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Study the Effect on Activity of Alumina Supported CuO-CeO_2-ZrO_2 Catalysts Prepared by Four Methods for CO Oxidation

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In the present study four catalysts, prepared by four different methods i.e. co-impregnation, citric acid sol-gel, urea nitrate combustion and urea gelation co-precipitation methods, have been used to study the effect of CO oxidation. The precursor $Cu(NO_3)_2 3H_2O$ has been used as for the preparation of catalysts having the composition $CuCe_{5.17}Zr_{3.83}O_x/\gamma$-$Al_2O_3$(25wt%). Catalysts were calcined at 500^0C and characterized by BET, XRD, TGA/DSC and SEM. A fixed weight (100 mg) of the catalyst was taken in a tubular fixed bed reactor at atmospheric pressure. 2.0% CO in air at a total feed rate of 60 ml/min was used in the reactor. The oxidation of CO to carbon dioxide was carried out at temperature ambient to 280°C. The preparation methods effect the catalytic activity of the catalysts as is discussed in the results. Excellent activity for CO oxidation is shown by the catalyst prepared by sol – gel method followed by co-impregnation, urea gelation and urea nitrate combustion methods. It exhibited the total conversion at 210°C. All the four catalysts prepared did not show any deactivation activity for 50 hours of continuous runs.

Keywords: CO Oxidation, Alumina, Sol-Gel, Combustion, Oxidation, Ceria, Catalyst

INTRODUCTION

Carbon monoxide is considered as an important air pollutant. It is mainly emitted from industries and transportation activities. Noble metals are considered to be efficient catalysts for CO oxidation (Ruth *et al*. 2000, Costello *et al*., 2002; Gardner *et al*., 1995; Sarkarand Khanra, 2005, Santra and Goodman, 2002).

However, noble metals being expensive and rare, oxides of transition metals, have been studied by many researchers for CO oxidation. (Marba'n, and Fuertes, 2005; El-Shobaky, and Ghozza, 2004, Zheng, *et al*. 2004, Mguig 2004, Federico 2004).

The catalysts containing oxides of Cu, Cr, Co, Mn, Ni, etc. have been studied by many workers and are well known to be active in catalytic oxidation of carbon monoxide and hydrocarbons. (Severino, *et al*. 1998, Hamada 1994, Royer and Duprez 2011).

The catalytic activity and selectivity of copper oxide based catalysts can be modified by loading the support or by introduction of different modifiers (Stankova, *et al*. 2001, Panatayov 1995) Supports applied to the catalysts are the oxides like Al_2O_3, SiO_2, TiO_2 and ZrO_2. (Artizzu, *et al*. 1999, Sun, *et al*. 2002, Carniti *et al*. 2000, Miyadera 1998, Aguila, *et al*. 2008).

Mostly γ-Al_2O_3 is used as the support for catalysts used in oxidation–reduction reactions. It has been found that in many cases, due to formation of metal aluminates, by the reaction between the transition metal oxide and Al_2O_3, the catalytic activities of γ- Al_2O_3, supported catalysts decreases with time. Due to its high oxygen storage capacity, ceria is extensively used as a promoter and/or support in many catalytic oxidation reactions. CeO_2 stabilizes the catalyst against metal dispersion and stores and releases oxygen (Cole *et al*. 2010, Liu and Fu 2004).

Mixed oxides mostly shows the higher catalytic activity than that of their individual oxides. (El-Shobaky 2004).

Ce-Zr mixed oxides inhibits the thermal sintering of CeO_2 (Monte and Kaspar 2005, Kašpar 2003) and enhances the reducibility of ceria hence the activity of Cu-Ce-Zr oxide catalysts is improved (Kapoor *et al*. 2001).

It has been also been reported that the incorporation of ZrO_2 into CeO_2 not only increases thermal resistance of the resulting mixed oxide but also improves other properties of the catalysts forming a Ce-Zr-O solid solution.(Monte and Kaspar 2005, Balducci 1995).

Cao *et al*. (2008) reported that the synergistic effect between CuO and the $Ce_{0.8}Zr_{0.2}O_2$ support, were responsible for the high catalytic activity for low temperature CO oxidation. The support has a strong influence on the activity of the catalysts (Ayastuy 2010).

