

Superior Activity of Au/CeO₂/SiO₂ Catalyst for CO Oxidation Reaction

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ABSTRACT

This article focuses on the synthesis, structural characterization and catalytic performance of the prepared Au/CeO₂/SiO₂ catalyst in CO oxidation. We had adopted simple co-precipitation method for the preparation of CeO₂/SiO₂ (1:1 mole ratio) nanocomposite system and deposition-precipitation method with urea (DPU) was employed to deposit gold (1 wt%) over the synthesized nanocomposite. The structural features of the resultant catalysts were performed by means of BET surface area, XRD, UV-vis diffuse reflectance spectroscopy, and TEM techniques. The ceria based samples show fluorite structure with cubic symmetry. The recognition that successful gold deposition over CeO₂/SiO₂ system was ascertained from the presence of Surface Plasmon Band (SPB) obtained in UV-vis DRS analysis of Au/CeO₂/SiO₂ catalyst. The nanometer dimension of the prepared catalysts was confirmed from both XRD and TEM analysis. The nano-structured Au/CeO₂/SiO₂ catalyst thus synthesized shows only 18–20% CO conversion at room temperature level (i.e. up to 40 °C). However, the CO conversion is drastically increased to ~100% when the reaction temperature is raised to 90 °C.

Key words: nanocomposite, Surface Plasmon Resonance (SPR), gold catalyst, CO oxidation.

1. INTRODUCTION

Carbon monoxide (CO) is a well known venomous environmental air pollutant. Even traces of CO causes severe environmental and health problems. Therefore, catalytic oxidation of CO at low temperatures has been a well studied reaction over the last decades [1,7-11,13]. In addition, the multi-fold fascinating practical applicability of this reaction has received intense importance among the researchers [1]. Of the various

oxide materials explored for CO oxidation, CeO₂ and its mixed oxides have been found to be the most effective catalysts. For instance, Reddy et al. prepared a series of different CeO₂-based mixed oxides for the oxidation of CO and diesel soot [1]. Indeed, the high catalytic activity of CeO₂ is thought to originate due to its remarkable redox properties and high oxygen storage capacity (OSC), which permits its rapid fluctuation

between Ce^{4+} and Ce^{3+} oxidation states under oxidizing and reducing environments, respectively [1,2]. Among the synthesized mixed oxides, the $\text{CeO}_2\text{-ZrO}_2$ (CZ) solid solution showed the superior performance both in CO (40% at $\sim 365^\circ\text{C}$ and 100% at $\sim 527^\circ\text{C}$) and soot oxidation whereas only 40% CO conversion (even at 527°C) was achieved by $\text{CeO}_2\text{-SiO}_2$ solid solution. The quite better catalytic activity of CZ system was attributed to the highest oxygen storage/release capacity of CZ. Thus, a great deal of research is still essential to design and synthesize low temperature active CeO_2 -based catalysts for CO conversion. Adopting the unique and beneficial aspects of CeO_2 , we have undertaken this study to improve the catalytic activity of $\text{CeO}_2\text{-SiO}_2$ nanocomposite in the low temperature range.

In the case of supported metal catalysts, the support material plays significant role on the performance of the catalysts. As an example, solid supports may provide a platform for the dispersion and stabilization of Au NPs rendering more surface gold atoms to the reactants, thereby escalating catalytic activity [3]. The distinctive features of CeO_2 namely the high oxygen storage and release capacity, facile oxygen vacancy

formation, and the presence of a narrow Ce 4f-band make it the best supporting material for catalysis by Au NPs [4]. Noble metal supported nanoparticulate CeO_2 materials are very potent catalysts for the elimination of toxic auto-exhaust gases, low-temperature water-gas shift (WGS) reaction, and the preferential oxidation of traces of CO in a large hydrogen excess (PROX) [5,6,7]. Among the possible catalytic materials, gold nanoparticles (Au NPs) exhibit superior catalytic performance in CO oxidation [8,9,10].

