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Influence of cerium precursors on the structure and reducibility of mesoporous $CuO\text{-}CeO_2$ catalysts for CO oxidation

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ABSTRACT

This work investigated the effects of cerium precursors [$Ce(NO_3)_3$ and $(NH_4)_2Ce(NO_3)_6$] on the structure, surface state, reducibility and CO oxidation activity of mesoporous $CuO\text{-}CeO_2$ catalysts. The catalysts were characterized by TG–DTA, XRD, LRS, N_2 adsorption–desorption, HRTEM, XPS, H_2-TPR and in situ FT-IR. The obtained results suggested that the precursors exerted a great influence on the properties of $CuO\text{-}CeO_2$ catalysts: (1) compared with the catalysts from Ce(III) precursor, the derived Ce(IV) precursor catalysts showed smaller grain size, higher BET surface area, narrower pore size distribution, whereas their reducibility and activities were not enhanced. (2) In contrast, the catalysts from Ce(III) precursor without excellent texture displayed high reducibility and activities for CO oxidation due to the high content of Ce^{3+}, following the redox equilibrium of $Cu^{2+} + Ce^{3+} \leftrightarrow Cu^{+} + Ce^{4+}$ shifting to right to form more stable Cu^{+} species, which was the origin of synergistic effect. The synergistic effect between copper and cerium was the predominant contributor to the improved catalytic activities of $CuO\text{-}CeO_2$ catalysts, instead of structural properties.

1. Introduction

In recent years, ceria (CeO_2) has been received increasing attentions and found tremendous applications in environmental catalysis due to its high oxygen storage-release capacity associated with Ce^{4+}/Ce^{3+} redox cycle [1,2]. It was well documented that the catalytic activities of ceria-based catalysts were greatly promoted not only by precious metals, but also by base metals, particularly copper species [3–6]. For instance, $CuO\text{-}CeO_2$ catalysts had been shown to be very active for CO oxidation, exhibiting specific activities comparable with or even superior to precious metal catalysts [7,8].

In principle, the high activity of $CuO\text{-}CeO_2$ is correlated with the synergism of copper–ceria interactions, which facilitates the electron exchanges between Cu^{2+}/Cu^{+} and Ce^{3+}/Ce^{4+}, with both components being significantly more readily reduced or oxidized than the corresponding independent ones [9–11]. The redox cycles between Cu^{2+} and Cu^{+} (and concomitantly Ce^{4+} and Ce^{3+}) are often regarded as the key steps of the reaction mechanism of CO oxidation and consequently, as well as in determining the catalytic behavior [12]. Thus, the $CuO\text{-}CeO_2$ catalysts with facile electron exchanges can easily form Cu^{+} species for CO adsorption, which is an important factor to promote activity of CO oxidation [13]. Another important factor is the presence of the oxygen vacancy provided by CeO_2, which can in turn generate active oxygen for the reaction [14]. Other than these, unique texture of ceria-based catalysts is also advantageous for their catalytic performances. For example, mesoporous $CuO\text{-}CeO_2$ catalysts had been reported to display superior activity toward CO oxidation in comparison with usually used CuO/CeO_2 catalysts [15–17]. Consequently, controllable synthesis of mesoporous $CuO\text{-}CeO_2$ catalysts, which possess facile redox process and a high concentration of oxygen vacancies, will be beneficial to the enhancement of activity toward CO oxidation.

Until now, $Ce(NO_3)_3$ and $(NH_4)_2Ce(NO_3)_6$ are two of the most widely used precursors to synthesize $CuO\text{-}CeO_2$ catalysts. Tang et al. [18] prepared $CuO\text{-}CeO_2$ catalysts by precipitation method and used $Ce(NO_3)_3$ as cerium precursor. They pointed out that the discrepancies in the dispersion of copper species and the degree of interaction between copper species and ceria determined the reversible redox properties, and consequently the catalytic performance of CO oxidation. Li et al. [19] obtained $CuO\text{-}CeO_2$ catalysts from $(NH_4)_2Ce(NO_3)_6$ by urea co-precipitation–gelation method. They found that the reducibility of ceria was promoted by the addition of copper, leading to the significantly enhanced activity in the water–gas shift reaction (WGS). However, to our knowledge,

