by the sol-gel and co-precipitation methods

Sample	Crystallite phase	Crystallite size (nm)
AlCP	Large	6.3
	Small	3.5
AlSE	Large	4.7
	Small	2.3

Table 2. Textural properties of the prepared γ -Alumina by different methods

γ -Alumina	$S_{BET}/m^2 \cdot g^{-1}$	$V/cm^3 \cdot g^{-1}$	D/nm
AlCP	305	0.2988	5.653
AlSE	284	0.3734	8.771
AlSM	97	0.1351	9.215

Table 3. Crystallite size of the prepared catalysts over γ -alumina by heterogeneous deposition-precipitation method

Sample	Crystallite phase	Crystallite size (nm)
Cu8/AlCP	Large	8.2
	Small	3.5
Cu8/AlSE	Large	6.1
	Small	3.3
Cu8/AlSM	Large	20.4
	Small	8.4

Table 4. Textural properties of the prepared catalysts over γ -alumina by heterogeneous deposition-precipitation method

Catalyst	$S_{BET}/m^2 \cdot g^{-1}$	$V/cm^3 \cdot g^{-1}$	D/nm
Cu8/AlCP	204	0.3107	6.0927
Cu8/AlSE	154	0.4121	10.682
Cu8/AlSM	53	0.1417	10.955

Table 5. Crystallite size of the bimetallic catalysts over γ -alumina

Sample	Crystallite phase	Crystallite size (nm)
La2-Cu6/AlSE	Large	6.1
	Small	2.9
La4-Cu4/AlSE	Large	5.8
	Small	2.8
La6-Cu2/AlSE	Large	4.6
	Small	2.6
Co2-Cu6/AlSE	Large	4.1
	Small	2.9
Co4-Cu4/AlSE	Large	5.2
	Small	2.8
Co6-Cu2/AlSE	Large	8.9
	Small	3.5
Ni2-Cu6/AlSE	Large	7.9
	Small	2.8
Ni4-Cu4/AlSE	Large	10.7
	Small	2.9
Ni6-Cu2/AlSE	Large	9
	Small	5.3

Fig. 1. Schematic diagram of the experimental set-up

Fig. 2. XRD patterns of AlCP and AlSE

Fig. 3. FESEM images for AlCP and AlSE

Fig. 4. Nitrogen adsorption-desorption results for AlCP, AlSE, and AlSM

Fig. 5. XRD patterns of Cu8/AlCP, Cu8/AlSE, and Cu8/AlSM

Fig. 6. FESEM images for Cu8/AlCP, Cu8/AlSE, and Cu8/AlSM

Fig. 7. TEM images for Cu8/AlSE

Fig. 8. Nitrogen adsorption-desorption results for Cu8/AlCP, Cu8/AlSE, and Cu8/AlSM

Fig. 9. a) XRD patterns for the prepared bimetallic catalysts over γ -alumina by heterogeneous deposition-precipitation method Cu-La

b) XRD patterns for the prepared bimetallic catalysts over γ -alumina by heterogeneous deposition-precipitation method Cu-Co

c) XRD patterns for the prepared bimetallic catalysts over γ -alumina by heterogeneous deposition-precipitation method Cu-Ni

Fig. 10. a) TEM images for La₂-Cu₆/AlSE

b) TEM images for Co₂-Cu₆/AlSE

c) TEM images for Ni₂-Cu₆/AlSE

Fig. 11. XPS spectra of the Cu₈/AlSE

Fig. 12. XPS spectra of the La₂-Cu₆/AlSE

Fig. 13. XPS spectra of the Co₂-Cu₆/AlSE

Fig. 14. XPS spectra of the Ni₂-Cu₆/AlSE

Fig. 15. Total oxidation of toluene over supported copper catalysts Cu8/AlSE, Cu8/AlCP and Cu8/AlSM with 0 and 94% relative humidity of the feed