The discovery by Haruta in 1989 that nanosize gold particles deposited on suitable metal oxides show surprisingly high catalytic activity in CO oxidation even at temperatures as low as -70°C , opened up a new chapter in heterogeneous catalysis by gold [11]. In the case of gold supported catalysts, several key factors such as gold particle size, preparation method, pretreatment conditions, and selection of the support truly have a significant impact on performance of the final catalysts [12,17]. Experimental results show that gold adheres to be oxidized when it is in contact with CeO_2 . Partially positive $\text{Au}^{\delta+}$ ions can adsorb CO sufficiently strongly, thereby converting it to CO_2 [13,14]. Generally, it is

seen that SiO₂ (an irreducible oxide) supported gold catalyst (Au/SiO₂) is far less active in comparison to reducible oxide supported gold catalysts (e.g., Au/CeO₂, Au/TiO₂, Au/FeO_x, etc.) due to poor dispersion of Au NPs observed as well as the “inert” nature of the SiO₂ support [15,16,17]. In contrast, CeO₂ supported gold catalysts are normally active in low-temperature CO oxidation [13,17,18]. Accordingly, addition of CeO₂ in to the irreducible oxide (e.g. SiO₂, Al₂O₃) supported gold catalysts resulted in the enhancement of CO oxidation activity [19].

In this work, we have paid attention to fabricate CeO₂-based gold nanocatalyst so as to achieve the resultant catalyst reasonably active in low temperature CO oxidation reaction. Although as mentioned

2. EXPERIMENTAL

2.1. Methods of catalyst preparation

First, we prepared CeO₂-SiO₂ (1:1 mole ratio based on oxides) composite by co-precipitation method. Then, 1 wt% Au was loaded on to the CeO₂-SiO₂ support by slightly modified deposition-precipitation with urea (DPU) method to make Au/CeO₂-SiO₂ catalyst. The detailed procedure is given in our previous work [21].

above, CeO₂-based mixed oxides are explored for CO oxidation, synthesis and evaluation of catalytic activity of gold supported CeO₂-based mixed oxides is very scarce. As far our knowledge, Qian et al. have comprehensively studied the catalytic performances of gold supported over 6% CeO₂/SiO₂ composite particles in CO oxidation [20]. However, their catalysts exhibited significant CO conversion only beyond high temperature. Therefore, we have employed a different synthetic strategy to prepare CeO₂/SiO₂ support as well as the Au/ CeO₂/SiO₂ catalyst with an intention to acquire practically low temperature CO conversion activity. We have analyzed the structure of the catalysts by BET surface area, XRD, UV-vis DRS, and TEM techniques.

2.2. Characterization of Catalysts

The BET surface areas were determined by N₂ physisorption at liquid N₂ temperature on a Micromeritics Gemini 2360 instrument using a thermal conductivity detector (TCD). The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Multiflex instrument using nickel-filtered CuK α (0.15418 nm) radiation source and a scintillation counter detector. The intensity

data were collected over a 2θ range of $10\text{--}80^\circ$. UV-vis diffuse reflectance spectra were recorded on a UV-visible spectrophotometer, Model U-4100 spectrophotometer (solid). Measurements are performed by pelletizing the samples with KBr in the mid-infrared region at an accelerating voltage of 200 V. Transmission electron microscopic (TEM) investigations were made on a JEM-2100 (JEOL) instrument equipped with a slow scan CCD camera.

2.3. Catalytic Activity Measurements

The catalytic activity of the synthesized catalysts was evaluated for the oxidation of CO at normal atmospheric pressure and temperatures in a fixed bed micro-reactor at a heating ramp of 5 K/min. About 80 mg catalyst sample (250–355 μm sieve fraction) was placed in the reactor for evaluation. Temperature was measured directly at the catalyst bed, using a thermocouple placed in the hollow part of the reactor. The gases used (supplied by Assam Air Products) are argon (>99.9% purity), 10% CO in argon (CO purity, >99.9%), and 10% O₂ in argon (oxygen purity, >99.9%). The total flow rates maintained by the mass flow controllers and flow meters were in the

range of 50–60 NmL/min (milliliters normalized to 273.15 K and 1 atm.). Prior to oxidation of CO, the catalysts were heated to 200 °C in 10% O₂/Ar gas mixture, using a heating ramp of 10 °C /min, and kept at the final temperature for 1 h. The oxidized sample was then purged in argon and cooled to the desired starting temperature. The partial pressures of CO and O₂ were in the range of 10 mbar. The conversion of CO was observed with the help of Gas Chromatograph (Perkin Elmer, Model: Clorus 580) equipped with TCD detector.

