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Bulletin of Chemical Reaction Engineering & Catalysis, 7 (2), 2012, 112 - 123

Research Article

Effect of Preparation Methods on Al_2O_3 Supported CuO-CeO_2-ZrO_2 Catalysts for CO Oxidation

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Received: 14th June 2012; Revised: 8th September 2012; Accepted: 19th September 2012

Abstract

To examine the effect of preparation methods, four catalyst samples having same composition ($CuCe_{5.17}Zr_{3.83}O_x$/g-Al_2O_3 (15wt%) were prepared by four different methods for CO oxidation. The catalysts were prepared by co-impregnation, citric acid sol-gel, urea nitrate combustion and urea gelation co-precipitation methods, and characterized by BET, XRD, TGA/DSC and SEM. The air oxidation of CO was carried out in a tubular fixed bed reactor under the following operating conditions: catalyst weight of 100 mg, temperatures of ambient to 250 °C, pressure of atmospheric, 2.5% CO in air, total feed rate of 60 ml/min. It was observed that the catalytic activity greatly influenced by the preparation methods. The highest activity of the catalyst prepared by the sol gel method appeared to be associated with its largest BET surface area. All the four catalysts were active for CO oxidation and did not show deactivation of catalytic activity for 50 hours of continuous runs. The ranking order of the preparation methods of the catalyst is as follows: sol-gel > co-impregnation > urea gelation > urea nitrate combustion. © 2012 BCREC UNDIP. All rights reserved

Keywords: CO oxidation, CuO-CeO_2-ZrO_2/Al_2O_3Catalysts, preparation methods, characterization

How to Cite: G. Rattan, R. Prasad, R.C.Katyal. (2012). Effect of Preparation Methods on Al_2O_3 Supported CuO-CeO_2-ZrO_2 Catalysts for CO Oxidation. *Bulletin of Chemical Reaction Engineering & Catalysis*, 7(2): 112-123. (doi:10.9767/bcrec.7.2.3646.112-123)

Permalink/DOI: http://dx.doi.org/10.9767/bcrec.7.2.3646.112-123

1. Introduction

The catalytic oxidation of carbon monoxide to carbon dioxide:

$$2CO + O_2 \Longrightarrow CO_2 \qquad (1)$$

is a very simple, straightforward single reaction (eqn. 1), and it has been investigated for several decades by many researchers [1-6] since the classic work of Langmuir [1] in 1922. Recently, CO oxidation has attracted renewed attention due to its importance in several areas of industrial significance for understanding fundamental processes associated with methanol synthesis, the water-gas shift reaction, the reforming of alcohols, etc. [7]; search of new energy sources related to removal of CO in H_2 fuel cells [8]; environmental cleanliness such as residential and industrial air purification; respiratory protection gas masks for fire fighters, mine rescue applications and chemical warfare protection; automotive emissions control; clean-up of flue gases; etc. [9-12].

A large number of catalysts for CO oxidation

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are reported in the literature which have been extensively reviewed [13-17] and can be classified in to three types: First type, noble metal (Pt, Pd, Rh) catalysts which are well-known CO oxidation catalysts with high activity and desirable temperature stability [2,14]. These catalysts exhibit very good activity in the temperature range of 150-250 °C.

However, the relatively high cost and limited availability of these metals may inhibit their large-scale applications. Thus, design and synthesis of more cost-effective and affordable noble metal-free catalysts are of particular interest [11]. Second type, gold catalysts are for room temperature oxidation of CO [12]. These catalysts have a potential to be practically applied in ambient conditions, especially in air purification systems and breathing apparatus. It is possible that gold could be usefully incorporated into automobile catalysts, considering that the price of other noble metals is rising rapidly. Third type, several kind of base metal oxide catalysts have been extensively studied for CO oxidation such as the oxide of Cu, Mn, Cr, Co, Ni, Fe, etc. alone or in combination [7,17].

Base-metal oxide being cheapest among other catalytic materials, have received considerable attention for CO oxidation. Copper oxide [9,18–20] and supported copper oxides [21-34] are known to be highly active for CO oxidation. The majority of the studies are devoted to supported copper oxide catalysts. The most often applied supports for such catalysts are the oxides: Al_2O_3 [20-22], SiO_2 [22], CeO_2 [22-33], ZrO_2 [30,31], TiO_2 [32], SmO_2 [33], ThO_2 [34], etc. As a support, CeO_2 plays an important role in Cu–CeO_2 catalyst that is reported to be very active for the complete CO oxidation, exhibiting a specific activity several orders of magnitude higher than that of conventional Cu-based catalysts and even comparable to precious metals [23,30,34,35]. Abundant availability of Cu and Ce, coupled with their lower costs compared to precious metals, make them strongly competitive. This type of composite catalyst also shows remarkably higher resistance to carbon dioxide, water poisoning, and sulphur compounds [36]. To date, there has been frequent most use of CuO-CeO_2 systems as additives to reduce the cost of noble metals in the three-way catalysts [37], for the purification of automotive exhaust gas. These have been thus widely studied with the aim to possibly replacing the expensive noble metal catalysts [23,24, 38-44].

