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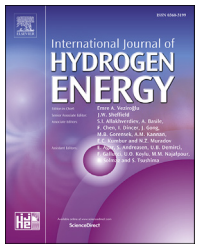

Promoted the reduction of Cu^{2+} to enhance $CuO-CeO_2$ catalysts for CO preferential oxidation in H_2-rich streams: Effects of preparation methods and copper precursors

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ABSTRACT

A series of $CuO-CeO_2$ catalyst samples synthesized by using various methods (CuCe-SF-N, CuCe-UGC-N, CuCe-SG-N and CuCe-ST-N) and copper precursors (CuCe-SF-N, CuCe-SF-C, CuCe-SF-A and CuCe-SF-S) were estimated for CO preferential oxidation in H_2-rich streams. It was found that both synthesis routes and copper precursors have an important effect on catalytic behaviors of $CuO-CeO_2$ catalyst. Compared to CuCe-UGC-N, CuCe-SG-N and CuCe-ST-N, CuCe-SF-N exhibits the lowest temperature and the widest temperature window for 100% CO conversion (about 50 °C), which should be attributed to synergistic effects of smaller crystallite size, the formation of more Cu^+ species together with the high ratio of $Ce^{3+}/(Ce^{3+}+Ce^{4+})$. Among the four catalysts prepared with different Cu precursors (CuCe-SF-N, CuCe-SF-C, CuCe-SF-A and CuCe-SF-S), the corresponding CO conversions of them are in the order of CuCe-SF-N > CuCe-SF-A > CuCe-SF-C » CuCe-SF-S. The lowest catalytic activity of CuCe-SF-S should be due to the presence of SO_4^{2-} species covered on the surface of the catalyst, which not only results in the formation of the less Cu active species but inhibits the interaction between Cu species and CeO_2. In addition, the optimal CuCe-SF-N catalyst displays relative stability during the 200 h time-on-stream test even in the presence of H_2O and CO_2.

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Introduction

Cu–Ce (CuO/CeO_2) catalyst has been extensively employed in many catalytic reactions that include CO preferential oxidation (CO-PROX), steam and oxidative reforming of methanol as well as water-gas shift (WGS) reaction [1–7]. As for CO-PROX, Cu–Ce catalyst is generally used to eliminate CO from H_2-rich streams due to its efficiency and simplicity, which will be further applied to proton exchange membrane fuel cell (PEMFC). In the past decades, Cu–Ce catalyst has attracted considerable attention in the field of CO-PROX due to the advantages of high activity and selectivity together with low cost, which has been regarded as one of the most promising candidates to replace the expensive noble metal-based catalyst [8–13].

It was well documented that Cu–Ce catalyst for CO-PROX is structure-sensitive and CO oxidation generally takes place at the interfaces of Cu–Ce catalyst. Moreover, according to the previous reports [14,15], both CuO and CeO_2 play essential roles during the course of CO-PROX while the interfaces of $CuO–CeO_2$ act as the active sites for CO-PROX. For instance, Stephanopoulos et al. [16] reported that the formation of more reduced (Cu^+) species within Cu–Ce catalyst is beneficial to the improvement of catalytic activity. This is because that adsorbed CO on the Cu^+ active sites on the surface of Cu–Ce catalyst will react with oxygen species offered by CeO_2 via the redox cycle of Ce^{4+}/Ce^{3+}. Furthermore, reduced Cu^+ active species were further formed by the interaction between CuO and CeO_2. Luo and coworkers [14,17] demonstrated that the CuO species with fine dispersion would be in favour of the enhancement of catalytic performances. These indicate that the important roles of the coordination site and the crystal orientation of active species for this structure-sensitive reaction. In general, the preparation method of Cu–Ce catalyst would result in significant differences both in physicochemical and structural properties, which, in turn, have an important influence on the catalytic behaviors. Therefore, the synthesis route of Cu–Ce catalyst has attracted considerable attention in the past decades, and many synthesis methods have been developed to prepare Cu–Ce catalyst with high-performances for CO-PROX, which involve impregnation, co-precipitation, deposition-precipitation, sol-gel, urea gelation/co-precipitation and so on [1,18–22]. Despite some significant progresses in the synthesis of Cu–Ce catalyst with high-performance for CO-PROX, however, these synthesis routes suffer from the disadvantages of a complex process, energy consumption and time consuming. Therefore, further studied in this area are desirable, particularly in relation to the synthesis routes with the advantages of fast and simple process, energy and time saving, and the reducing and/or avoiding the utilization of solvents.