3. RESULTS AND DISCUSSION

3.1. BET Surface Area

The specific BET surface area analysis of the synthesized catalysts reveals that the composite oxide sample, CeO₂/SiO₂ acquires a relatively larger surface area (152.95 m²/g) than the gold containing sample, Au/CeO₂/SiO₂ (140.37 m²/g). Accordingly, it could be inferred that loading of gold causes a gradual decrease in surface areas observed for the supports. This could be due to dissemination of the Au NPs into the pores of the support, thereby narrowing its pore diameter and blocking some of the micropores [22].

3.2. XRD studies

The powder X-ray diffraction (PXRD) patterns of the synthesized catalysts investigated in this work are shown in figure 1. As it is apparent from this figure, both the samples (with or without gold) exhibited moderately sharp and intense diffraction peaks. The corresponding diffraction peaks could be ascribed to the cubic fluorite structure of CeO₂ (JCPDS 43-10020).

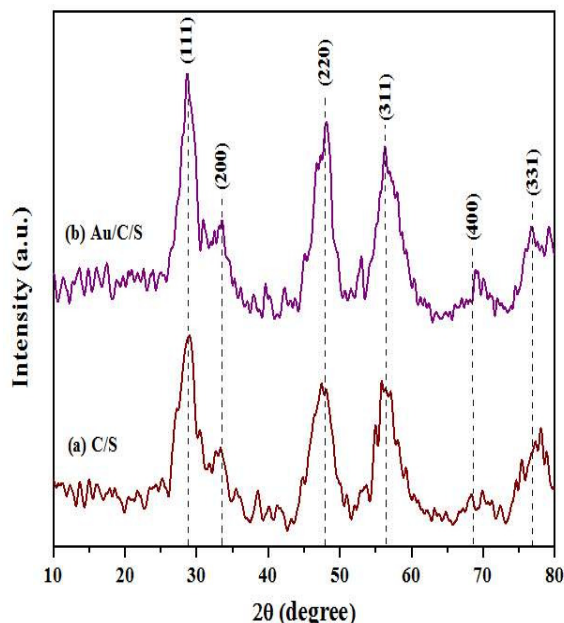


Figure 1. Powder X-ray diffraction pattern of (a) CeO₂/SiO₂ (C/S) sample calcined at 500 °C and (b) Au/CeO₂/SiO₂ (Au/C/S) sample calcined at 200 °C.

No individual peaks for SiO₂ is observed in the diffraction pattern, which may be due to the amorphous nature of SiO₂ phase, existing at the preparation temperature, 773 K [1,2,22]. The XRD pattern also did not

exhibit any mixed phases for CeO₂/SiO₂ nanocomposite [2,22]. Besides, the structural features of CeO₂ in Au/CeO₂/SiO₂ catalyst do not differ from the pattern observed for corresponding CeO₂/SiO₂ support. Remarkably, No other peaks were observed, disclosing high purity of the samples. In addition, the patterns did not show any reflections due to gold or gold oxide, implying either low gold content beyond the detection limit or that well dispersion of the Au NPs on the support surface [23]. The broad nature of the diffraction patterns reflects the nanocrystalline behavior of the resulting CeO₂-based materials. The CeO₂ crystallite sizes were calculated from the most intense (111) XRD peak using Scherrer's equation. The estimated average crystallite sizes of CeO₂ have been found to be 5-6 nm. It is also seen that crystallite sizes of CeO₂ in the gold containing sample are rather bigger than the gold deprived samples and hence retain smaller surface area. Consequently, an exciting observation could be made that gold deposition promotes to accelerate the growth of CeO₂ crystals. In fact, deposition of gold onto CeO₂ results in the enrichment of oxygen vacancies and Ce³⁺ ion concentration [24]. Since the ionic radii of Ce³⁺ (0.114

nm) is higher than Ce^{4+} (0.097 nm), accordingly fortification of Ce^{3+} concentration leads to increase the lattice parameter of CeO_2 .

3.3. UV-vis DRS studies

The UV-vis DR spectra of the as-prepared catalysts are shown in figure 2. The diffuse reflectance spectra of both samples show three common absorption bands situated at 232, 290 and 330 nm. The first two bands could be assigned to charge transfer phenomenon of $\text{O}^{2-} \rightarrow \text{Ce}^{3+}$ and $\text{O}^{2-} \rightarrow \text{Ce}^{4+}$ transitions, respectively and third band is due to inter-band (IBT) transition [1,2]. Interestingly, the UV-vis DR spectra of the gold supported samples displayed an intensified light absorption in the visible region [23]. In a similar manner, the Au/C/S sample showed an additional broad absorption peak positioned at ~540 nm. This distinguished absorption is well known by the term so-called surface Plasmon resonance (SPR) effect earned by the optically excited free conduction band electrons of Au NPs [23,25]. Consequently, occurrence of this surface plasmon band (SPB) clearly ensures the presence of gold particles embedded on the support surface.