Huang and Tsai [18] studied CO oxidation activities over unsupported Cu, Cu_2O, and CuO and reported the activity order as follows: Cu_2O > Cu > CuO. Thus, Cu_2O exhibits the highest activity than the other two copper species. Qin et al. [45] reported the activity for ceria supported catalyst in the following order: CuO-CeO_2 > CuO > CeO_2. This fact is correlated with the synergistic interaction between CuO and CeO_2, resulting in exceptional redox properties at the interface created between them, with both components being significantly more readily reduced or oxidized than the corresponding independent components[24]. Further, Zhang et al. [27] reported that the reduced catalyst, Cu-CeO_2 is more active than CuO-CeO_2 for CO oxidation. Martinez-Arias et al. [46] concluded that the partially reduced state of the copper oxide phase and the redox properties at the copper-ceria interface are two factors contributing to CO oxidation. Liu and Stephanopoulos [23] proposed a reaction model, in which Cu^+ species were stabilized by the interaction between CuO and CeO_2 and the Cu^+ species provide surface sites for CO chemisorption while the CeO_2 provides the lattice active oxygen through a Ce^{4+}/Ce^{3+} redox cycle for faster CO oxidation. Thus the high activity of partially reduced CuO-CeO_2 catalyst is attributed to the strong interaction and synergism between the copper oxide and ceria, with the active role of the pairs Ce^{4+} +Cu^{1+} Ce^{3+} +Cu^{2+} [23,36]. The catalytic performance of copper oxide in CO oxidation is enhanced by the generation of oxygen vacancies in the support, which provokes higher oxygen mobility and diffusion from the lattice to the interface of copper oxide-ceria and high oxygen storage capability [47-50].

However, it is known that the pure CeO_2 has poor thermal stability [52]. Recently, it has been reported that the incorporation of ZrO_2 into CeO_2 not only increases thermal resistance of the resulting mixed oxide [53,54] but also improves other properties of the catalysts forming a Ce-Zr-O solid solution [55]. The main features which contribute to the success of these components are: (i) higher thermal resistance compared to conventional ZrO_2-free three way catalyst (TWC) [56], (ii) a higher reduction efficiency of redox couple Ce^{4+}/Ce^{3+} [57], (iii) excellent oxygen storage/release capacity (OSC), compared to pure ceria [58], (iv) increase the mobility of lattice oxygen [59] and (iv)the possibility of preventing the undesired formation during reaction of $CeAlO_3$, which contributes to the deactivation of the TWC [60]. The modifications of these properties of the catalysts ultimately result in better performance in CO oxidation [61-63]. Thus, CeO_2-ZrO_2 mixed oxides are extensively used in TWC [54,64]. Cao et al. [62] reported that the synergistic effect between CuO and the $Ce_{0.8}Zr_{0.2}O_2$ support, the highly dispersed CuO nano-particles, the meso-porous framework, the high-surface area and the uniform distribution of nano-scale particles size were responsible for the high catalytic activity of the catalysts for low temperature CO oxidation. Wang et al. [63] observed that the CuO/CeO_2 exhibited higher catalytic activity for CO oxidation than $CuO/Ce_{0.8}Zr_{0.2}O_2$ catalysts when the calcination temperature was lower than 600°C. However, the result was just the opposite when the catalysts calcined at 800°C. This indicated that $CuO/Ce_{0.8}Zr_{0.2}O_2$ had better thermal resistance than CuO/CeO_2 catalysts; higher thermal stability of the catalyst is more desirable than very high activity with lower stability.

The support has a strong influence on the activity of the catalysts [22,64]. Aguila et al. [22] studied the effect of the support, Al_2O_3, ZrO_2, and SiO_2, on the activity for CO oxidation of a series of CuO and CeO_2 monometallic and bimetallic catalysts prepared by co-impregnation of the support with the adequate amount of Cu and Ce nitrates to obtain a loading of 2% Cu and/or 8% Ce. They reported that the bimetallic supported catalysts followed the activity sequence $CuO–CeO_2/SiO_2 > CuO–CeO_2/ZrO_2 > CuO–CeO_2/Al_2O_3$. In the absence of CeO_2, the most active monometallic catalyst was the CuO/ZrO_2 system. The authors proposed that the different degree of interaction between CuO and CeO_2 particles, induced by the support, can explain the activity results for the bimetallic catalysts.

