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Short communication

Catalytic oxidation of carbon monoxide over nanostructured CeO_2–Al_2O_3 prepared by combustion method using polyvinyl alcohol

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Abstract

The catalytic oxidation of carbon monoxide over nanostructured CeO_2–Al_2O_3 mixed oxide powders prepared by gel combustion method using polyvinyl alcohol and metal nitrates as starting materials was studied in this paper. The prepared samples were characterized by thermal analysis, X-ray diffraction, field-emission scanning electron microscopy and Brunauer–Emmett–Teller nitrogen adsorption method at 77 K. The effects of molar ratios of starting materials, pH value of precursor solution and calcination temperature on phase formation, phase composition and morphology of prepared samples were investigated. The dependence of CO conversion efficiency on Ce/Al molar ratio was also studied. The results showed that the bee's nest-like nanostructure with the pore wall consisting of CeO_2–Al_2O_3 mixed oxide nanocrystals was observed for samples calcined at temperatures in the range of 600–850 °C. For the optimized sample with this nanostructure, an average grain size of 10 nm, an average pore size of 300 nm, a specific surface area of 87.5 m^2/g, and a CO conversion efficiency as high as 99.7% at 160 °C were obtained.

Keywords: Nanostructured CeO_2–Al_2O_3 catalyst; Polyvinyl alcohol; Combustion method; Carbon monoxide oxidation

1. Introduction

Ceria-based mixed oxides such as CeO_2–MnO_x, CeO_2–Al_2O_3, CeO_2–ZrO_2, etc. have been studied intensively as catalysts for exhaust gas treatment [1–7]. Ceria is well-known to be an oxide containing cerium ions in both +3 and +4 oxidation states. This ability of ceria of reversible exchange of oxygen enables this oxide to be applied as an oxygen buffer [4]. It was indicated that the oxygen buffering behavior of ceria can be improved by incorporating other certain di- or trivalent cations into its lattice. These incorporated cations are suggested to enhance the catalytic activities of ceria-based mixed oxides by creating oxygen vacancies. Among these mixed oxides, CeO_2–Al_2O_3 system, in which Al_2O_3 acts a role as a catalytic support material, has drawn much attention as catalyst for selective catalytic reduction of NO [8] or CO oxidation [9]. For this binary system, the existence of the second phase was experimentally demonstrated to suppress the crystallization and phase transition of both CeO_2 and Al_2O_3 [10]. Up to date, in order to improve the catalytic activity of nanosized CeO_2–Al_2O_3 system, numerous approaches such as controlling the microstructure of this nanocomposite, preventing phase transition of alumina into the non-catalytic active α-Al_2O_3 from other catalytic active polymorphic types, are carried out [11,6].

This work reports our research results on the synthesis and carbon monoxide conversion of nanostructured CeO_2–Al_2O_3 mixed oxide powders prepared by gel combustion method using polyvinyl alcohol (PVA). The effects of molar ratios of starting materials, pH value, calcination temperature on the phase formation, phase composition, morphology of prepared samples and the variation of CO conversion over nanostructured CeO_2–Al_2O_3 catalyst as a function of Ce/Al molar ratio were also studied.

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2. Experimental

2.1. Catalyst preparation

The analytical grade nitrate salts of cerium and aluminum ions with Ce/Al molar ratios of 5/5; 4/6; 3/7; 2/8; and 1/9 were dissolved in PVA solution with the metal cations/PVA molar ratio of 1/3. After adjusting pH value to 4 with ammonia, this mixture was heated at 80 °C until the viscous gel was obtained. The samples were then calcined at 500, 600, 750, 850, and 950 °C for 2 h.

2.2. Catalyst characterization

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the gel precursor were carried out on a Setaram TGA-50 and DTA-50 thermal analyzer from room temperature to 800 °C in air. X-ray diffraction (XRD) measurements of the prepared samples were performed using a Siemens D 5000 diffractometer with CuK$_\alpha$ radiation at a step size of 0.03° in the 2θ range of 15–80°.

The morphology of prepared samples was investigated by using a Hitachi S-4800 field emission scanning electron microscope (FE-SEM).

The BET specific surface area was determined by nitrogen adsorption at 77 K using a Micrometics ASAP 2010 surface area and porosimetry analyzer, operating in a single point mode.

