Comparison of Different Preparation Methods on Al₂O₃ Supported CuO-CeO₂-ZrO₂ Catalysts for CO Oxidation

Gaurav Rattan¹*, R. Prasad², R.C. Katyal³

¹Department of Polymer Science & Chemical Technology, DTU, Delhi 110042
²Department of Chemical Engineering & Technology, B.H.U., Varanasi 221005
³University Institute of Chemical Engineering & Technology, P.U., Chandigarh 160014
*e-mail: g_rattan1107@yahoo.co.in

Abstract- Catalyst (CuCe₅.₁₇Zr₃.₃₅Oₓγ-Al₂O₃ (5wt%) have been prepared by four different methods for CO oxidation. The oxidation of CO was carried out in a tubular fixed bed reactor which has been designed and fabricated in the laboratory. The following operating conditions were maintained: catalyst weight 100 mg, temperature - ambient to 250°C, pressure - atmospheric, 2.5% CO in air, total feed rate 60 ml/min. It was observed that the catalytic activity was greatly influenced by the preparation methods. The catalyst prepared by the sol gel method followed by calcinations at 500°C exhibited excellent activity for CO oxidation with total conversion at 210°C. The ranking order of the preparation methods of the catalyst is as follows: sol gel.>co–impregnation>urea gelation co precipitation > urea nitrate combustion method. All the four catalysts are active for CO oxidation.

Keyword: catalytic activity, sol gel., CO oxidation, co-impregnation, urea gelation
1. Introduction

The catalytic oxidation of carbon monoxide (CO) to carbon dioxide (CO₂):

\[ 2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2 \]

is a very simple, straightforward reaction, and it has been investigated by many researchers [1-4]. CO oxidation has attracted renewed attention due to its importance in several areas of industrial significance for understanding fundamental associated with methanol synthesis, water gas shift reactions, reforming of alcohols, etc [5]. Other applications include removal of CO in hydrogen fuel cells [6], environmental cleanliness, protective radiation synthesis, reforming of alcohols, etc [5]. Research in this area has mainly focused on the improvement of catalytic activity at low temperatures. The catalysts for CO oxidation reported in the literature can be noble metals or base metals.

Noble metal (Pt, Pd, Rh) catalysts are well-known CO oxidation catalysts with high activity and desirable temperature stability [2,3,19]. 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 inhibit their large-scale applications. Thus, design and synthesis of more cost-effective and affordable base metal catalysts are of particular interest.

Gold catalysts are used for preferential oxidation of carbon mono-oxide (CO-PROX) in rich H₂ atmosphere at temperature under 100°C and are resistant to water and CO₂ [8]. Third, several kind of base metal oxide catalysts have been studied such as the oxide of Cu, Mn, Cr, Co, Ni, Fe alone or in combination [1,4,7,12]. Base-metal oxides are considered as the cheapest among other catalytic materials, have received considerable attention for CO oxidation.

Cu is a well-known base metal used for CO oxidation. The CuO-CeO₂ catalyst was reported to be very active for the complete CO oxidation, exhibiting activity higher than that of conventional Cu-based catalysts and even comparable to precious metals [11]. The supports used mostly for such catalysts are the oxides: Al₂O₃, SiO₂, CeO₂, ZrO₂, TiO₂, SmO₂, ThO₂ etc.

It is well known that ceria is extensively used as a promoter and/or support in many catalytic oxidation reactions due to its Ce³⁺/Ce⁴⁺ redox cycle and high oxygen storage capacity. Hence, it is used as a promoter and/or support in CuO catalysts for CO oxidation. Meanwhile, the dispersion of copper oxides can be greatly promoted by the addition of a small amount of ceria. Recently, it has been reported that the incorporation of ZrO₂ into CeO₂ not only increases thermal resistance of the resulting mixed oxide [13,14] but also improves other properties of the catalysts forming a Ce-Zr-O solid solution [15]. The main features which contribute to the success of these components are: (i) higher thermal resistance (ii) a higher reduction efficiency of redox couple Ce⁴⁺/Ce³⁺ (iii) excellent oxygen storage/release capacity (OSC) (iv) increase the mobility of lattice oxygen (v) the possibility of preventing the undesired formation during reaction of CeAlO₃, which contributes to the deactivation of the TWC. The modifications of these properties of the catalysts ultimately result in better performance in CO oxidation [16-18]. These have been thus widely studied with the aim to possibly replacing the expensive noble metal catalysts.

Huang and Tsai [20] studied CO oxidation activities over unsupported Cu, Cu₃O, and CuO and reported the activity order as follows: Cu₃O > Cu > CuO. Thus, Cu₃O exhibits the highest activity than the other two copper species. Qin, et al. [21] reported the activity for ceria supported catalyst in the following order: CuO-CeO₂ > CuO > CeO₂. This fact is correlated with the synergistic interaction between CuO and CeO₂, resulting in exceptional redox properties at the interface created between them.

The CuO-CeO₂-ZrO₂ 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. However, little attention has been paid on the alumina supported CuO-CeO₂-ZrO₂ 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, the homogeneity of components, the morphology, etc. which in turn strongly affect the catalyst activity [22].

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-CeO₂ catalysts. Additionally, little attention has been paid on the alumina supported CuO-CeO₂-ZrO₂ catalyst for CO oxidation. Although there are number of methods for preparation of catalysts [23], in the present work, CuO-CeO₂-ZrO₂/γ-Al₂O₃ catalysts were prepared by four different methods and their catalytic performance was evaluated for CO oxidation.