The CuO-CeO_2-ZrO_2 catalyst shows good performance in the CO oxidation and cheaper than precious metal catalysts, it could be made further cheaper using alumina support without sacrificing the performance in the reaction. Because of the abundant pores and large surface area present in alumina, it has a great potential in further improving the catalytic performance. The alumina wash-coated monolith has been used in TWC converters. However, little attention has been paid on the alumina supported CuO-CeO_2-ZrO_2 catalyst for CO oxidation. Further, it is a recognized fact that the method of preparation of the catalysts determines the dispersion and size distribution of metal crystallites, their spatial distribution on the support, the homogeneity of components, the morphology, etc. which in turn strongly affect the catalyst activity [45,66]. In recent years, there has been a significant progress towards understanding the relationship between the preparation method and the final properties of catalysts and catalytic supports. As a consequence, a variety of methodologies have been developed by different workers for the preparation of high activity CuO-CeO_2 catalysts. Recently, the authors of this paper have reviewed seventeen methods of preparation of CuO-CeO_2 catalysts [67] and their various applications.

In spite of the more and more interest drawn on CuO-CeO_2-ZrO_2 catalysts for CO and other pollution abatement, and for various industrial applications, literatures on the selection of synthesis methods determining the physiochemical features or factors related to catalyst performance remain quite limited [63]. Additionally, little attention has been paid on the alumina supported CuO-CeO_2-ZrO_2 catalyst for CO oxidation. Therefore, keeping the mentioned facts in mind, the present investigation was undertaken to explore the significance of preparation methods on the morphology and performance of the alumina supported CuO-CeO_2-ZrO_2 catalyst for CO oxidation. For this purpose, CuO-CeO_2-ZrO_2/g-Al_2O_3 catalysts have been prepared by four different methods, characterized by various techniques and evaluated for CO oxidation.

2. Experimentals

2.1. Catalyst Preparation

γ-alumina supported-copper-ceria-zirconia catalysts having identical composition with molar ratio of Cu/(Cu+Ce+Zr) = 0.1 and of Ce/Zr = 1.35 with 15 wt% g-Al_2O_3 (100–120 mesh size particles) 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). All the catalysts have identical composition represented by $CuCe_{5.17}Zr_{3.83}O_x$/g-Al_2O_3(15wt%). This composition was found to be optimum for CO oxidation during the Ph.D work of one of the authors [68].

2.1.1. Co-impregnation method

Co-impregnation method is the simplest method of catalyst preparation used in this study following the procedure described by Aguila et al. [22]. The Cu-$Ce_{5.17}$-$Zr_{3.83}O_x$/g-Al_2O_3(15wt%) catalyst sample was prepared by co-impregnation on the requisite amount of support with a distilled water solution containing $Cu(NO_3)_2.3H_2O$, $Ce(NO_3)_3.6H_2O$ and $ZrO(NO_3)_2.H_2O$, defined by above mentioned molar ratios. Then the resulting slurry was evaporation over a steam bath with constant stirring to near dryness. Final drying was carried out at 105 °C in an oven overnight, and calcined at 500 °C for 3 hours under static air in a muffle furnace. The catalyst powders were cooled to room temperature in a decicator containing $CaCl_2$ and then kept in an air tight bottle. The sample was marked as Cat-CI.

2.1.2. Citric acid sol-gel method

The method followed here is described by Liang et al. [69]. The nitrates of the components of the catalysts were dissolved in distilled water according to the required molar ratio. Citric acid was added as the complexing agent with a 1.3:1 ratio of the acid to metal ions including Ce^{3+}, Zr^{4+} and Cu^{2+}. Appropriate amount of polyglycol was added followed by the 10% citric acid and the blended solution was thoroughly mixed over a magnetic stirrer. Then required amount of alumina was added into the solution and heated at 80°C with constant stirring over a magnetic stirrer till transparent gel was formed. The resulting gel was dried at 105 °C overnight in an oven. The received powders were submitted to decomposition at 300 °C for 1 h and calcination at 500 °C for 3 h under static air in a muffle furnace. The catalyst powders were cooled to room temperature in a decicator containing $CaCl_2$ and then kept in an air tight bottle. The sample was named as Cat-SG.

2.1.3. Urea–nitrate combustion method

Urea combustion with nitrates is a single pot technique for the preparation of the catalysts. The catalyst sample was prepared following the method described by Avgouropoulos et al. [38]. Nitrates of copper, cerium and zirconium, and urea, $CO(NH_2)_2$ were mixed in appropriate molar ratio in a minimum volume of distilled water to obtain a transparent solution. The urea/nitrate stoichometic molar ratio was equal to 5(3-x)/6 where x denotes the Cu/(Cu+Ce+Zr) molar ratio. The urea/nitrate ratio taken was equal to 4.17 while Cu/(Cu+Ce+Zr) molar ratio was equal to 0.1. The mixed solution was heated for a few minutes at 80 °C and the resulting viscous gel was introduced in an open muffle furnace preheated at 500 °C, in a fuming cupboard. The gel started boiling with frothing and foaming and in a couple of minutes ignited spontaneously with rapid evolution of large quantity of gases, yielding a foamy voluminous powder. The powder obtained after combustion contains small amounts of carbonaceous residues. In order to burn off carbon residues, the powders were mixed thoroughly and further heated at 500 °C for 2.0 hr in the furnace. The catalyst sample obtained was stored in air–tight bottle after cooling. The sample was labeled as Cat-UC.