Fig. 16. a) Total oxidation of toluene over Cu8/AlSE at feed relative humidity of 0- 94% and reaction temperatures of 250°C

b) Total oxidation of toluene over Cu8/AlSE at feed relative humidity of 0- 94% and reaction temperatures of 300°C

c) Total oxidation of toluene over Cu8/AlSE at feed relative humidity of 0- 94% and reaction temperatures of 350°C

d) Total oxidation of toluene over Cu8/AlSE at feed relative humidity of 0- 94% and reaction temperatures of 400°C

Fig. 17. a) Total oxidation of toluene over the prepared catalysts at feed relative humidity of 94% and reaction temperatures of 350°C for La2-Cu6/AlSE, La4-Cu4/AlSE, La6-Cu2/AlSE, and Cu8/AlSE

b) Total oxidation of toluene over the prepared catalysts at feed relative humidity of 94% and reaction temperatures of 350°C for Co2-Cu6/AlSE, Co4-Cu4/AlSE, Co6-Cu2/AlSE, and Cu8/AlSE

c) Total oxidation of toluene over the prepared catalysts at feed relative humidity of 94% and reaction temperatures of 350°C for Ni2-Cu6/AlSE, Ni4-Cu4/AlSE, Ni6-Cu2/AlSE, and Cu8/AlSE

Fig. 18. Long term performance of La2-Cu6/AlSE for oxidation of toluene at feed relative humidity of 94% and reaction temperature of 350°C

Figure 1.

Schematic diagram of the experimental set-up

Figure 2.

XRD patterns of AlCP and AlSE

Figure 3.

FESEM images for AlCP and AlSE

Figure 4.

Nitrogen adsorption-desorption results for AlCP, AlSE, and AlSM

Figure 5.

XRD patterns of Cu₈/AlCP, Cu₈/AlSE, and Cu₈/AlSM

Figure 6.

FESEM images for Cu₈/AlCP, Cu₈/AlSE, and Cu₈/AlSM

Figure 7.

TEM images for Cu₈/AlSE

Figure 8.

Nitrogen adsorption-desorption results for Cu8/AlCP, Cu8/AlSE, and Cu8/AlSM

Figure 9.

XRD patterns for the prepared bimetallic catalysts over γ -alumina by heterogeneous deposition-precipitation method a) Cu-La, b) Cu-Co, and c) Cu-Ni

a)

b)

c)

Figure 10.

TEM images for a) La₂-Cu₆/AlSE, b) Co₂-Cu₆/AlSE, and c) Ni₂-Cu₆/AlSE

a)

c)

Figure 11.

XPS spectra of the Cu₈/AlSE

Figure 12.

XPS spectra of the La₂-Cu₆/AlSE

Figure 13.

XPS spectra of the Co₂-Cu₆/AlSE

Figure 14.

XPS spectra of the Ni₂-Cu₆/AlSE

Figure 15.

Total oxidation of toluene over supported copper catalysts Cu8/AlSE, Cu8/AlCP and Cu8/AlSM with 0 and 94% relative humidity of the feed

Figure 16.

Total oxidation of toluene over Cu₈/AlSE at feed relative humidity of 0- 94% and reaction temperatures of a) 250°C, b) 300°C, c) 350°C, and d) 400°C

a)

b)

c)

d)

Figure 17.

Total oxidation of toluene over the prepared catalysts at feed relative humidity of 94% and reaction temperatures of 350°C for a) La₂-Cu₆/AlSE, La₄-Cu₄/AlSE, La₆-Cu₂/AlSE, and Cu₈/AlSE, b) Co₂-Cu₆/AlSE, Co₄-Cu₄/AlSE, Co₆-Cu₂/AlSE, and Cu₈/AlSE, and c) Ni₂- Cu₆/AlSE, Ni₄-Cu₄/AlSE, Ni₆-Cu₂/AlSE, and Cu₈/AlSE

a)

b)

c)

Figure 18.

Long term performance of La₂-Cu₆/AlSE for oxidation of toluene at feed relative humidity of 94% and reaction temperature of 350°C