Preparation and Characterization of Nanosized CuO-CeO$_2$ Mixed Oxide with High Surface Area*

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CuO-CeO$_2$ mixed oxide with high surface (about 70 m$^2$/g) and average particle size (from 4 to 10 nm) was prepared by the auto-combustion method. The characteristics of CuO-CeO$_2$ mixed oxide were examined by means of X-ray diffraction (XRD), H$_2$-temperature-programmed reduction (H$_2$-TPR) and the nitrogen adsorption and desorption (BET), transmission electron microscopy (TEM). H$_2$-TPR results indicated that there are three CuO species in the mixed oxide, namely, the finely dispersed CuO, the bulk CuO and the Cu$^{2+}$ in the CeO$_2$ lattice. The calculating results from Powder Cell 2.4 software showed that, when CuO-CeO$_2$ mixed oxide was formed, the cell parameter values of CeO$_2$ was smaller than that of pure CeO$_2$, indicating that some CuO entered the CeO$_2$ lattice. [DOI: 10.1380/ejssnt.2011.463]

Keywords: Nano particles; Copper oxide; Ceria; Auto-combustion method

I. INTRODUCTION

In recent years, much research has focused on cerium oxide-based transition metal catalysts because of their applications in different processes. CuO-CeO$_2$ catalysts have been widely studied for reactions such as NO reduction, complete CO oxidation, preferential oxidation (PROX), the water-gas shift (WGS) and the wet oxidation of phenol due to high activity and selectivity for these reactions.

CeO$_2$ performs the following functions: (1) it stabilizes the catalyst against metal dispersion; (2) it stores and releases oxygen; (3) it improves CO oxidation and NO reduction. It is also well known that CeO$_2$ is promoter additive. CeO$_2$ is attractive as a carrier or mixed carrier in transition metal oxides, with unique catalytic properties and as a replacement for expensive noble-metal catalyst. CeO$_2$ can maintain the reductant/oxidant ratio of exhaust near the stoichiometric value through the highest conversion of automotive pollutants. All the above factors indicate the importance of the Ce$^{4+}$/Ce$^{3+}$ redox couple in improving the performance of three-way catalysts. In addition, the structure of CeO$_2$ is similar to CaF$_2$ and its reducibility is improved due to transition metal cation entering the CeO$_2$ lattice [1].

In the present work, we focused on preparing CuO-CeO$_2$ mixed oxide by a sol-gel combustion technique. The process exploits the advantages of cheaper precursor, a simple preparation method and a resulting ultrfine, homogeneous, highly active powder. The auto-combustion reaction has the following characteristics: the precursor can be ignited at a low temperature (150-500°C) and rise to a high temperature (1000-1400°C) rapidly without any external energy. A large amount of gas yield and nano-particles with large specific surface areas can be obtained during the combustion. The reaction maintains the combustion itself once the reaction mixture is ignited. The characterization of rapid heating and rapid cooling of the auto-combustion reaction suppresses the aggregation between the particles. What is more important is that the functional molecules can be used to adjust the particle-size and morphology during the formation of sol-gel and impurities would not appear after the precursor goes through an auto-combustion reaction [2].

In this paper, the characteristics and the copper species were studied by means of X-ray diffraction (XRD), H$_2$-temperature-programmed reduction (H$_2$-TPR), the nitrogen adsorption and desorption and the Powder Cell 2.4 calculating techniques.

II. EXPERIMENTAL

Ce(NO$_3$)$_3$·6H$_2$O, Cu(NO$_3$)$_2$·3H$_2$O were used as a source of Ce$^{3+}$, Cu$^{2+}$. Citric acid was chosen as a ligand and a determinant factor in the formation of the sol-gel, PVA as an adjusting agent of particles-size and morphology.

A mixture of Ce(NO$_3$)$_3$ and Cu(NO$_3$)$_2$, polyvinyl alcohol (PVA), citric acid with a molar ratio of Cu/(Cu+Ce) = 0.1, citric/(Cu+Ce) = 1 and the amount ratio of PVA/Ce(NO$_3$)$_3$+Cu(NO$_3$)$_2$ = 20 wt.% were dissolved in a minimum volume of distilled water in order to obtain a transparent solution. The mixed solution was heated for a few minutes at 80-90°C, the solution was heated 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 150°C overnight to form spongy material, i.e., catalyst precursor. Then the precursor was put in a furnace and heated at 300°C. 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 287-300°C. The gel started boiling with rapid frothing and foaming. After some minutes, it ignited spontaneously with rapid evolution of a large quantity of gases, yielding a foamy, voluminous powder.

In order to burn-off small amounts of carbon residues remaining after auto ignition, the powder was further heated at 500°C for 1 h.

X-ray diffraction (XRD) pattern was measured using a D8 Advance, Bruker (German) with Cu K$_\alpha$ radiation.

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operated at 40 kV and 40 mA. The intensity data were collected at 25°C in a 2θ range from 20° to 80°. The microstructural parameters of sample were determined by the Powder Cell 2.4 software (material analysis using diffraction).

Specific surface area (SBET), the pore volume and the pore size distribution of the sample was determined from a single point Brunauer-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). A 0.2011 g amount of sample was placed in a quartz reactor which was connected to a homemade TPR apparatus and the reactor was heated from 293 K to 973 K at a heating rate 10 K/min. The reaction mixture consists of 10% H₂ and 90% Ar.