2.1.4. Urea gelation co-precipitation (UGC) method

The method described by Liu et al. [70] was followed to prepare the catalyst. The preparation procedure consisted of mixing the aqueous metal nitrate solutions in the ratios Ce/Zr = 1.35, Cu/(Cu+Ce+Zr) = 0.1 and urea/nitrate = 4.14. 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. After that 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 calcium in a muffle furnace at 500 °C for 3 hours. The sample was termed as Cat-UG.

2.2 Catalyst Characterization

Textural characterization of the catalyst samples were 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 Ka radiation for crystal phase identification of the catalysts. The patterns were recorded at room temperature with a 2θ range from 20 to 80°. Images of the catalysts were obtained on a high-resolution SEM, Hitachi-3700 N, Japan for surface morphological studies of the catalysts. TGA/DSC thermograms of the catalysts precursors were recorded by Perkin Elmer, STA-6000, simultaneous thermal analyser.

2.3 Catalytic activity testing

The catalytic activity was evaluated in a compact tubular packed bed flow reactor [71] at atmospheric pressure in a temperature range of ambient to 300 °C. No pretreatment was applied before each catalytic test. A gas mixture of 2.0 % CO in air was fed at a total inlet flow rate of 60 ml min^{-1} (ambient temperature and pressure). Air fed was made free of moisture and CO_2 by passing it through CaO and KOH pellets drying towers. Hundred milligram of the catalyst was diluted to 5 ml with Al_2O_3 of same size (100-150 mesh) and placed into the reactor. It is well known that the presence of mass and heat transfer resistance may lead to under estimate the catalytic activities of catalysts for CO oxidation. In order to minimize the transfer limitations and thus differentiate the activity sequence of these catalysts, less mass of

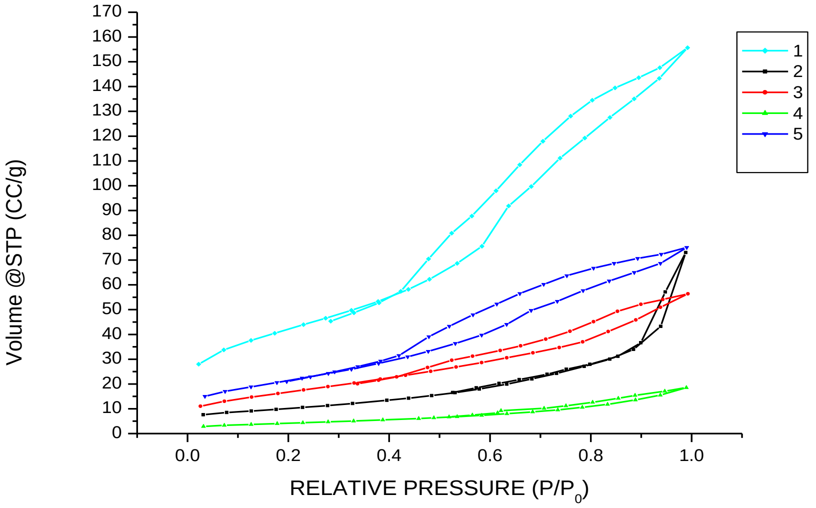


Figure 1. N_2 adsorption-desorption isotherm : (1) ɣ-Al_2O_3, (2) Cat-CI, (3) Cat-UG, (4) Cat-UC, (5) cat-SG.

Table 1. Textural characteristic of the various catalysts and support, ɣ-Al_2O_3

Catalyst	S_{BET} (m²/g)	Average pore Radius (Å)	Total pore volume (cc/g)
Cat-UG	61.592	28.32	0.087, <1319.8 Å
Cat-CI	35.900	62.95	0.113, < 834.0 Å
Cat-SG	78.375	29.63	0.116, <1015.3 Å
Cat-UC	15.225	37.66	0.029, <932.3 Å
ɣ-Al_2O_3	150.314	32.04	0.241, <1224.4 Å

catalyst further diluted with inert material and relatively moderate flow rate were chosen in the catalytic tests. The catalytic experiments were carried out under steady state conditions. Typically, the reactor was heated to the desired temperature with the help of a microprocessor based temperature controller. A temperature control of ±0.5⁰C was achieved. After 60 min 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, 80 and 80 ⁰C respectively. The activity was expressed by the conversion of CO calculated by the following formula (Eqn. 2):

$$X_{CO} = (C_{COin} - C_{COout}) / C_{COin} \qquad (2)$$

Multiple samples of the outlet gas were taken and averaged to ensure that the catalytic system had reached steady state. The conversion calculated using the integrated peak area differences between the CO fed initially and the effluent CO from the reactor with an accuracy of about 1%. 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.

