

SYNTHESIS OF NANOSIZED CuO-CeO₂ MIXED OXIDE BY CITRATE SOL-GEL METHOD

Hoang Thi Huong Hue, Nguyen Dinh Bang

Faculty of Chemistry, Hanoi University of Science, VNU

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Abstract

Nano-particles of CuO-CeO₂ with the average particle size (10 - 40 nm) and surface area (45.3 m²/g) was obtained from a mixed solution of Ce(NO₃)₃, Cu(NO₃)₂, citric acid by the citrate sol-gel method as precursors. The characteristics of CuO-CeO₂ mixed oxide were examined by means of X-Ray diffraction (XRD), H₂-temperature-programmed reduction (H₂-TPR) and the nitrogen adsorption and desorption (BET), transmission electron microscopy (TEM). The results indicated that there are CuO species in the CuO-CeO₂ mixed oxide: the Cu²⁺ mostly exists in Cu_xCe_{1-x}O_{2-δ} solid solution, the left in the finely dispersed CuO species on the surface of CeO₂ and the bulk CuO. The calculating results from Powder Cell 2.4 software showed that, when CuO-CeO₂ mixed oxide was formed, the cell parameter values of CeO₂ was smaller than that of pure CeO₂, indicating that some Cu²⁺ entered the CeO₂ lattice.

1. INTRODUCTION

Volatile organic compounds (VOCs), emitted from a variety of industrial processes and transportation activities, are considered as an important class of air pollutants. Catalytic oxidation is one of the most developed techniques used for the elimination of VOCs, as it requires lower temperatures than thermal oxidation. Typical catalysts for VOC oxidation are mainly noble metals, which show high activity at low temperatures, but they are costly and have low stability in the presence of chloride compounds. Metal oxides (Fe, Cr, Cu, Mn and Co) are a cheaper alternative to noble metals as catalysts for VOC oxidation [1]. They present sufficient activity, although they are less active than noble metals at low temperatures. CuO-CeO₂ mixed metal oxides comprise a promising family of catalysts and have been studied by many investigators in reactions, such as, the combustion of CO and CH₄ [2], the water-gas shift reaction [3], the reduction of NO [4], and the wet oxidation of phenol [5]. The high activity of CuO-CeO₂ is attributed to the promoting effect of ceria due to its high oxygen storage capacity and facile Ce⁴⁺/Ce³⁺ redox cycle.

Several methods for the preparation of CuO-CeO₂ mixed oxide have been reported, such as combustion [6], sol-gel [7], co-precipitation [8] and impregnation [4]. In this work, the CuO-CeO₂ mixed oxide with nanosize was prepared using a citrate sol-gel method. The CuO species in the mixed oxide was investigated.

2. EXPERIMENTAL

2.1. Preparation of CuO-CeO₂ mixed oxide

CuO-CeO₂ mixed oxide was prepared using the citrate sol-gel method. Aqueous solutions of 1M Ce(NO₃)₃ and 1M Cu(NO₃)₂ were mixed with an aqueous solution of 2M citric acid (the molar ratio of Cu/Cu+Ce = 0.1, citric/Cu+Ce = 1). The mixed solution was heated at 80 - 90°C by a stirrer until a viscous gel was obtained. In this process, the mixture color turned from blue to green. The gel was dried at 110°C over night to form spongy material, i.e., catalyst precursor. Then the precursors was put in a furnace and heated at 450°C to result in a black mixture of CuO-CeO₂ (the activation temperature was chosen on the basis of TGA results, which showed that the decomposition of citrate precursors under air flow takes place at 200 - 300°C).

2.2. Characterization

- X-ray diffraction (XRD) pattern was measured using a D8 Advance, Bucker (German) with CuK α radiation operated at 40kV and 40 mA. The intensity data were collected at 25°C in a 2 θ range from 20⁰ to 80⁰. The cell parameter values of pure CeO₂ and CeO₂ in mixed oxide were determined by the XRD and the Powder Cell 2.4 software (material analysis using diffraction).

- Specific surface area (S_{BET}), the pore volume and the pore size distribution of the sample was determined from a single point Braunauer- Emmett-Teller (BET) analysis of nitrogen adsorption and

desorption isotherms at 77 K recorded on an ASAP 2010 Micromeritic (USA).

- Transmission electron microscopy (TEM) investigation was carried out using a JEM 1010, JEOL (Japan) microscope operated at 80 kV.

- Reducibility and the copper species of CuO-CeO₂ mixed oxide was measured by H₂-temperature-programmed reduction (H₂-TPR) using an AutoChem II 2920 V3.03 Micromeritics (USA) instrument. The sample (0.1733 g) was first treated in a He stream at 300°C for 0.5 h. After being cooling to room temperature in the same atmosphere, the sample was finally heated with a mixture of 10 %H₂ in 90%Ar from room temperature to 700°C at a rate of 10°C/min.