2.3. Catalytic activity tests

CO oxidation over nanostructured CeO_2–Al_2O_3 mixed oxides was carried out in a conventional flow reactor at ambient pressure and the reaction temperature ranged from room temperature to 450 °C. For the oxidation of CO, 200 mg of the CeO_2–Al_2O_3 nanocomposite was loaded inside a tubular fixed-bed flow quartz reactor. 570 ppm CO was added to a gas mixture including 20 vol% O_2 and 80 vol% N_2 to serve as gas reactants. The total flow rate was 1000 cm^3/min, corresponding to a space velocity of 3000 cm^3/g/h. The CO concentration was analyzed by a Landcom II gas analyzer. The CO conversion efficiency was calculated as follows:

$$\text{CO conversion } (\%) = ([\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}) \times 100/[\text{CO}]_{\text{in}},$$

where $[\text{CO}]_{\text{out}}$ and $[\text{CO}]_{\text{in}}$ are the CO concentrations in the product gas and feed gas, respectively.

3. Results and discussion

3.1. Thermal analysis

The DTA, TGA and derivative thermogravimetric (DrTGA) curves of the gel precursor were shown in Fig. 1. The broad endothermic peak at 58 °C with the weight loss of 20.7% in the TG curve was observed as a result of the vaporization of residual water and small organic molecules. Three exothermic peaks at 189, 336, and 381 °C with the corresponding weight loss of 21.3%, 20.4%, and 25.5%, respectively, might be associated with the decomposition of nitrate ions, the removal of organic residues and the pyrolysis of PVA. No further changes in TGA and DrTGA curves were observed when heating the sample over 600 °C.

3.2. Effect of calcination temperature on phase composition of CeO_2–Al_2O_3 nanocomposite

Fig. 2 showed XRD diagrams of samples with Ce/Al molar ratio of 5/5 calcined at 500, 600, 750, 850, and 950 °C. For the cases of the samples calcined at 500 and 600 °C, no crystalline phase was observed. It is found that fluorite structure CeO_2-based phase fully crystallized with all diffraction peaks coincided with those of standard pattern (PDF card no. 34-0394) for only samples calcined at 850 and 950 °C.

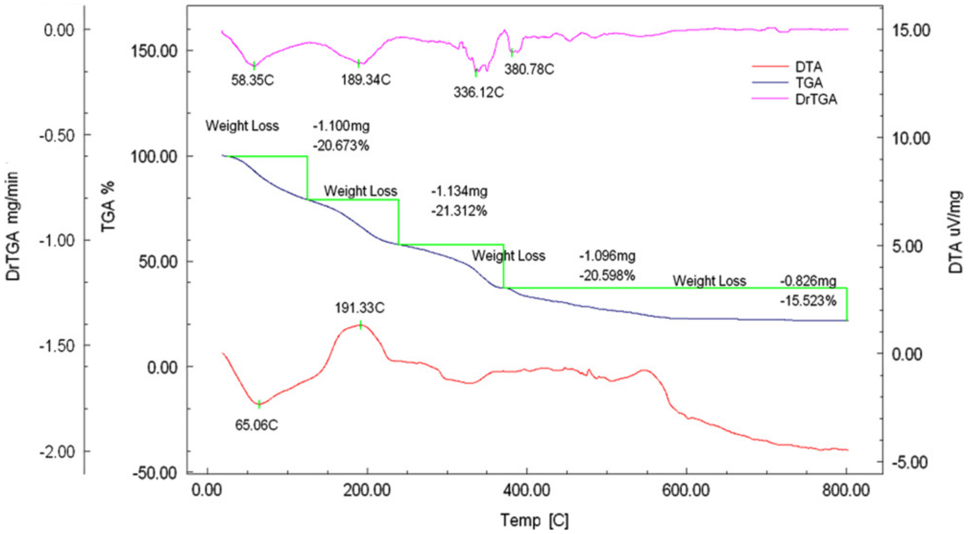

Fig. 1. TGA and DTA curves of the as-prepared gel.