3. Results and Discussion

3.1 Effect of preparation methods on physico-chemical properties of the catalysts

The nitrogen adsorption–desorption isotherms of the support, ɣ-Al_2O_3 and catalyst, Cu-$Ce_{5.17}$-$Zr_{3.83}O_x$/g-Al_2O_3 (15wt%) prepared by sol-gel method are shown in Figure 1. The isotherms of the support and prepared catalyst are of 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-CI is relatively very short in comparison to other catalysts. The textural properties of the support and prepared catalysts by N_2 sorptometry are listed in Table 1.

The pore volume was measured by N_2 sorption at its relative pressure, P/P_0 = 0.992. It is evident from Table 1 that the textural properties (BET surface area, average pore radius and pore volume) vary significantly for the support and catalysts prepared by different methods. The catalysts areas were several folds less than the support, ɣ-Al_2O_3

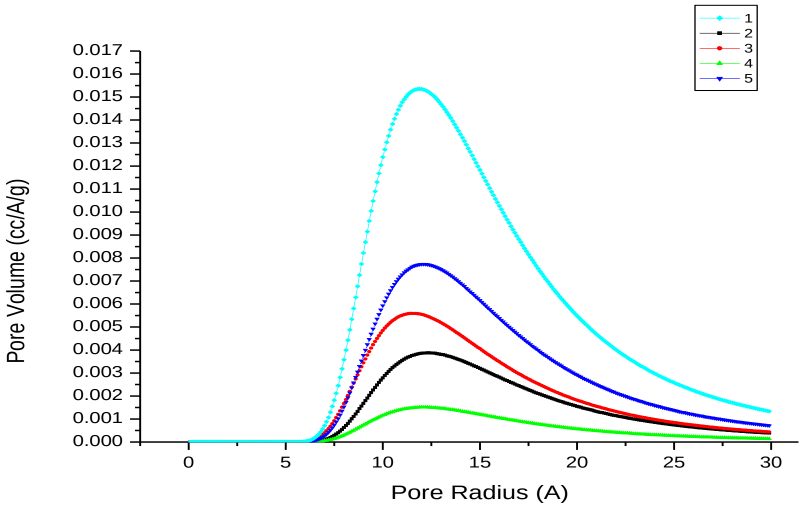
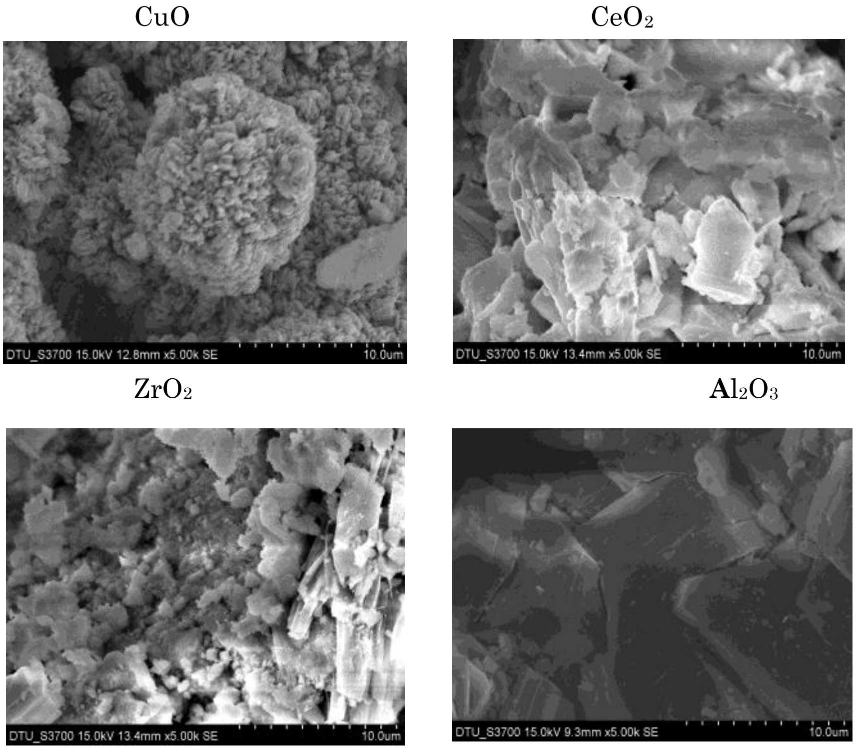


Figure 2. Pore size distribution of (1) γ-Al_2O_3, (2) Cat-CI, (3) Cat-UG, (4) Cat-UC, (5) cat-SG.