To understand the relation between the preparation methods and the properties of catalysts, number of preparation methods for $CuO-CeO_2$ catalysts have been developed by different workers. A review of different methods of preparation of $CuO-CeO_2$ catalysts and their various applications have been reviewed in earlier work (Prasad and Rattan, 2010).

Very little work has been reported on the alumina supported $CuO-CeO_2-ZrO_2$ catalyst for CO oxidation. Marbán and Fuertes (2005), prepared $CuO–CeO_2$ catalysts by sol–gel using citrates and have reported low degree of agglomeration. CuO/CeO_2 catalysts prepared with synthesis combined with impregnation method exhibited better catalytic performance (Zeng et.al. 2004). The effect of preparation methods on alumina supported $CuO-CeO_2-ZrO_2/ Al_2O_3$, (15%) catalyst for CO oxidation have been studied in our earlier work (Prasad and Rattan 2012).

The present investigation forms a part of continuing study undertaken to explore the significance of preparation methods on the activity of the alumina supported $CuO-CeO_2-ZrO_2$ catalyst for CO oxidation. In the present work, $CuO-CeO_2-ZrO_2/\gamma-Al_2O_3$ (25%) catalysts have been prepared by four different methods, characterized by various techniques and evaluated for CO oxidation.

EXPERIMENTAL

Catalyst Preparation

γ-Alumina (25 wt% , 100–120 mesh size particles) supported-on copper-ceria-zirconia catalysts having composition $CuCe_{5.17}Zr_{3.83}O_x$ with molar ratio of Cu/(Cu+Ce+Zr) = 0.1 and of Ce/Zr = 1.35 were prepared using all AR-grade chemicals by four different methods, namely, Co-impregnation method (CI), Citric acid sol-gel method (SG), Urea-nitrate combustion method (UC), and Urea gelation co-precipitation method (UG).

The procedure described byAguila *et al.* (2008), was used for the preparation of catalyst sample by co-impregnation method. The requisite amount of support with a distilled water solution containing $Cu(NO_3)_2.3H_2O$, $Ce(NO_3)_3.6H_2O$ and $ZrO(NO_3)_2.H_2O$, were mixed and the resulting slurry was evaporated with constant stirring and drying was carried at 105°C, calcined at 500°C for 3 hours under static air in a muffle furnace. The catalyst powders were cooled to room temperature then stored in air tight bottle and marked as Cat-CI.

The method described by Liang *et al.* (2008) was used to prepare the catalyst by Citric acid sol-gel method. The nitrates of the components of the catalysts were dissolved in distilled water, Citric acid and polyglycol were added and the solution was thoroughly mixed. Required amount of alumina was added into the solution with constant stirring and heating at 80°C till transparent gel was formed. The gel was dried at 105°C, powders obtained were decomposed at 300°C and calcined at 500°C for 3 h. The catalyst powders were cooled to room temperature then stored in an air tight bottle marked as Cat-SG.

The method described by Avgouropoulos *et al.* (2003) was used to prepare the catalyst sample by Urea–nitrate combustion method (UC). Nitrates of copper, cerium and zirconium, and urea, $CO(NH_2)_2$ were mixed with distilled water in appropriate molar ratio. The mixed solution was heated at 80°C and the resulting viscous gel was preheated at 500°C in a fuming cupboard. In a couple of minutes the gel started boiling and ignited spontaneously yielding a foamy voluminous powder. The catalyst sample Cat-UC, obtained was stored in air–tight bottle.

Urea gelation co-precipitation method**,** as described by Liu, *et al.*(2004), consisted of mixing the aqueous metal nitrate solutions in the ratio of as described in the above method . The solution was heated at 100°C under vigorous stirring and distilled water was added, boiling the resulting gel for 8 hrs. at 100°C. The resulting gel was filtered and the precipitates were washed twice with distilled water at 50–70°C and then the cake was dried in an oven at 120°C for overnight. After drying it was crushed into smaller particles and resulting powder was calcined in a muffle furnace at 500°C for 3 hours. The sample was termed as Cat-UG.