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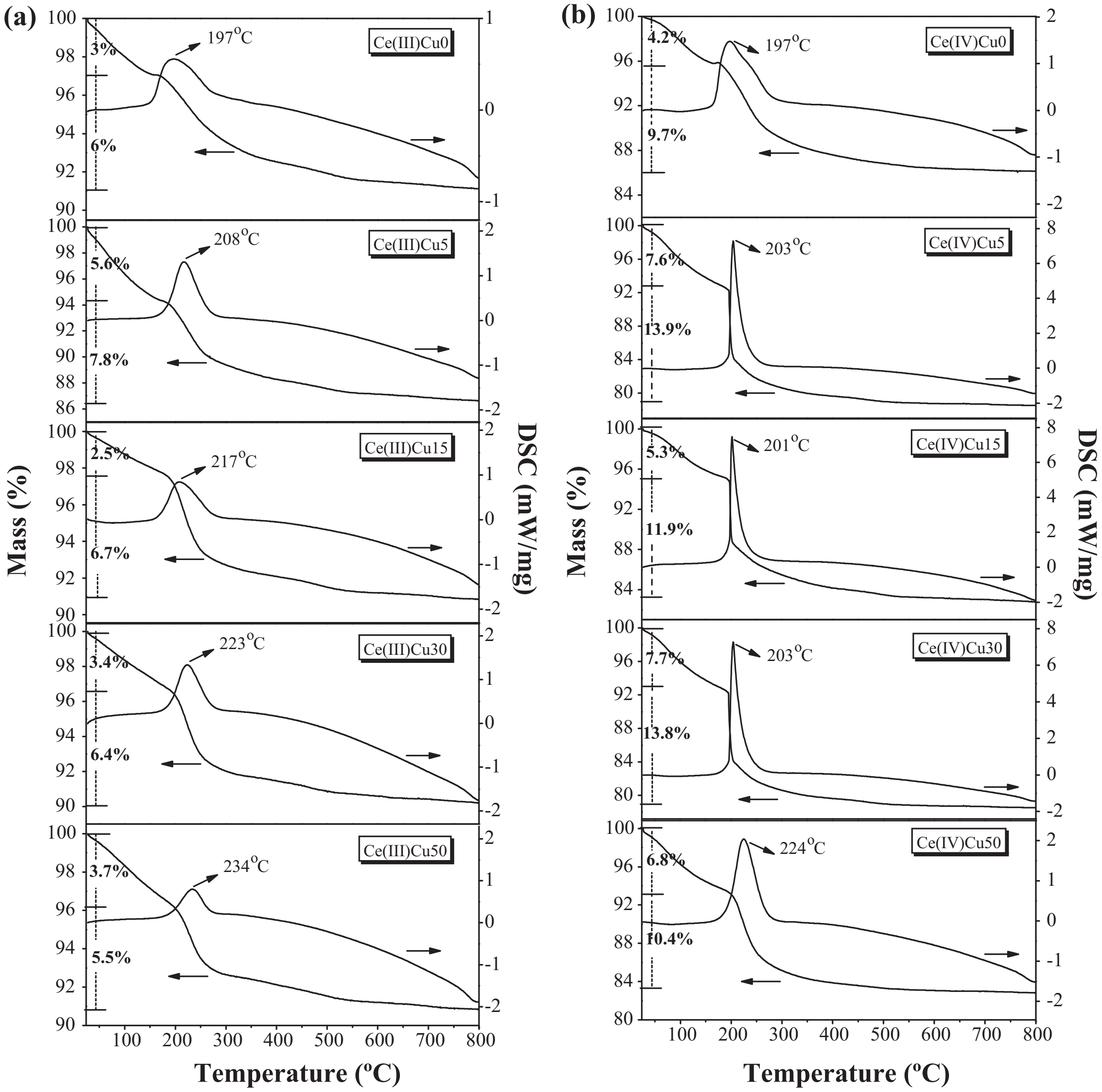

Fig. 1. TG–DTA curves of the uncalcinated samples: (a) Ce(III)Cu*x*; (b) Ce(IV)Cu*x*.

little attention has been paid to comparing the effect of cerium precursors on the structure, surface state, redox property and CO oxidation activity of mesoporous CuO-CeO_2 catalysts. On the other hand, previous researches proved that many factors could influence the activity of CuO-CeO_2 catalysts, such as surface area, porous structure [15], synergistic effect between copper and cerium [12], oxygen vacancy [14], etc. Nevertheless, the contributions of these factors to the catalytic activity and the predominant contributor to the enhanced activity are still not clear.

In this work, a series of mesoporous CuO-CeO_2 catalysts were prepared by a surfactant-assisted co-precipitation method and characterized by means of TG–DTA, XRD, LRS, N_2 adsorption–desorption, HRTEM, H_2-TPR, in situ FT-IR and CO oxidation model reaction. The studies have mainly focused on (1) exploring the influence of cerium precursors (i.e. $Ce(NO_3)_3$ or $(NH_4)_2Ce(NO_3)_6$) on the structure, surface state, reduction property and CO oxidation activity of CuO-CeO_2 catalysts; (2) investigating the contribution of structural property and synergistic effect to the reducibility and catalytic activity of CO oxidation, and deciding the major contributor to improve the activity.

2. Experimental

2.1. Catalyst preparation

All chemicals were of analytical grade and used as received without further purification. CuO-CeO_2 catalysts with different Cu contents were synthesized by a surfactant-assisted co-precipitation method. In a typical synthesis procedure, 6 mmol cetyltrimethyl ammonium bromide (CTAB) was dissolved in 200 mL distilled water at room temperature, followed by the addition of 10 mmol $Ce(NO_3)_3{\cdot}6H_2O$ or $(NH_4)_2Ce(NO_3)_6$ and a calculated amount of $Cu(NO_3)_2{\cdot}3H_2O$. After that, an aqueous solution of NaOH ($0.2\ \mathrm{mol\ L^{-1}}$) was added dropwise to the pre-mixed solution under vigorous stirring until pH 9. The obtained suspension was aged at 90 °C for 3 h. The precipitate was filtered, washed and dried at 110 °C for 12 h. Subsequently, the resultant powders were calcined at 400 °C for 5 h in air. The catalysts were denoted as Ce(III)Cu*x* or Ce(IV)Cu*x*, where *x* stands for the percentage of Cu/(Cu + Ce) molar ratio. The nominal contents of Cu were 0, 5, 15, 30 and 50 mol%, respectively.