CuO

CeO_2

ZrO_2

Al_2O_3

Figure 3. SEM micrographs of CuO, CeO_2 and ZrO_2 obtained by decomposition of respective nitrates at 500 °C, and γ-Al_2O_3 support.

depending upon the method of preparation. This observation is in agreement with literature reports [72]. Among the four methods used, UC method has the smallest specific area.

The SEM micrographs of CuO, CeO_2 and ZrO_2 obtained by decomposition of respective nitrates at 500°C, as well as of g-Al_2O_3 are shown in Figure 3. The SEM micrographs of Cu-$Ce_{5.17}$-$Zr_{3.83}O_x$/g-Al_2O_3 (15wt%) catalysts prepared with different methods are shown in Figure 4. The micrographs

catalyst (15.225 m²/g), and SG method has the highest specific area catalyst (78.373 m²/g). Other two samples Cat-UG and Cat-CI have specific area of 61.592 and 35.900 m²/g respectively.

Pore size distribution of the support and catalysts are shown in Figure 2. It can be seen that pores are distributed in a narrow range of 7-40 Å, with dominating pore radius around 12 Å in all the catalysts as well as alumina support used in the catalyst preparation.

As can be seen, with Cat-CI and Cat-SG the

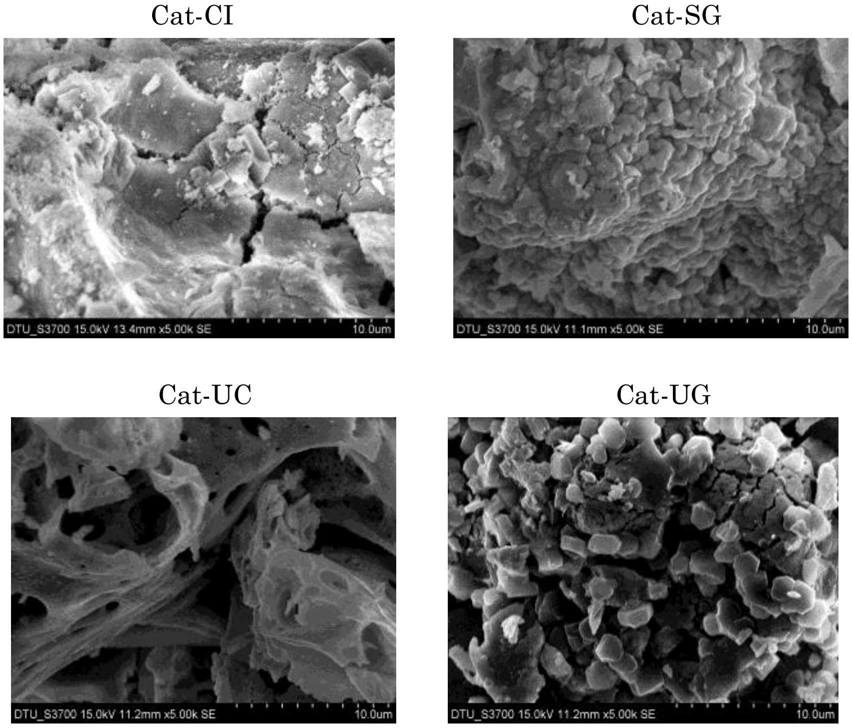

Cat-CI
Cat-SG
Cat-UC
Cat-UG

Figure 4. SEM micrographs of catalysts; Cat-CI, Cat-SG, Cat-UC and Cat-UG

former surface has larger block and multiple cracks but the latter were much smaller highly porous grains with uniform distribution as marigold flower. Cat-UC shows sintered bulk particles having spongy large voids with irregular sizes and shape. The Cat-SG synthesized by the sol-gel method presented a strong tendency to the state of particles agglomeration, forming noticeably porous structures. This morphology aspect is very appropriate from the point of view that potential catalytic properties are expected of these materials. It is worth pointing out that the Cat-SG presents a relatively homogeneous size distribution of agglomerates. The surface morphologies of Cat-SG and Cat-UG are somewhat similar except little bigger particles are present in the latter one.