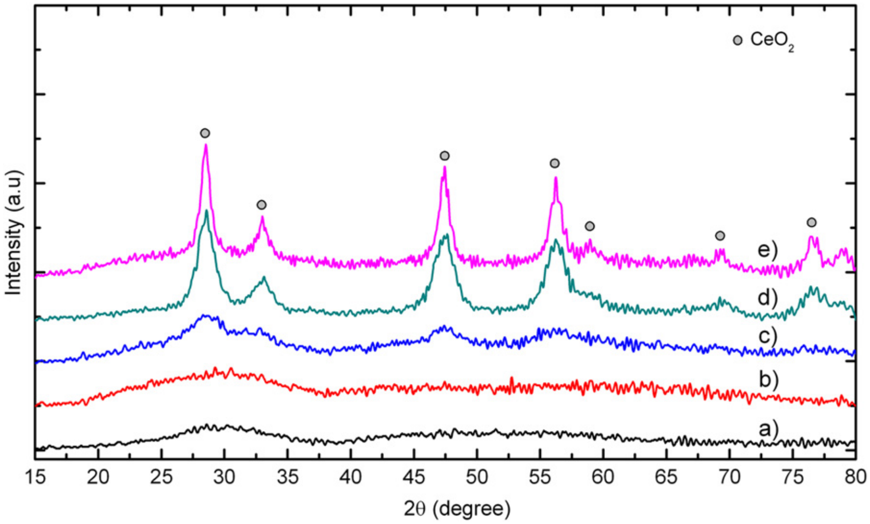

Fig. 2. X-ray diffraction diagrams of the CeO_2–Al_2O_3 powder samples prepared by calcination of the precursor at: (a) 500 °C; (b) 600 °C; (c) 750 °C; (d) 850 °C; and (e) 950 °C or 2 h.

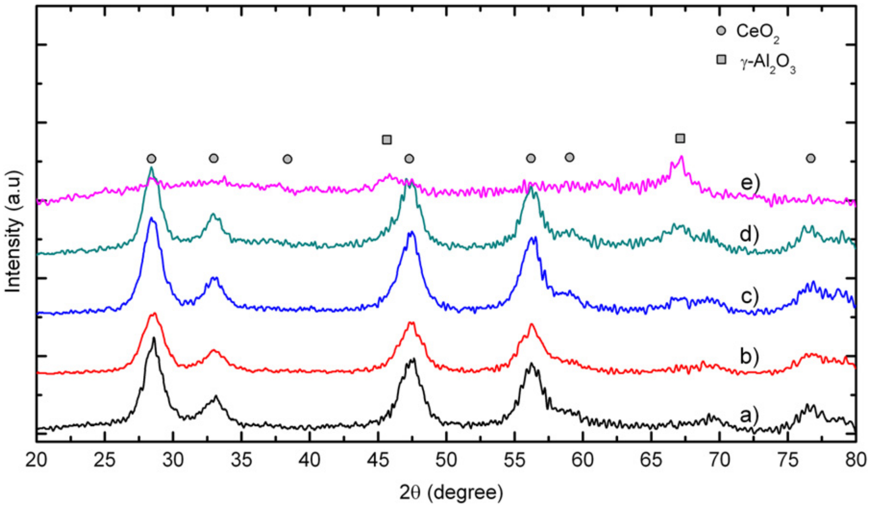

Fig. 3. X-ray diffraction diagrams of the CeO_2–Al_2O_3 powder samples with Ce/Al molar ratios of: (a) 5/5; (b) 4/6; (c) 3/7; (d) 2/8; and (e) 1/9 calcined at 850 °C for 2 h.

3.3. Effect of Ce/Al molar ratio on phase composition of CeO_2–Al_2O_3 nanocomposite

The prepared samples calcined at 850 °C with Ce/Al molar ratio of 1/9, 2/8, 3/7, 4/6, and 5/5 were subjected to study the effect of molar ratio on phase composition of CeO_2–Al_2O_3 nanocomposite. For the sample with Ce/Al molar ratio of 1/9, only γ-Al_2O_3 existed in XRD diagram due to low amount of cerium ions (Fig. 3). The γ-Al_2O_3 phase was also detected in the samples with Ce/Al molar ratio of 2/8 and 3/7. In contrast, for all measured samples with Ce/Al molar ratio $\geq 1/9$, the amount of CeO_2-based crystalline phase with the fluorite structure increased with Ce/Al molar ratio.