Catalyst Characterization

Textural characterization of the catalyst samples prepared was done by nitrogen adsorption-desorption at -196°C using

Quantachrome Nova 2200e surface area analyzer. X-ray diffraction (XRD) patterns of the catalysts were collected on a 'X'-Pert Pro Model, Panalytical Co. (Philips) Netherland, powder diffracto-meter using Cu Kα radiation for crystal phase identification of the catalysts. The patterns were recorded at room temperature with a 2θ range from 20 to 80°. For surface morphological studies of the catalysts a high-resolution SEM, Hitachi-3700 N, Japan, was used. TGA/DSC thermograms of the catalysts precursors were recorded by Perkin Elmer, STA-6000, simultaneous thermal analyser.

Catalytic activity

As described earlier (Prasad and Rattan 2009), a compact tubular packed bed flow reactor is used to find the catalytic activity of the catalyst samples prepared. The tests were conducted at atmospheric pressure and temperature range from ambient to 300°C under steady state conditions. No pretreatment was applied before each catalytic test. A gas mixture of 2.0 % CO in air a flow rate of 60 ml min^{-1} was introduced to the reactor. Air used was passed through CaO and KOH to remove moisture and CO$_2$.

Hundred milligram of the catalyst diluted to 5 ml with Al$_2$O$_3$ of same size (100-150 mesh) was placed into the reactor. A temperature controller (±0.5^{0}C) was used to heat the reactor. After 60 minutes of steady state the effluent gases were analyzed online by a GC equipped with porapack Q column, FID detector and methanizer for the detection of CO and CO$_2$ using N$_2$ as the carrier gas. Oven, injector and detector temperatures were set at 60^0, 80^0 and 80^{0}C respectively. The activity (X) was expressed by the conversion of CO calculated by using the equation:

$$X_{CO} = (C_{COin} - C_{COout})/C_{Coin} \quad (1)$$

Multiple samples of the outlet gas were taken and averaged to ensure the steady state. Temperatures for the light off, 50% conversion of CO and 100% conversion of CO: T_i, T_{50} and T_{100} were used as an index to evaluate the activity of the catalysts.

RESULTS AND DISCUSSION

Fig.1 shows the nitrogen adsorption–desorption isotherms of the catalysts, Cu-Ce$_{5.17}$-Zr$_{3.83}$O$_x$/γ-Al$_2$O$_3$ (25 wt %) prepared by all four method. The isotherms of the prepared catalysts are similar to type II according to De Boer classification. A hysteresis loop with a sloping adsorption curve and desorption curves is observed at high relative pressure (P/P$_0$) range. The hysteresis loop of Cat-UC is relatively very short in comparison to other catalysts.

The textual properties of the prepared catalysts are listed in Table 1. The pore volume was measured by N$_2$ sorption at its relative pressure, $P/P_0 \approx 0.987$. It is evident from the data that the textural properties (BET surface area, average pore radius and pore volume) vary significantly for the catalysts prepared by different methods. Among the four samples used, Cat-UC method has the least specific area catalyst (19.439 m^2/g), and Cat-SG method has the highest specific area (67.413 m^2/g) and