X-ray diffraction patterns of the support g-Al_2O_3 and the catalysts prepared by four different methods are shown in Fig. 5. The main reflections at 29.12, 33.23, 48.00 and 56.89 of 2θ in the XRD patterns of all the samples correspond to the cubic, fluorite structure typical of CeO_2 [73], and there is no indication of the presence of other phases. From Figure 5, it can be seen that no reflections characteristic of CuO structure is present, which may be due to the high dispersion of too small particle sizes of the CuO on the surface of the support to be identified by the X-ray diffraction method. It is important to note that the main alumina peaks at ($2\theta = 45.8^o$ and 66.8^o) disappeared in all the catalyst samples. This

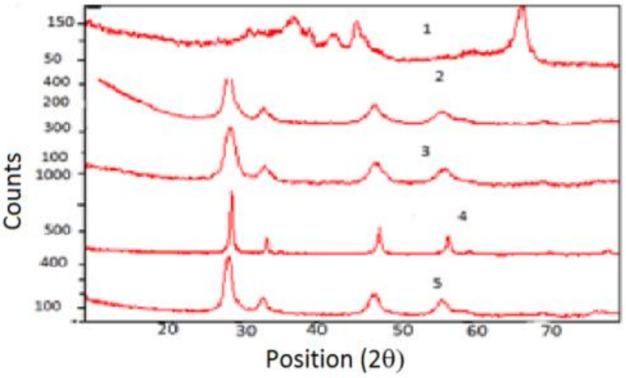


Figure 5. XRD patterns of (1) γ-Al_2O_3, (2) Cat-CI, (3) Cat- SG, (4) Cat-UC, (5) cat- UG.

indicates that there is no segregation of phases in the synthesized catalytic systems.

The diffraction patterns of all the catalyst samples are similar, except that diffraction peaks of Cat-UC, which are sharp and intense than for others. This may be attributable to the bigger crystalline phase resulted by urea combustion method whereas catalysts prepared by other methods show broad peaks suggesting the presence of smaller size and less crystalline phase. This is probably due to higher local temperature of the content of the pot during uncontrolled combustion in the furnace maintained at 500 ^{0}C, which causes sintering. This is evident by the reported lowest BET surface area and also clearly seen in the SEM micrograph of the Cat-UC.

In order to determine the thermal decomposition temperature, TG-DSC profiles of the $Cu\text{-}Ce_{5.17}\text{-}Zr_{3.83}O_x/g\text{-}Al_2O_3$ (15 wt%) catalysts' precursors, used for the preparation by co-impregnation and sol-gel method, were measured, as shown in Figure 6. It can be seen that the endothermic peak between 50 and 200 °C in the DSC curve,

3.2 Effect of preparation methods on Activity of the catalysts

The results of CO oxidation activity as a function of temperature of the catalysts having same composition, $CuCe_{5.17}Zr_{3.83}O_x/gAl_2O_3$ (15 wt%) prepared by four different methods are displayed in Figure 7 and also given in Table 2. A significant influence of the preparative method on the activity of the different catalysts is evident. 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 190 °C in comparison to the catalysts prepared by the other methods. The temperature T_{100} (225 °C) of Cat-CI was about 5 °C less than that of Cat-UG (230 °C). The activity of Cat-UC was somewhat inferior compared with other catalysts, showing T_{100} at the highest temperature of 250 °C. Although at lower temperature (<110 °C) Cat-UC showed the best activity but beyond this temperature inferior activity could be seen from Figure 7 for this catalyst. The Cat-SG exhibited the highest activity as this method offers better control over textural characteristics. It is evident from Table 2 that the BET accompanied by a significant weight loss on TG, was attributed to the evaporation of the adsorbed water and structure water. The main weight loss between 200 and 400 °C on the TG curve, accompanied with a strong exothermic peak at 225 °C and a shoulder around 255 °C, can be attributed to the decomposition and the combustion of carbon species. The total weight loss of 52.3 and 57.5% occurred in case of catalyst precursors prepared by co-impregnation and sol-gel methods respectively. No crystalline phase transformation is observed below 500 °C. No distinct weight loss can be seen above 500 °C, which indicates that the carbon species in the samples could be completely removed after calcinations at 500 °C in air. Since, calcinations at high

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

Preparation Method	Temperature (^{0}C)		
	T_{10}	T_{50}	T_{100}
CI	96	158	226
SG	75	137	190
UC	37	205	250
UG	50	180	230