3. RESULTS AND DISCUSSION

3.1. Surface area and structure

Fig.1a shows the nitrogen adsorption-desorption isotherms of CuO-CeO₂ mixed oxide. The isotherm displayed a hysteresis loop with a sloping adsorption branch and a relatively steep desorption branch at a medium pressure ($P/P_0 = 0.4 - 0.5$), which was

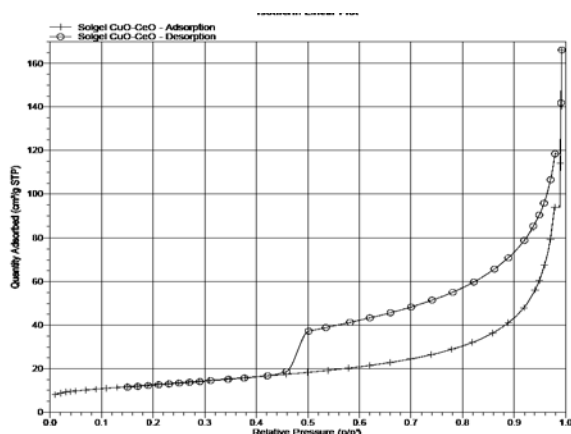


Fig. 1(a): Nitrogen adsorption-desorption isotherms of CuO-CeO₂ mixed oxide

typical of type IV (IUPAC classification), and characteristic of inorganic porous oxides. The BET surface area of the CuO-CeO₂ mixed oxide is measured to be 45.3 m²/g.

Fig.1b shows the corresponding pore size distribution of CuO-CeO₂ mixed oxide. The pore size distribution calculated from the desorption branch using the BJH method is shown in Fig.1b, which shows that the dominant peak is in the mesoporous range, with a main peak around 2.5 nm. XRD pattern of CuO-CeO₂ mixed oxide are shown in Fig. 2.

Fig. 2 showed that reflections in the 2θ region 25 - 80°, it can be seen that diffraction peaks of the face-centered cubic fluorite oxide-type structure of CeO₂ at $2\theta = 28.5^\circ$, 33.4° and 47.5° in the CuO-CeO₂ mixed oxide. Diffraction peaks of CuO phase was not detected in CuO-CeO₂ mixed oxide, even when the 2θ region 30°-50°, where CuO peaks were expected, was expanded. Peaks of Cu₂O were also not detected. The absence of copper oxide peaks may be attributed to highly dispersed CuO on the surface of ceria or the formation of Cu-CeO solid solution [2, 5, 7, 8]. The average crystallite sized of CeO₂ in mixed oxide, as calculated using Scherrer's equation, is about 30 nm.

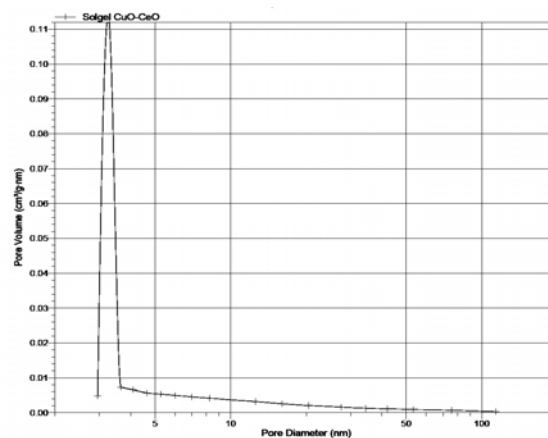


Fig. 1(b): the corresponding pore size distribution of CuO-CeO₂ mixed oxide

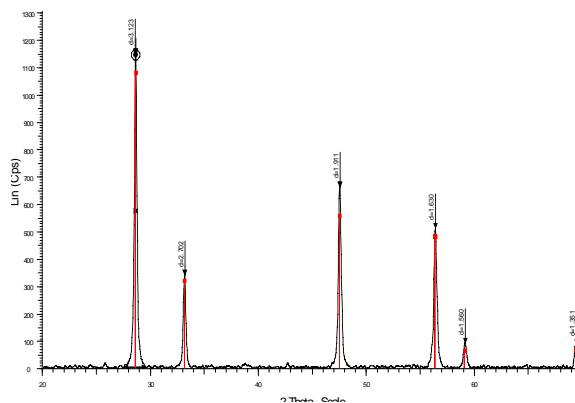


Fig. 2: XRD pattern of CuO-CeO₂ mixed oxide

The size and morphology of CuO-CeO₂ was shown in Fig. 3.

As shown in Fig. 3, the small size particles (10-40 nm) were obtained. The result is in accordance with the calculated by Scherer equation based on the XRD result.