In this paper, we reported a facile route to rapidly synthesize $CuO–CeO_2$ catalysts within 30 min, and the influences of our preparation method with respect to other synthesis route as well as copper precursors on catalytic performances for CO-PROX were investigated. In order to illustrate the interrelationship between physicochemical properties and catalytic performances, the aforementioned catalysts were characterized by N_2 adsorption-desorption, XRD, H_2-TPR, TEM, Raman and FT-IR. In addition, stability of catalyst for CO-PROX even in the presence of CO_2 and H_2O was studied.

Materials and methods

Materials

Cerium nitrate hexahydrate ($Ce(NO_3)_3·6H_2O$), cupric nitrate ($Cu(NO_3)_2·3H_2O$), cupric chloride ($CuCl_2·2H_2O$), cupric acetate ($Cu(CH_3COO)_2·H_2O$), cupric sulfate ($CuSO_4·5H_2O$), citric acid ($C_6H_8O_7$), cetyltrimethylammonium bromide ($C_{16}H_{33}(CH_3)_3NBr$, CTAB) and urea ($CO(NH_2)_2$) were purchased from Shanghai chemical regent company of China. All the above chemicals are of analytical grade and were used as the received.

Synthesis of $CuO–CeO_2$ catalysts

$CuO–CeO_2$ catalysts prepared by the use of solvent-free (SF) method were briefly described as follows: the calculated amounts of $Ce(NO_3)_3·6H_2O$, $Cu(NO_3)_2·3H_2O$ and $(NH_2)_2CO$ were mixed and grinded at room temperature (RT) to ensure the loading of Cu (7.5 wt%, based on Cu), and the transparent viscous gel was obtained within a few minutes. After that, the resulting gel was calcined at 700 °C in air for 20–30 min. In order to investigate the influence of copper sources, only $Cu(NO_3)_2·3H_2O$ was replaced by $Cu(CH_3COO)_2·H_2O$, $CuCl_2·2H_2O$ or $CuSO_4·5H_2O$ to prepare other catalyst samples. The $CuO–CeO_2$ catalyst samples prepared by our synthesis route were denoted as CuCe-SF-X, where "X" represents Cu sources (X = N, C, A and S; N = cupric nitrate, C = cupric chloride, A = cupric acetate, S = cupric sulfate, respectively).

The synthesis procedures of $CuO–CeO_2$ sample with the aid of surfactant template (ST) were depicted as follows: 12 mmol of CTAB was dissolved in 200 ml of deionized water with vigorously stirring at RT for 1 h. Next to, the calculated amounts of $Cu(NO_3)_2·3H_2O$ and $Ce(NO_3)_3·6H_2O$ were added into the above solution to keep the loading of Cu (7.5 wt%), and the mixed solution was kept stirring for 0.5 h. Then, the pH value of the mixed solution was adjusted to 10.0 by the addition of 0.2 M NaOH. After that, the resulting solution was still kept to be stirred at RT for 12 h and aged at 90 °C for 3 h, respectively. Subsequently, the obtained product was filtered, washed with hot water and dried at 110 °C for 6 h. At last, the resulting sample was calcined at 700 °C in air for 1 h, and the corresponding catalyst was nominated as CuCe-ST-N.

Urea gelation/co-precipitation method was used to synthesize $CuO–CeO_2$ catalyst sample according to the processes and recipes reported in the previous references [23–26], which were described as follow: the calculated amounts of $Ce(NO_3)_3·6H_2O$, $Cu(NO_3)_2·3H_2O$ and $(NH_2)_2CO$ were added into deionized water to form the transparent solution and maintain the loading of Cu (7.5 wt%). After that, the mixture solution was thermally treated at 80–100 °C to evaporate and remove excess water and to obtain the precipitate (or gel). Subsequently, the resulting precipitate was washed and dried at 80–100 °C in turn. Finally, the resulting product was calcined at 700 °C in air for 1 h, and the catalyst sample prepared with this method was designated as CuCe-UGC-N.

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