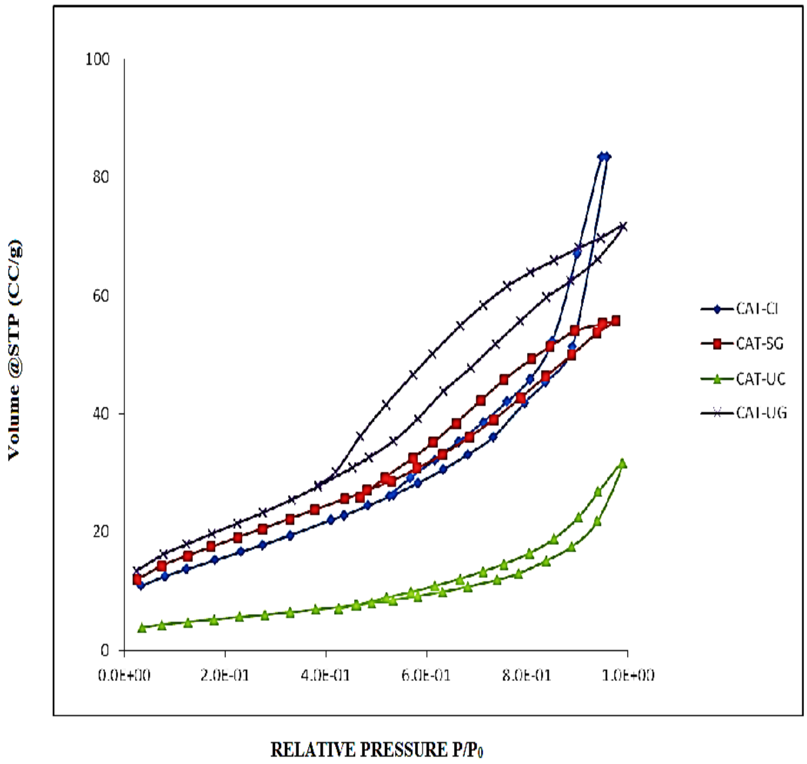


Fig. 1: N_2 adsorption-desorption isotherm of (1) Cat-CI, (2) Cat-SG, (3) Cat-UC, (4) cat-UG.

Table 1. Textural characteristic of the various catalysts

Catalyst	S_{BET} (m^2/g)	Average pore Radius (Å)	Total pore volume (cc/g)
Cat-CI(D6)	58.835	47.50	0.1396, pores <650.7 Å
Cat-SG (E6)	67.413	26.37	0.889, pores <714.6Å
Cat-UC(F6)	19.439	50.38	0.049, pores <804.2 Å
Cat-UG(G6)	67.391	29.05	0. 111, < 929.4Å

pore volume close to cat- UG.

Pore size distribution of the catalysts is shown in Fig. 2. It can be seen that pores are distributed in a narrow range of 7-30 Å, with dominating pore radius around 12-14 Å in all the catalysts.

The SEM micrographs with a magnification of 5000X of $Cu\text{-}Ce_{5.17}\text{-}Zr_{3.83}O_x/\gamma\text{-}Al_2O_3$ (25 wt %) catalysts prepared with different methods are shown in Fig.3. It is very clear that the morphologies of the catalysts are very different from their components. Thus the preparation method exerts significant influence on the morphologies of the catalysts. From the figure above it is observed that smaller and randomly oriented large number of crystals are seen for in the image for cat-CI. The

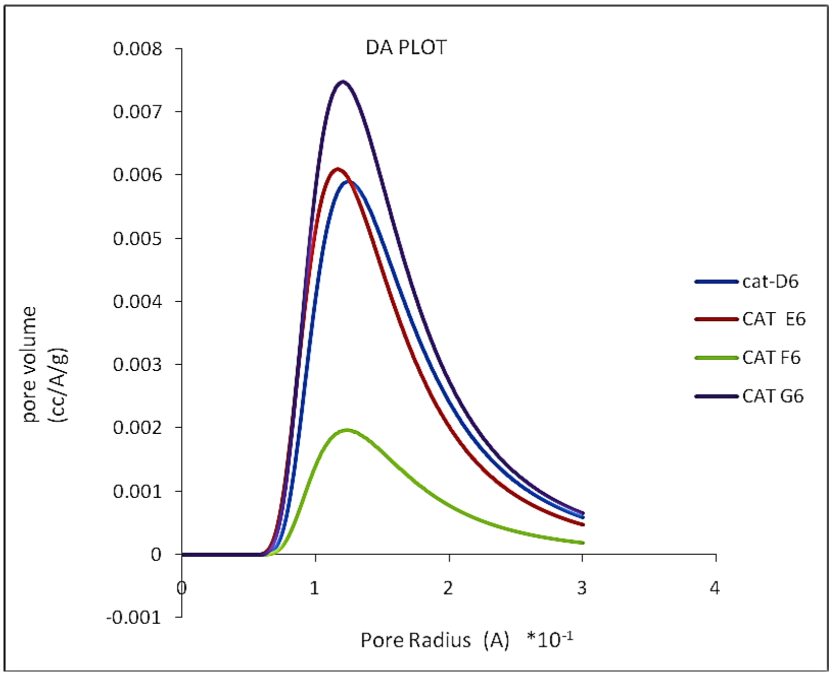


Fig. 2: Pore size distribution of Cat-CI, Cat-UG, Cat-UC, Cat-SG.