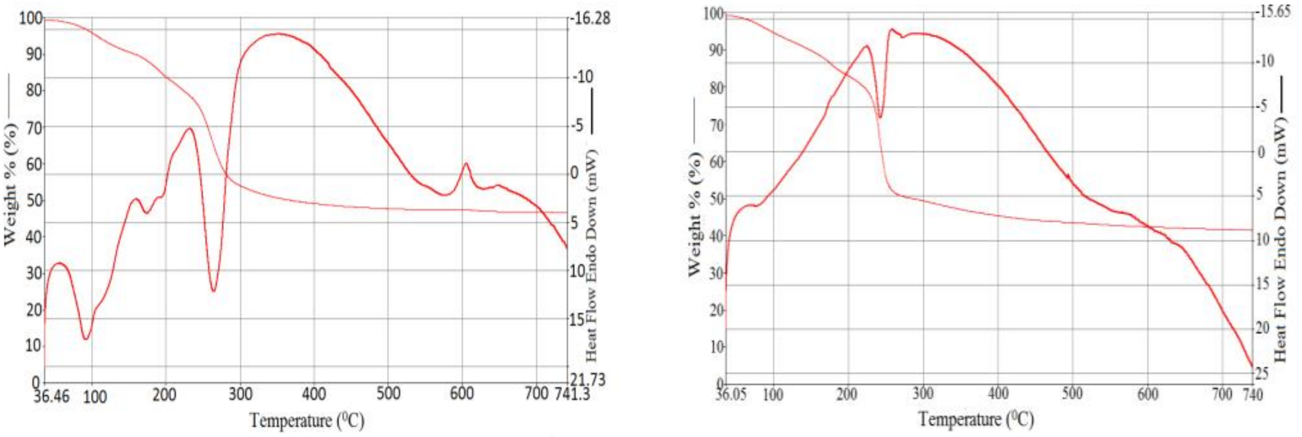


Figure 6. TGA/DSC thermograms of the precursors of $CuCe_{5.17}Zr_{3.83}O_x/\gamma Al_2O_3$ (15 wt%) catalysts prepared by (1) co-impregnation and (2) sol-gel methods.

temperature could result in decline in the surface area and increase in the crystallite size of catalysts, also taking into account the TG/DSC results the optimum calcinations temperature in air was found to be 500 °C. surface area (78.375 m²/g) of this catalyst is the highest in comparison to the other catalysts studied. On the other hand the inferior activity of Cat-UC could be due to its lowest BET surface area (15.225 m²/g).

Cat-UC has lower light-off temperature (LOT) at lower conversions than that of Cat-SG, this is probably Cat-UC has more energetic active sites but lower site density than that of Cat-SG. More energetic active sites of Cat-UC oxidizes CO at lower temperature than Cat-SG. This is evidenced by comparative BET surface areas. S_{BET} for Cat-SG is more than five times of Cat-UC. Higher active site density of relatively less energetic sites of Cat-SG than Cat-UC perhaps resulted lower light off temperature at higher conversions for Cat-SG.

In sol-gel method hydrophilic colloidal solutions are formed of micelles that remain separated because of electrical charges on their surfaces and in the surrounding solution. These charges create repelling forces which prohibit coagulation of the micelles. Such micelles are produced via chemical reactions of polymerization and poly-condensation. Thus, highly dispersed catalyst is resulted by sol-gel method. The Cat-UC synthesized by urea combustion method possessed sintered large particles probably due to higher local temperature of the content of the pot during uncontrolled combustion in the furnace maintained at 500 °C, which causes sintering. This is clearly seen in the SEM micrograph, evident by the sharp and intense diffraction peaks and lowest BET surface area of the Cat-UC. Therefore, sol-gel is the best method of preparation of the catalyst, $CuCe_{5.17}Zr_{3.83}O_x/gAl_2O_3$ (15 wt%) for the oxidation of CO. 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 did not show deactivation of catalytic activity for 50 hours of continuous runs at 200 °C, of course at different levels of CO conversions: Cat-SG 100%, Cat-CI 89%, Cat-UG 80%, and Cat-UC 55%.

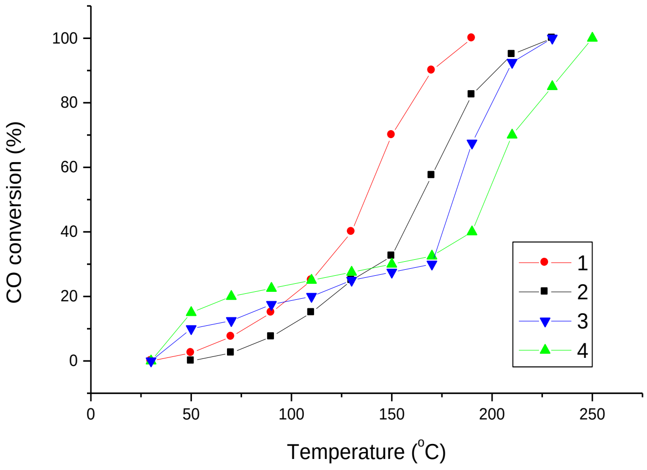


Figure 7. Effect of preparation methods on CO oxidation activity of the catalysts, (1) Cat-SG, (2) Cat-CI, (3) Cat-UG and (4) Cat-UC

4. Conclusions

Four catalysts sample having same composition ($CuCe_{5.17}Zr_{3.83}O_x/g\text{-}Al_2O_3$ (15 wt%) have been prepared by four different methods and examined for CO oxidation. The catalytic performance for the said reaction and morphology of the catalysts strongly depend upon preparation methods. The catalyst prepared by sol gel method shows the best catalytic performance, this is ascribed 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 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.

Acknowledgements

The authors gratefully acknowledge the Department of Science & Technology, Government of India, for the use of equipments and instrument provided under the SERC (Engineering Science) Project Grant NO. SR/S3/ME/027/2006.

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