III. RESULTS AND DISCUSSIONS

The XRD pattern of CuO-CeO₂ was presented in Fig. 1. Figure 1 showed that reflections in the 2θ are in the region 25°-80°. Diffraction peaks of the face-centered cubic fluorite oxide-type structure of CeO₂ can be seen at 2θ = 28.5°, 33.4° and 47.5° in the CuO-CeO₂. Diffraction lines due to CuO were not detected in CuO-CeO₂ mixed oxide, even in the 2θ region 30°-50°, where CuO peaks were expected. 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-Ce-O solid solution [3-7].

The typical H₂-TPR profile of CuO-CeO₂ is shown in Fig. 2. The TPR profile of CuO-CeO₂ showed mainly one reduction peak at about 184°C. In addition, there were two shoulder peaks at about 158°C and 219°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 29°C and 390°C [3, 4, 6]. Luo et al. [5] 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. Also, it is known that the finely dispersed CuO is easy to be reduced. Moreover, as pointed out by Martinez-Arias et al. [9], CeO₂ can also enhance the reducibility of finely dispersed CuO clusters, leading...
to lower reduction temperature. Thus, the shoulder peak at 158°C is ascribed to finely dispersed CuO: it is known that the finely dispersed CuO is easy to be reduced [8]. The mainly peak at 184°C is due to the reduction of the Cu\(^{2+}\) in the Cu\(_x\)Ce\(_{1-x}\)O\(_{2-x}\) solid solution and the shoulder peak at 219°C is attributed to bulk CuO [5, 9]. However, amount of CuO phase is very small so that a separate CuO phase can be found in the XRD result.

The formation of Cu\(_x\)Ce\(_{1-x}\)O\(_{2-x}\) 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 Cu\(^{2+}\) (0.072 nm) is smaller than that of Ce\(^{4+}\) (0.097 nm) [10]. Indeed, we observed a decrease in the cell parameter from 5.411 Å in pure CeO\(_2\) to 5.404 Å in CuO-CeO\(_2\), which confirms Cu\(^{2+}\) ion substitution in the CeO\(_2\) matrix and the Cu\(_x\)Ce\(_{1-x}\)O\(_{2-x}\) solid solution is formed. Therefore, it can be concluded that there are CuO species in the CuO-CeO\(_2\) mixed oxide: the Cu\(^{2+}\) is mostly exist in Cu\(_x\)Ce\(_{1-x}\)O\(_{2-x}\) solid solution, the left in the finely dispersed CuO species on the surface of CeO\(_2\) and the bulk CuO.

The size and morphology of CuO-CeO\(_2\) was shown in Fig. 3. Figure 3 showed that the small size and well-dispersed particles (4-10 nm) were obtained. The BET results showed that the total pore volume of pores less than 729.5 Å with at P/P\(_0\) = 0.9729 was 0.1559 cm\(^3\)/g, the adsorption average pore diameter (APD= 4 pore volume/BET surface area) was 89.1 Å and the BET surface area was 70 m\(^2\)/g.

IV. CONCLUSIONS

High surface area, small size CuO-CeO\(_2\) mixed oxide was obtained by the auto-combustion method. Three different CuO species exist on CuO-CeO\(_2\) mixed oxide: the finely dispersed CuO species on the surface of CeO\(_2\), the bulk CuO and the Cu\(^{2+}\) in the CeO\(_2\) lattice (the Cu\(_x\)Ce\(_{1-x}\)O\(_{2-x}\) solid solution). This is the mainly copper species in the CuO-CeO\(_2\) mixed oxide.

[1] A. Trovarelli, Catal. Rev. Sci. Eng. 38, 439 (1996).
[2] J. Gao, Y. Qi, W. Yang, X. Guo, S. Li, and X. Li, Mater. Chem. Phys. 82, 444 (2003).
[3] G. Avgouropoulos, T. Ioannides, and H. Matralis, Appl. Catal. B 56, 87 (2005).
[4] J. Xiaoyuan, L. Guanglie, Z. Renxian, M. Jianxin, C. Yu, and Z. Xiaoming, Appl. Catal. B 173, 208 (2001).
[5] M.-F. Luo, Y.-P. Song, J.-Q. Lu, X.-Y. Wang, and Z.-Y. Pu, J. Phys. Chem. C 111, 12686 (2007).
[6] H. Zou, X. Dong, and W. Lin, Appl. Surf. Sci. 253, 2893 (2006).
[7] S. Hočevar, U. O. Krašovec, B. Orel, A. S. Arico, and H. Kim, Appl. Catal. B: Environ. 28, 113 (2000).
[8] G. Avgouropoulos and T. Ioannides, Appl. Catal. B 67, 1 (2006).
[9] A. Martinez-Arias, M. Fernandez-Gercia, O. Galvez, J. M. Coronado, J. A. Anderson, J. C. Conesa, J. Soria, and G. Munuera, J. Catal. 195, 207 (2000).
[10] N. F. P. Ribeiro, M. M. V. M. Souza, and M. Schmal, J. Power Sources 179, 329 (2008).