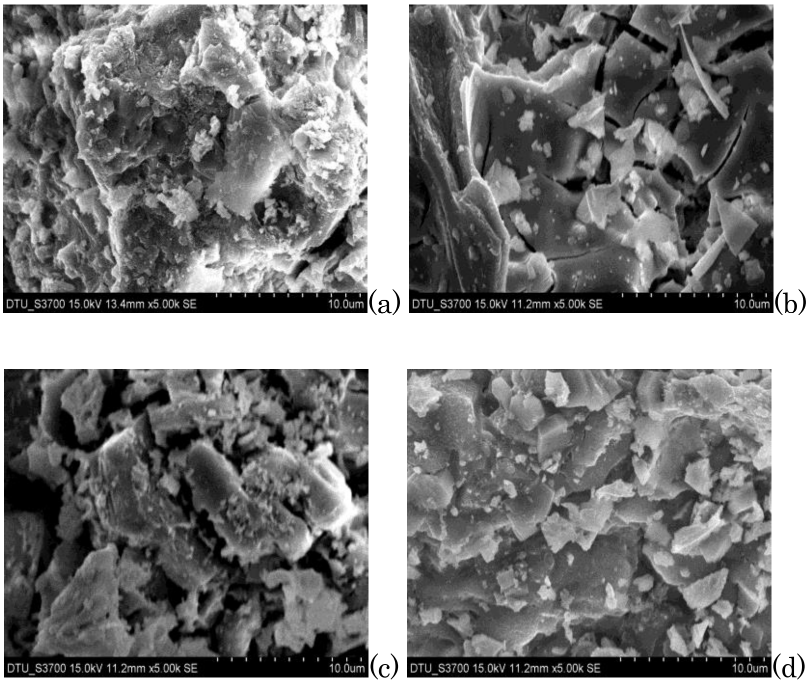


Fig. 3: SEM micrographs of catalysts (a) cat-CI (b) cat-SG (c) cat-UC (d) cat-UG at 5.00X

surface adsorption should be quite good.

Cat-SG shows formation of precipitates with crack type of voids and plane area on the surface as compared to other samples. Catalyst cat-UC has more randomly oriented surfaces. Cat-UG shows large number of broken crystals of random shape.

Figure 4 shows the TG-DSC profiles for Cu-Ce$_{5.17}$-Zr$_{3.83}$O$_x$/γ--Al$_2$O$_3$(25%), catalyst