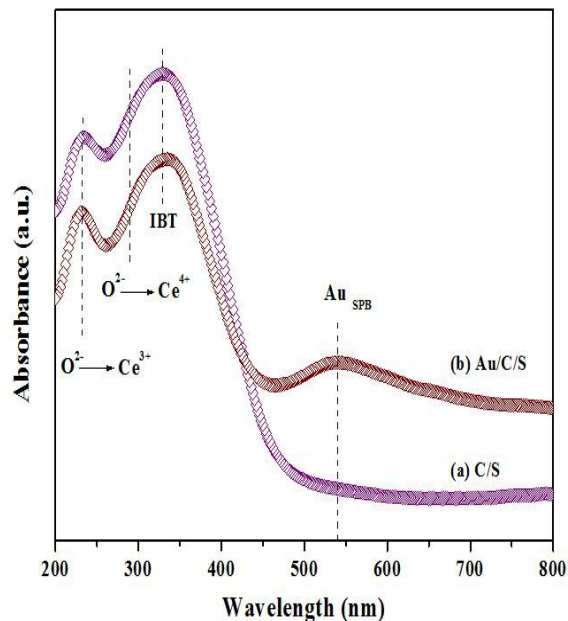


Figure 2. UV-Vis DRS pattern of (a) $\text{CeO}_2/\text{SiO}_2$ (C/S) and (b) $\text{Au}/\text{CeO}_2/\text{SiO}_2$ (Au/C/S) samples.

3.4. TEM studies

TEM investigations were carried out to know the particle size and morphology of the as-prepared samples. The representative TEM images are shown in figure 3 (a & b).

The selected area diffraction (SAED) patterns are shown as inset in figure 3a & 3b. It could be seen in figure 3a that CeO_2 nanocrystals are dispersed over the amorphous SiO_2 particles in a non-homogeneous fashion and some of the CeO_2 crystals seem to agglomerate [1,2]. The average crystallite size of CeO_2 is found to be 5-6 nm which is nicely matched with the

CeO₂ crystallite size found in XRD study. Moreover, density of Au NPs on the surface of CeO₂/SiO₂ is apparently narrow.

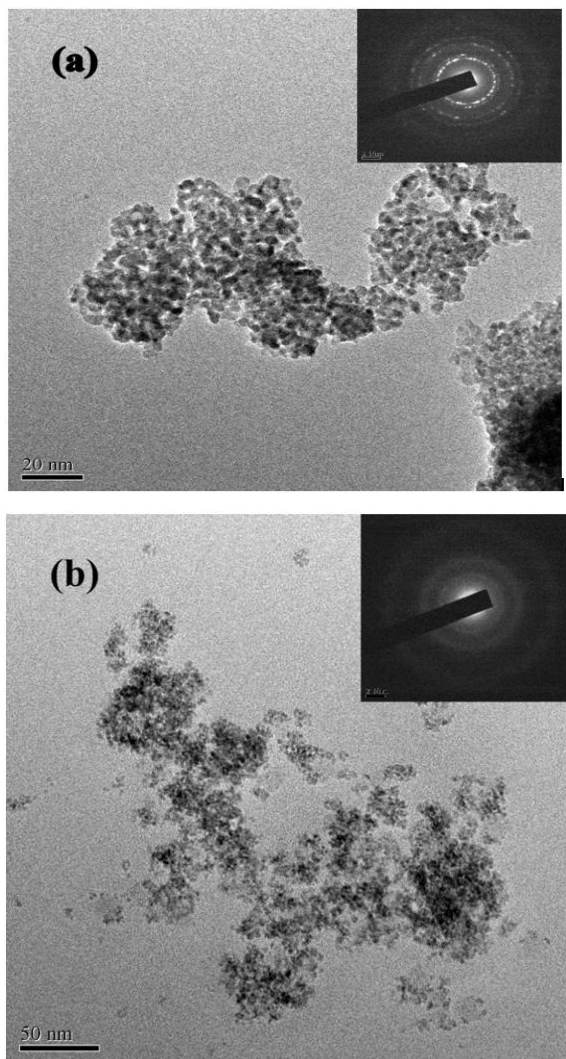


Figure 3. TEM image of (a) CeO₂/SiO₂ (C/S) and (b) Au/CeO₂/SiO₂ (Au/C/S) samples with respective SAED patterns shown as insets.

