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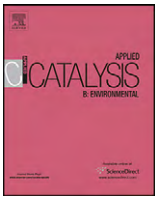

Preferential oxidation of CO in H_2-rich stream over $CuO/Ce_{1-x}Ti_xO_2$ catalysts

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ABSTRACT

$CuO/Ce_{1-x}Ti_xO_2$ prepared by sol–gel impregnation was used as catalysts for the preferential oxidation (PROX) of CO in H_2-rich stream. The effects of support composition, catalyst calcination temperature as well as the presence of H_2O and CO_2 in the reaction stream on the catalytic performance of $CuO/Ce_{1-x}Ti_xO_2$ were investigated. The results indicated that the catalyst $CuO/Ce_{0.8}Ti_{0.2}O_2$ exhibits the highest activity and the optimal temperature for the catalyst calcination is 500 °C. The presence of H_2O and CO_2 in the reaction stream has a negative effect on the catalytic activity and stability of $CuO/Ce_{0.8}Ti_{0.2}O_2$. The negative effect of CO_2 on the catalyst stability is stronger than that of H_2O, suggesting that the accumulation of carbonate species may be the main reason for catalyst deactivation. The characterization by means of XRD, HRTEM, and H_2-TPR indicated that the doping of TiO_2 in CeO_2 enhances the surface area of the composite oxide support, decreases its particle size, and promotes the dispersion of active copper species. The strong interaction between TiO_2 and CeO_2 in the support as well as the interfacial interaction between CuO and the support may also contribute to the high catalytic activity of $CuO/Ce_{0.8}Ti_{0.2}O_2$.

1. Introduction

With the intense development of low temperature proton-exchange membrane fuel cell (PEMFC), the preferential oxidation (PROX) for removing trace amounts of CO from H_2-rich stream to avoid anode poisoning has attracted extensive attention in the past decades. A number of catalysts have been developed for the CO PROX reaction, which include the noble metal-based catalysts (Pt, Pd, Ru, Rh) [1–4], gold-based catalyst [5–8], and transition metal-based catalysts (Co, Cu, Mn) [9–11]. The platinum-group metals catalysts have desirable activity and stability at 150–200 °C, but they are not selective enough in the presence of H_2O and CO_2 [12]. Gold-based catalysts are more active than platinum-group metal catalysts at relatively low temperatures [13,14]. However, the transportation application of the noble metal-based catalysts may be limited by their high cost. Compared with the noble metal-based catalysts, the mixed oxide CuO–CeO_2 is very attractive for CO PROX due to its excellent performances and low cost [15–17]. It is more active and selective than Pt-group-based catalysts at low temperature [18] and also more selective and stable than the gold catalysts. For the industrial application, on the other side, the catalyst should have high stability and durability to the presence of H_2O and CO_2, because the reformate H_2-rich stream underwent a water–gas shift reaction contains 15–25 vol.% CO_2 and about 10 vol.% H_2O. However, CuO–CeO_2 is susceptible to the presence of CO_2 and H_2O in the reactant stream [19–21]. When the feed stream contains 10–25 vol.% H_2O and 10–25 vol.% CO_2, the temperature window for CO conversion above 99.0% is very narrow (about 5–20 °C) [12,22,23].

The redox behavior of cerium oxide can be modified by incorporation of other elements and the formation of mixed oxides. The capability of the redox couple Ce^{4+}–Ce^{3+} is strongly enhanced if other elements are introduced into the CeO_2 lattice by forming solid solutions [24–27]. Lin et al. [24] reported that a synergistic interaction between CuO and $Ce_{0.7}Sn_{0.3}O_2$ makes the reduced $CuO/Ce_{0.7}Sn_{0.3}O_2$ catalyst be easily oxidized, which is responsible for the high CO oxidation activity at low temperature. Chen et al. [25] reported that the incorporation of Sn^{4+} into CeO_2 in the $CuO/Ce_xSn_{1-x}O_2$ catalysts promoted the selective oxidation of CO. They also found that an appropriate amount of zirconium $(1-x=0.1)$ incorporated into CeO_2 for $CuO/Ce_xZr_{1-x}O_2$ and $CuO/Ce_xZr_{1-x}O_2$-Al_2O_3 catalysts could not only increase the mobility of lattice oxygen but also promote the activity of selective CO oxidation; when the amount of Zr^{4+} exceeded 10% $(1-x>0.1)$, however, this promotion effect on CO oxidation was weakened [26,27].