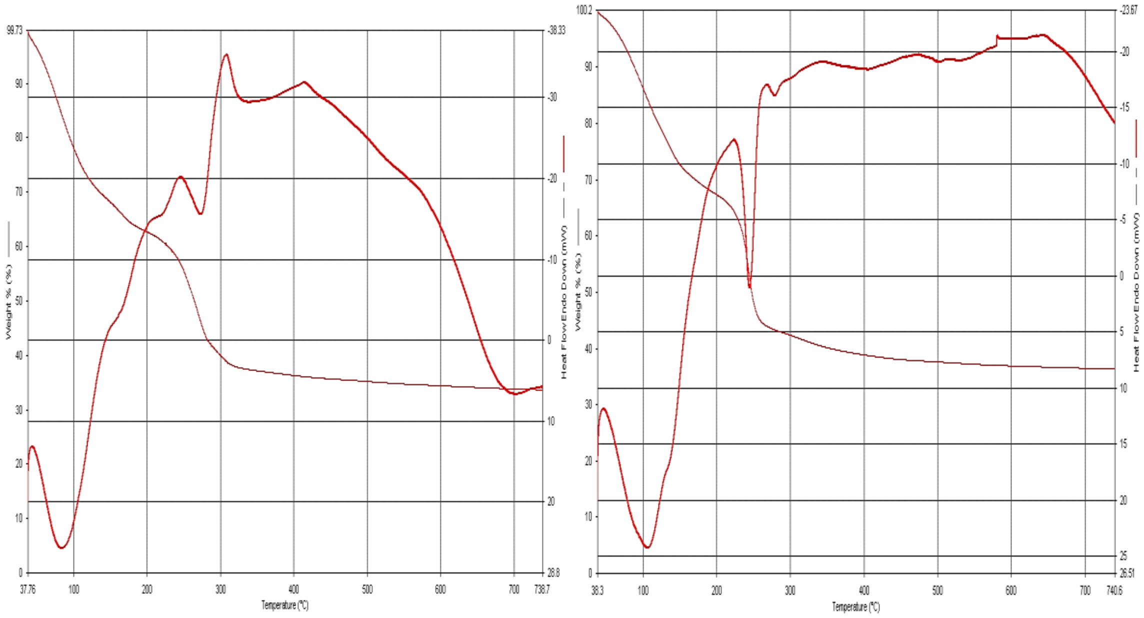


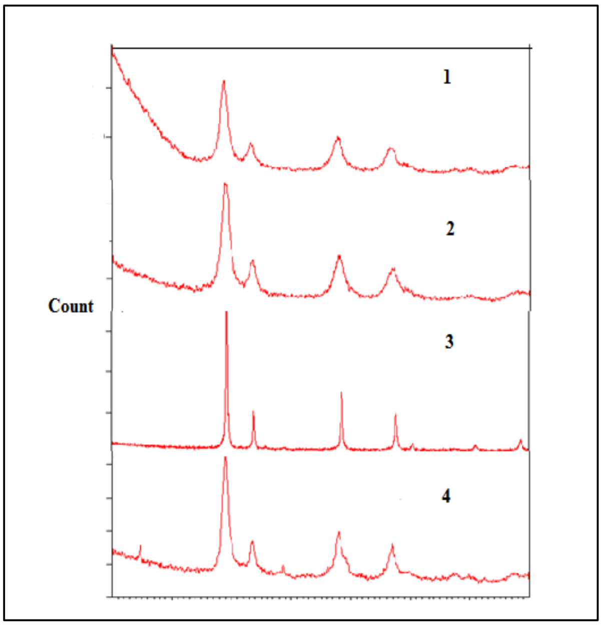
Fig. 4: TGA/DTA patterns for the precursors of catalysts cat-CI and cat-SG

precursors, used for the preparation by co-impregnation method and sol-gel method.

For precursor sample of cat-CI the weight is nearly constant after temperature of about 400°C and loss of weight was attributed to the evaporation of the adsorbed water and structure water. The total weight loss is about 65%. The loss of weight is in two steps and heat flow curve shows that decomposition is exothermic.

In case of precursor sample of cat-SG, The total weight loss is about 65% at 450°C. However weight loss in case of catalyst precursor used continues to loose.

X-ray diffraction patterns of catalysts prepared by four different methods using 2θ positions between 20° and 80° are shown in Fig. 5. The main reflections at 29.1, 33.2, 48.0 and 57.0 of 2θ in the XRD patterns of all the samples correspond to the cubic, fluorite structure typical of CeO_2, and there is no indication of the presence of other phases.



Position [(^{0}2θ) (Copper Cu)]

Fig. 5: XRD patterns of (1) Cat-CI, (2) Cat-SG, (3) Cat-UC, (4) cat- UG.