From FE-SEM images of prepared samples with Ce/Al molar ratio of 5/5 calcined at 500, 600, 750, 850, and 950 °C for 2 h, the bee's nest-like nanostructure was observed for samples calcined at 600, 750, 850 °C (Fig. 4). However, there is only the sample calcined at 850 °C that exhibits the bee's nest-like nanostructure (Fig. 4 (d)) together with the pore wall consisting of fully crystallized fluorite structure CeO_2-based nanocrystals (Fig. 3 (d)). This sample possesses an average grain size of 10 nm, an average pore size of 300 nm, and a specific surface area of 87.5 m^2/g. It is obvious that the applied combustion method using polyvinyl alcohol provides not only the bee's nest-like nanostructure but also the average grain size of about 10 nm or samples calcined at 500, 600, 750, 850 °C. This small average grain size can be comparable with that reported by previous works [8,9]. For sample calcined at 950 °C, the pore arrangement was nearly destroyed and the average grain size increased significantly to 25 nm (Fig. 4e).

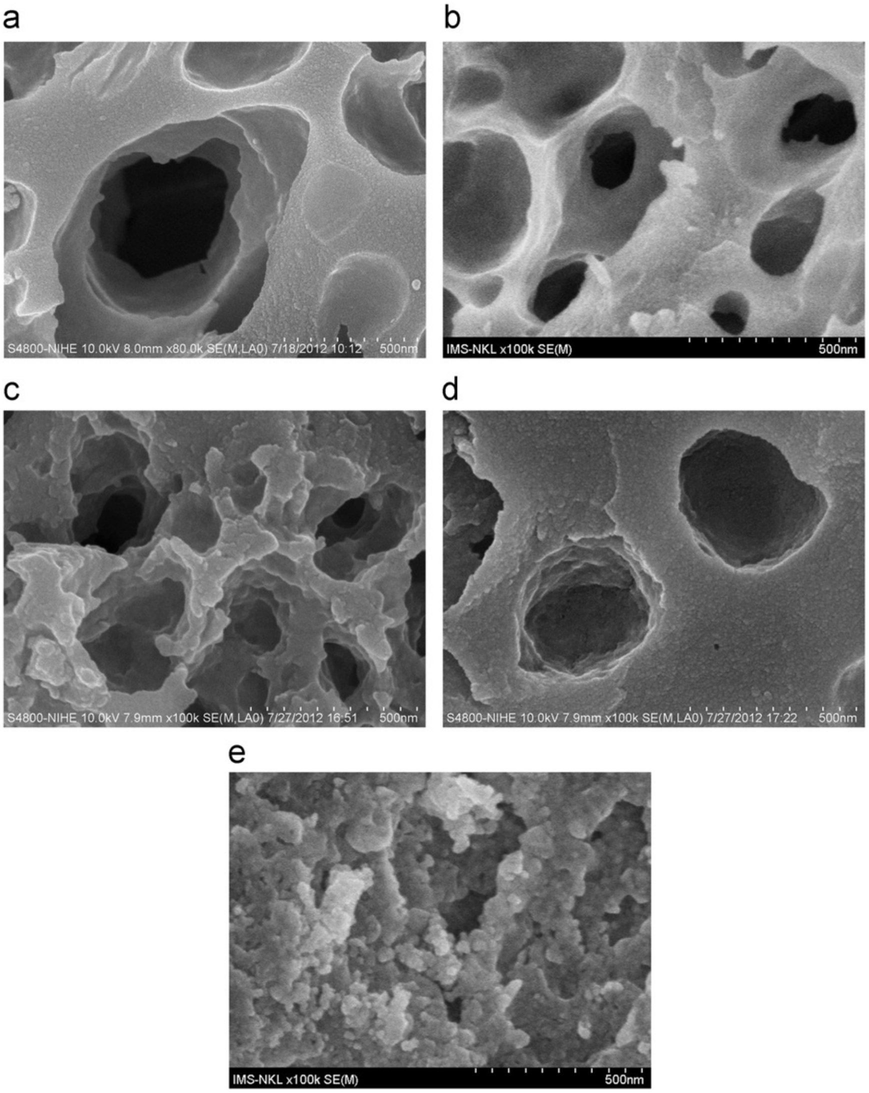

Fig. 4. FE-SEM images of the CeO_2–Al_2O_3 powder samples with Ce/Al molar ratio of 5/5 calcined at (a) 500 °C; (b) 600 °C; (c) 750 °C; (d) 850 °C; and (e) 950 °C for 2 h.