In this case, also a non-homogeneous Au distribution is seen on the crystalline CeO₂

surface as well as on amorphous SiO₂ matrix with an average of 4-5 nm Au particles. The SAED patterns show nanocrystalline behavior of the synthesized materials [1].

3.5. CO oxidation activity studies

The CO oxidation activity profile of Au/CeO₂/SiO₂ catalyst is shown in figure 4. The profile exhibits corresponding CO conversion as a function of reaction temperature.

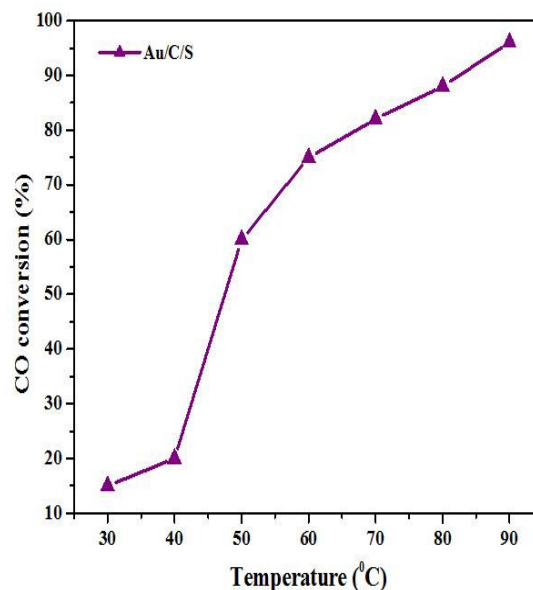


Figure 4. Conversion of CO versus temperature profile of Au/CeO₂/SiO₂ (Au/C/S) sample.

It is seen that catalytic CO conversion efficiency is not so high (18–20% only) at room temperature level (i.e. up to 40 °C). However, the CO conversion is drastically increased to ~100% when the reaction

temperature is raised to 90 °C. Recently, Qian et al. prepared a series of gold (2 wt%) supported over CeO₂/SiO₂ catalysts by DP method and evaluated their catalytic performances in CO oxidation using 100 mg of the catalysts [20]. We have got almost full CO conversion at 90 °C (the highest temperature investigated) where they found only 50% conversion even at 110 °C followed by complete conversion at 210 °C. Accordingly, it could be concluded that the catalytic efficiency of our Au/CeO₂/SiO₂ (1 wt% Au) catalyst (80 mg) for CO oxidation is significant. The superior activity may be mainly due to the preparation procedure of our catalysts. In principle, smaller the Au particle size, more is the CO oxidation activity and maximum activity of Au NPs have been observed with diameter lower than ~5 nm [26,27]. Hence, another prominent parameter could be assigned for the enhanced catalytic activity of our Au/CeO₂/SiO₂ catalyst is the relatively smaller Au particle (4 nm) size. Thus we can claim that our catalyst is rather low temperature active in CO oxidation as it gives 50% CO conversion at 45 °C. Our report is showing remarkable CO oxidation activity catalyzed by Au/CeO₂/SiO₂ within the temperature range 30–90 °C.

4. CONCLUSIONS

We have prepared CeO₂/SiO₂ composite employing a simple co-precipitation technique. Au/CeO₂/SiO₂ was prepared by deposition-precipitation with urea (DPU) method. The as-prepared catalysts were characterized by BET surface area, XRD, UV-vis DRS, and TEM techniques. XRD and TEM study disclosed the nano dimensional character of the prepared catalysts. UV-vis DRS technique showed successful Au loading. The effective catalytic CO conversion activity of Au/CeO₂/SiO₂ is attributed to high surface area of the CeO₂/SiO₂ support. Eventually, it has been seen that deposition of Au on to CeO₂/SiO₂ by modified DPU method affords an efficient catalyst in CO oxidation. Thus, it could be concluded that DPU is an authentic and promising approach for synthesizing CeO₂-based Au catalysts showing low temperature CO oxidation activity.

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