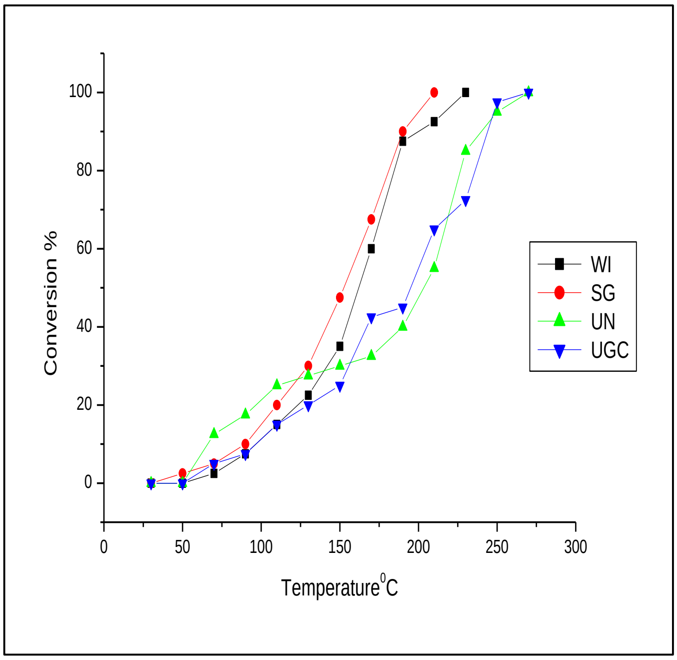


Fig. 6: Effect of preparation methods on CO oxidation activity of the catalysts

Effect of preparation methods on catalyst activity

Many factors affect the activity of catalysts and are mainly related to the interaction between ceria and copper species (Martınez, A. *et al* 2003). Pure zirconia is considered as hardly reducible oxide, thus the redox properties of copper supported on it is strongly hindered. Incorporation of Zr into the ceria lattice is known to improve redox properties of the cerium oxide. Aguila *et al.* (2008) in their work compared the activity of CuO- CeO_2 supported on three supports Al_2O_3, ZrO_2 and SiO_2, catalysts. The most noticeable synergistic effects are seen when using Al_2O_3, and SiO_2 as support. A significant influence of the preparative method on the activity of the different catalysts is evident.

The results of CO oxidation activity as a function of temperature of the catalysts having same composition, $CuCe_{5.17}Zr_{3.83}O_x/\gamma Al_2O_3$ (25 wt %), prepared by four different methods are given in Fig. 6 and Table 2.

Table 2. Effect of catalyst preparation method on the light-off temperature of the catalysts

Catalyst	**Temperature (⁰C)**		
	T_{10}	**T_{50}**	**T_{100}**
cat-CI	100	160	230
cat-SG	90	155	210
cat-UC	60	200	265
cat-UG	100	200	260

It is very clear that the catalyst prepared by sol-gel method (Cat-SG) exhibited the highest activity showing the lowest temperature, T_{100} for complete conversion of CO at 210°C in comparison to the catalysts prepared by the other methods. The temperature T_{100} (230°C) of Cat-CI was about 30°C less than that of Cat-UG (260°C).

The activity of Cat-UG and Cat-UC compared with other catalysts, showing T_{100} at the highest temperature of 265°C.

Although at lower temperature (T_{50}) cat-UC and cat-UG showed the equal activity but beyond this temperature inferior activity could be seen from Fig. 6 for these catalysts. The cat-SG exhibited the highest activity and offers better control over textural characteristics. It is evident from Table 1 that the BET surface area (67.413 m^2/g) of this catalyst is the highest in comparison to the other catalysts studied.

CONCLUSIONS

Catalysts sample prepared by four different methods having the composition ($CuCe_{5.17}Zr_{3.83}O_x/\gamma$-$Al_2O_3$ (25 wt %) have been examined for CO oxidation. It is found that the catalytic performance for the said reaction and morphology of the catalysts strongly depend upon preparation methods (Ayastuy *et al*. 2010). The catalyst prepared by sol gel method, Cat-SG, shows the best catalytic performance among the four. This highly dispersed catalyst is resulted due to uniform dispersion of copper species in the catalyst. The catalyst sample prepared by urea nitrate combustion method presents lowest performance due to sintering. The Cat-UC synthesized possessed sintered large particles probably due to higher local temperature during uncontrolled combustion in the furnace maintained at 500°C. This is clearly seen in the SEM micrograph, evident by lowest BET surface area of the Cat-UC. The ranking order of the preparation methods of the catalyst is as follows: sol-gel > co-impregnation > urea gelation > urea nitrate combustion. All the four catalysts are active for CO oxidation and do not show deactivation of catalytic activity for 50 hours of continuous run at 200°C, of course at different levels of CO conversions.

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