2. Catalyst Preparation

Gama alumina supported-copper-ceria-zirconia catalysts having composition with molar ratio of Cu/(Cu+Ce+Zr) = 0.1 and of Ce/Zr = 1.35 with 5 wt% γ-Al₂O₃ (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 having identical composition represented by CuCe$_{5.17}$Zr$_{3.83}$O$_{7}$ γ-Al$_{2}$O$_{3}$(5wt%).

2.1.1. Co-impregnation method (CI)

Co-impregnation method is the simplest method of catalyst preparation used in this study following the procedure described by Aguila et al. [24]. The CuCe$_{5.17}$Zr$_{3.83}$O$_{7}$/γ-Al$_{2}$O$_{3}$(5wt%) catalyst sample was prepared by co-impregnation using Cu(NO$_{3}$)$_{2}$·3H$_{2}$O, Ce(NO$_{3}$)$_{3}$·6H$_{2}$O and ZrO(NO$_{3}$)$_{2}$·H$_{2}$O, in above mentioned molar ratios. Then the resulting slurry was evaporated 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 desiccator containing CaCl$_{2}$ and then kept in an air tight bottle. The sample was marked as Cat-Cl.

2.1.2. Citric acid sol-gel method (SG)

The method followed to prepare the catalyst by citric acid sol-gel method is as described by Liang et al [25]. 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. 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 formation of transparent gel. The resulting gel was dried at 105°C overnight in an oven. The received powders were decomposed at 300°C for 1 h and calcined at 500°C for 3 h under static air in a muffle furnace. The catalyst powders were cooled to room temperature in a desiccator 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 (UC)

The catalyst sample was prepared following the method described by Avgouropoulos et al. [26]. 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 ratio taken was equal to 4.14. 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 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 and labeled as Cat-UC.

2.1.4. Urea gelation co-precipitation (UG) method

The method described by Liu et al [11] 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 wascalcium in a muffle furnace at 500°C for 3 hours. The sample was termed as Cat-UG.

2.2 Catalytic activity

The catalytic activity was evaluated in a tubular packed bed flow reactor which has been designed and fabricated in the laboratory [27]. No pretreatment was applied before each catalytic test. A gas mixture of 2.5 % CO in air was fed at a total inlet flow rate of 60 ml min$^{-1}$ (ambient temperature and pressure). Hundred milligram of catalysts was diluted to 5 ml with Al$_{2}$O$_{3}$ (60-120 mesh size) and placed into the reactor. It is well known that the presence of mass and heat transfer resistance may lead to underestimate the catalytic activities of catalysts for CO oxidation. The catalytic experiments were carried out under steady state condition. Typically, the reactor was heated to the desired temperature with a microprocessor based temperature controller. A temperature control of 0.5°C was achieved. After 60 min of steady state the effluent gases were analyzed online by GC analysis. The activity was expressed by the conversion of CO. Multiple samples of the outlet gas were taken and averaged to ensure that the catalytic system had reached steady state. Temperatures for the light off, 50% conversion of CO and 100% conversion of CO: $T_{r}$, $T_{50}$ and $T_{100}$ were used as an index to evaluate the activity of the catalysts. The activity was expressed by the reduction of CO, $X_{CO}$, calculated by the following formula:

$$X_{CO} = (C_{CON} − C_{COout}) / C_{CON}$$
where $C_{\text{COin}}$ and $C_{\text{COout}}$ are the inlet and outlet concentrations of carbon monoxide.

![Graph](image)

Fig. 1 Effect of preparation methods on Activity of the catalysts

Multiple samples of the outlet gas were taken and averaged to ensure that the catalytic system had reached steady state.

### 2.2.1 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$_{1.83}$O$_{2}/\gamma$-Al$_2$O$_3$(5wt%) prepared by four different methods are displayed in Fig. 1 and also given in Table 1. 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 210 °C in comparison to the catalysts prepared by the other methods. The temperature $T_{100}$ (250 °C) of Cat-CI was about 20°C less than that of Cat-UG (270 °C). The activity of Cat-UC was the least compared with other four prepared catalysts showing 100% CO conversion at the highest temperature 290 °C. The highest activity of cat-SG may be due to the reason that catalyst is highly dispersed. Lowest activity of Cat-UC synthesized by urea combustion method may be due to sintering of large particles. The same trend is seen in $T_{50}$ and $T_{50}$ also.

Thus the ranking order of the preparation methods of the catalyst in CO oxidation activity is as follows: sol gel > co-impregnation > urea gelation co precipitation > urea nitrate combustion method.

### 2.2.2. Effect of Reaction Temperature

Catalysts prepared were evaluated at temperature range from 30 to 300°C. The results of the catalysts were presented in Figures 1. Catalytic activity increases with increase in temperature after a certain temperature. Catalyst prepared by citric acid sol gel (SG) method and calcined at 500°C results 100% conversion at 210°C.

### 3. Conclusions

Catalyst (CuCe$_{5.17}$Zr$_{1.83}$O$_{2}/\gamma$-Al$_2$O$_3$(5weight %) prepared by four different methods were studied. The correlations between preparation methods were obtained. The catalytic activity of CuO-CeO$_2$-ZrO$_2$ catalysts strongly depends on preparation route. The catalysts prepared by sol-gel method showed the best catalytic activity, this is ascribed to uniform dispersion of copper species in the catalyst. The sample prepared by urea nitrate combustion method presents lower performance which may be due to sintering. All the four catalysts are active for CO oxidation and do not show de-activation of catalytic activity.

### References