The doping of ceria with other elements did not always enhance the activity of CuO-CeO_2 catalyst in CO oxidation. Ratnasamy et al. [28] investigated the CO PROX activity of CuO-CeO_2, CuO-CeO_2-ZrO_2 and CuO-ZrO_2 catalysts prepared by coprecipitation method; they observed that CuO-CeO_2 exhibited superior activity than CuO-CeO_2-ZrO_2 and CuO-ZrO_2. Martínez-Arias et al. [29] revealed that

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$CuO/Ce\text{-}M\text{-}O_2$ catalyst ($M = Zr, Tb$) prepared by precipitation using a reverse microemulsion method exhibited inferior activity to the CuO/CeO_2 catalyst. Manzoli et al. [30] and Caputo et al. [31] also found that doping cerium with zirconia has no beneficial effect on CO PROX performance. The inconsistent conclusion may be originated from the different methods for preparing catalysts and the various doping elements. However, we can still get a rough estimation that the $CuO/Ce_{1-x}M_xO_2$ catalysts with low level cerium doping ($x \leq 0.3$) show better CO PROX performance than the heavy doping ones ($x \geq 0.5$), especially for the cerium-containing catalysts doped with zirconia [26,31].

The incorporation of Ti into CeO_2 can significantly improve the storage capacity of mobile oxygen of CeO_2 [32]. In this respect, the Ce–Ti–O composite oxides were prepared and investigated as promising supports [32–34]. The catalysts supported on the Ce–Ti–O composite oxides have been used in the reactions such as stream forming of ethanol [35], partial oxidation of methane [36], oxidation of volatile organic compounds (VOCs) [37], and photocatalytic degradation of chlorophenol [38]. We also found that Pd supported on the ceria–titania composite oxides ($Pd/CeO_2–TiO_2$) prepared by sol–gel precipitation followed by supercritical fluid dry (SCFD) exhibited high activity for CO oxidation at low temperature [39]. The temperature-programmed reduction (TPR) using H_2 and CO as reducing agents suggested that the Pd–Ce interaction in $Pd/CeO_2–TiO_2$ favored the reduction of both PdO and CeO_2, which contributed to the high activity for CO oxidation at low temperature [40–42]. The pretreatments of calcination and reduction exhibited significant effects on the catalytic behavior of $Pd/CeO_2\text{-}TiO_2$ [43,44]. Moreover, $Pd/CeO_2\text{-}TiO_2$ can still perform well in CO oxidation under the relatively actual conditions in the presence of H_2O and CO_2 [45,46]. Recently, Sangeetha and Chen reported that $Au/CeO_2–TiO_2$ exhibited high activity in the CO PROX reaction at low temperature [47]. It is then supposed that the modified oxygen storage capacity of CeO_2 by TiO_2 may also promote the activity of supported Cu species for CO oxidation in H_2-rich stream. However, as far as we know, copper supported on Ce–Ti–O composite oxides used for CO PROX was scarcely reported.

Therefore, in this work, the $CuO/Ce_{1-x}Ti_xO_2$ catalysts with various Ti/(Ce + Ti) atomic ratios were prepared by sol–gel impregnation. The effects of support composition, catalyst calcination temperature as well as the presence of H_2O and CO_2 in the reaction stream on the catalytic performance of $CuO/Ce_{1-x}Ti_xO_2$ for CO PROX in H_2-rich stream were investigated.

2. Experimental

2.1. Catalyst preparation

CeO_2, TiO_2 and $Ce_{1-x}Ti_xO_2$ composite oxides were prepared by sol–gel precipitation method at room temperature as described elsewhere [39,40]. Briefly, the alcosol was obtained through the hydrolysis of $Ce(NO_3)_3{\cdot}6H_2O$ and $Ti(SO_4)_2$ in ethanol under stirring. The precipitation was achieved with the solution of $NH_3{\cdot}H_2O$ at ambient temperature. After aging and filtration, the precipitate was washed with deionized water until no $SO_4{}^{2+}$ ions were detected with $Ba(NO_3)_2$ solution. To drive out of the water in the wet precipitate, the material was then washed with ethanol. The resulting alcogel was dried at 110 °C and finally calcined at 500 °C in air for 4 h.