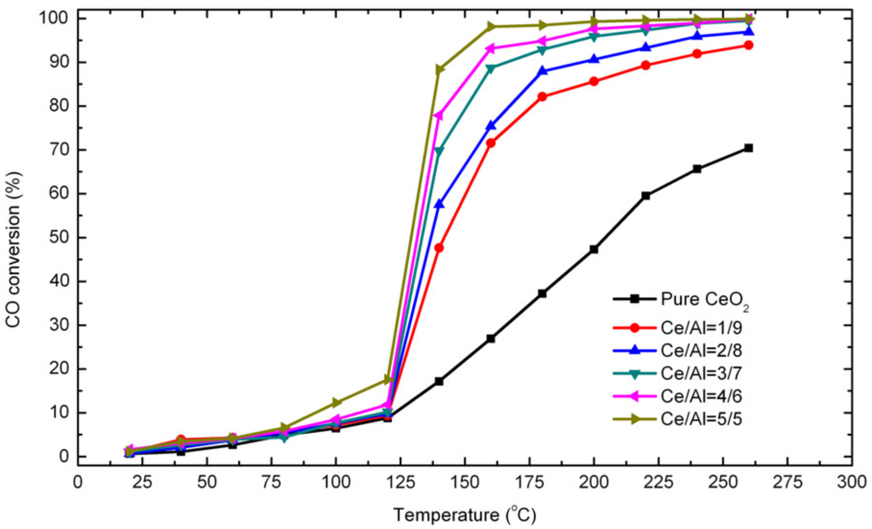

Fig. 5. CO conversion over (a) pure CeO_2 and CeO_2–Al_2O_3 nanocomposites with Ce/Al molar ratio of (b) 1/9; (c) 2/8; (d) 3/7; (d) 4/6; and (e) 5/5 calcined at 850 °C.

3.4. CO oxidation catalytic tests

A series of CeO_2–Al_2O_3 nanocomposites with different Ce/Al molar ratios was subjected to CO oxidation tests. In order to investigate the catalytic activity of the bee's nest-like nanostructure, all samples were calcined in air at 850 °C for 2 h. It is observed that their CO conversion is higher than the one of pure CeO_2 (Fig. 5). In addition, the catalytic activity at 160 °C increased from 70.7% to 99.9% with Ce/Al molar ratio in the range of 1/9–5/5. This could be explained on the basis that both Ce^{3+} and Ce^{4+} species coexisted in above samples and Ce^{4+} cations, with their high oxidation state, served as the catalytic active sites. Consequently, the increase in cerium ion content in CeO_2–Al_2O_3 mixed oxides can promote the catalytic activity to a certain extent. In our work, the highest CO conversion efficiency was found for CeO_2–Al_2O_3 catalyst with $(Ce^{3+}+Ce^{4+})/Al^{3+}$ molar ratio of 5/5. With this molar ratio, the CO oxidation conversion of 99.7% was achieved at 160 °C. This conversion temperature is significantly lower than that reported for CeO_2–Al_2O_3 system prepared by combustion method using a fuel mixture containing glycine, urea, hexamine and oxalyl dihydrazide [9]. This might originate from the bee's nest-like nanostructure that facilitates the CO conversion at low temperature.

4. Conclusion

Nanostructured CeO_2–Al_2O_3 mixed oxide powders with Ce/Al molar ratio ranging from 1/9 to 5/5 were synthesized by combustion method using PVA as polymeric agent. The effects of molar ratios of starting materials, pH value of precursor solution, and calcination temperature were investigated. The bee's nest-like nanostructure with the pore wall consisting of CeO_2–Al_2O_3 mixed oxide nanocrystals was observed for samples calcined at temperatures in the range of 600–850 °C. For the optimized sample with this nanostructure, an average grain size of 10 nm, an average pore size of 300 nm, a specific surface area of 87.5 m^2/g, and a CO conversion efficiency as high as 99.7% at 160 °C, was obtained. CO conversion efficiency was found to be significantly affected by Ce/Al molar ratio and reached the maximum value with Ce/Al molar ratio = 5/5.

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