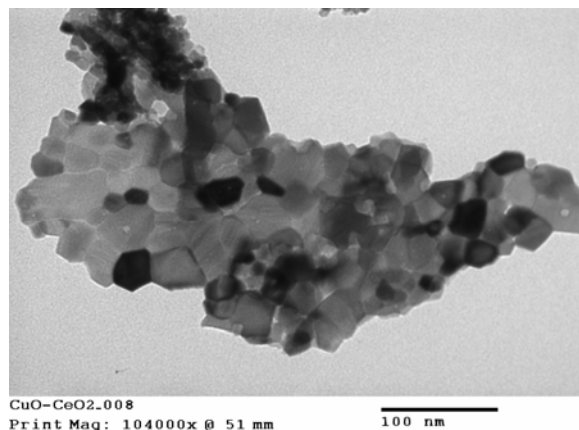


Fig. 3: TEM image of CuO-CeO₂ particles

3.2. Temperature-programmed reduction

In order to determine the existing states of CuO on CuO-CeO₂ mixed oxide, we have employed H₂-TPR characterization. Fig. 4 shows the H₂-TPR profiles of CuO-CeO₂.

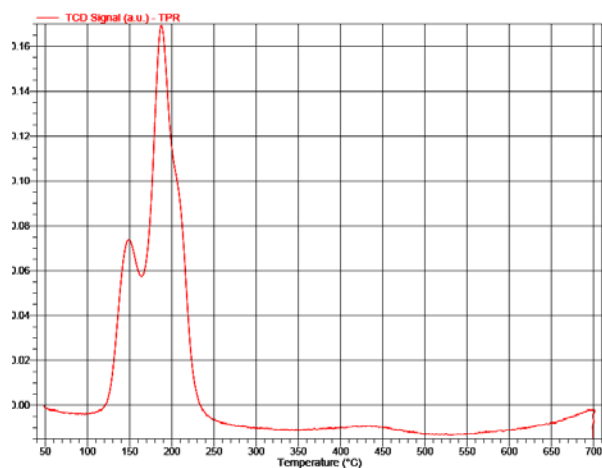


Fig. 4: H₂-TPR profile of CuO-CeO₂

The TPR profile of CuO-CeO₂ showed mainly one reduction peak at about 188°C and the others at 149°C. In addition, there was one shoulder peak at about 206°C. These peaks are mainly related to the reduction of different copper species. The reduction of pure CuO is reported in the literature to occur between 290 and 390°C [7, 9, 10]. Meng-Fei Luo et al. regard the low temperature peak as reduction of copper species strongly interacting with CeO₂ and the higher temperature peak as reduction of less or

non-interaction CuO species [7]. Also, it is known that the finely dispersed CuO is easy to be reduced. Moreover, as pointed out by Martinez- Arias et al., CeO₂ can also enhance the reducibility of finely dispersed CuO clusters, leading to lower reduction temperature [11]. Thus, the peak at 149°C is ascribed to finely dispersed CuO, it is known that the finely dispersed CuO is easy to be reduced. The mainly peak at 188°C is due to the reduction of the Cu²⁺ in the Cu_xCe_{1-x}O_{2-δ} solid solution and the shoulder peak at 206°C is attributed to bulk CuO [7, 11]. However, amount of CuO phase is very small so that a separate CuO phase can not be found in the XRD result.

The formation of Cu_xCe_{1-x}O_{2-δ} solid solution was confirmed by the Powder Cell 2.4 software (material analysis using diffraction), which showed that a reduction in the lattice parameter of ceria upon introduction of CuO, because the ionic radius of Cu²⁺ (0,072 nm) is smaller than that of Ce⁴⁺ (0,097nm) [12]. Indeed, we observed a decrease in the cell parameter from 5.41134 Å in pure CeO₂ to 5.4062 Å in CuO-CeO₂, which confirms Cu²⁺ ion substitution in the CeO₂ matrix and the Cu_xCe_{1-x}O_{2-δ} solid solution is formed.

Therefore, it can be concluded that there are CuO species in the CuO-CeO₂ mixed oxide: the Cu²⁺ is mostly exist in Cu_xCe_{1-x}O_{2-δ} solid solution, the left in the finely dispersed CuO species on the surface of CeO₂ and the bulk CuO.

4. CONCLUSIONS

Nano-particles of CuO-CeO₂ with the average particle size (10 - 40 nm) and high surface (45.3 m²/g) were obtained from a mixed solution of Ce(NO₃)₃, Cu(NO₃)₂, citric acid by the citrate sol-gel method as precursors. There are three CuO species in the CuO-CeO₂ mixed oxide: the Cu²⁺ mostly exists in Cu_xCe_{1-x}O_{2-δ} solid solution, the left in the finely dispersed CuO species on the surface of CeO₂ and the bulk CuO.

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Corresponding author: **Hoang Thi Thuong Hue**

Faculty of Chemistry, Hanoi University of Science, VNU

19 Le Thanh Tong, Hoan Kiem, Hanoi

Email: huevoco@gmail.com

Tel. 0986236174