CuO-supported catalysts were prepared by the incipient wetness impregnation method with aqueous $Cu(NO_3)_2$ solution. The catalyst was then dried at 110 °C for 12 h and calcined in air at the temperature of 400–800 °C for 4 h. The nominal value of Ti/(Ce + Ti) atomic ratios (x) was in the range of 0–1 for the $Ce_{1-x}Ti_xO_2$ composite oxides, and the CuO loading was 10.0 wt.% for the $CuO/Ce_{1-x}Ti_xO_2$ catalysts.

2.2. Catalyst characterization

The powder X-ray diffraction (XRD) was performed on an advanced X-ray diffractometer (Bruker AXS D8, Germany). The diffraction patterns of the samples were recorded at room temperature with Cu Kα radiation (154.06 pm, 40 kV, and 40 mA) in the range of 2θ between 10° and 90°. The average crystallite size was estimated from the line broadening of the most intense XRD reflections with Scherrer formula, and the cell parameter of cubic CeO_2 is obtained by the MDI Jade5 software.

The Brunauer–Emmett–Teller (BET) surface area of the catalysts was measured by nitrogen adsorption at −195.8 °C with a TriStar 3000 Gas Absorption Analyzer (Micromeritics Instrument Co., USA). The samples were degassed at 200 °C and 6.7 Pa for 2 h prior to the measurement.

The high-resolution transmission electron microscopy (HRTEM) images of the samples were obtained using a JEM 2010 microscope operating at 200 kV and equipped with an energy-dispersive X-ray (EDX) instrument. The catalyst was crushed to a fine powder, and then a holey carbon film copper grid was dipped into the crushed powder. The mean particle size is estimated from a statistic result of 100 particles randomly selected in TEM images.

The temperature-programmed reduction of H_2 (H_2-TPR) was performed in a quartz microreactor, and 50 mg sample was used in each measurement as described elsewhere [40,41]. The samples were first pretreated under an air flow (30 ml/min) at 300 °C for 1 h, followed by purging with Ar (30 ml/min) at the same temperature for 1 h and then cooled down to room temperature (RT). After that, a flow of 5% H_2 in Ar (30 ml/min) was switched into the system and the sample was heated up to 700 °C from room temperature at a rate of 10 °C/min. The amount of H_2 uptake during the reduction was measured by a thermal conductivity detector (TCD), which was calibrated by the quantitative reduction of a given amount of CuO to the metallic copper.

2.3. Catalytic tests and analytical procedure

The catalytic test for CO PROX in a hydrogen-rich stream was carried out in a quartz tubular flow microreactor with an internal diameter of 6.0 mm at atmospheric pressure as described previously [7,8]. The reacting stream consisted of 1.0% CO (by volume, hereinafter), 1% O_2, 50% H_2, 10% H_2O (when used), 15% CO_2 (when used), and balanced N_2. H_2O was introduced to the feed through a bubbler saturator. The total flow rate is 100 ml/min, and the weight of the catalyst used in each run is 500–200 mg, corresponding to a space velocity of 12,000–60,000 ml g^{-1} h^{-1}. The catalyst bed was about 1.0–2.5 cm in height and placed in the constant temperature zone (3–4 cm high) of the microreactor. Before the light-off tests, the catalyst was pretreated at 300 °C for 1 h in air with a flow rate of 30 ml/min. Then the catalytic reaction was performed from room temperature up to 200 °C at a heating rate of 2 °C/min.

CO, CO_2 and O_2 in the reaction stream and effluent were analyzed online with gas chromatographs as described elsewhere [7,8]. CO conversion was determined either based on CO_2 formation or CO consumption (when excess CO_2 was added):

$$\text{CO conversion}\,(x_{\text{CO}}) = \frac{[\text{CO}_2]_{\text{out}}}{[\text{CO}]_{\text{out}} + [\text{CO}_2]_{\text{out}}} \times 100\%\ \text{or}$$

$$\text{CO conversion}\,(x_{\text{CO}}) = \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}} \times 100\%\,(\text{when excess CO}_2\text{ was added}).$$