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Oxygen activation on Cu/Mn–Ce mixed oxides and the role in diesel soot oxidation

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ABSTRACT

The Cu- and Mn-doped ceria were prepared using the citric acid sol–gel method. The structural and redox properties of the mixed oxides were investigated by means of XRD, BET, O_2-TPD, CO-TPR and CO reduction under isothermal conditions. TPO tests were performed to evaluate the catalytic activity for soot oxidation. The results showed that Mn^{x+} cations entered into the ceria lattice to form solid solutions, which increased the amount of oxygen vacancies and promoted surface oxygen chemisorption. Cu_xO clusters were more likely to be dispersed on the surface of ceria particles. The interaction between copper and cerium greatly enhanced the rapid release of lattice oxygen of the oxides in the reducing atmosphere. These two mixed oxides showed improved catalytic activities and selectivities to CO_2 for soot oxidation compared with pure ceria. The order of activities under different contact conditions was believed to be related to active oxygen species released by the catalysts.

1. Introduction

CeO_2 has been widely used in automobile exhaust three-way catalysts (TWCs) due to its outstanding oxygen storage capacity (OSC) [1–3]. Ceria-based catalysts recently gain more attention on the utilization for diesel soot oxidation [4–7]. It is presented by Bueno-López et al. [4] through the ^{18}O isotope exchange experiment that the active oxygen on the surface of CeO_2 is a determining factor for soot catalytic oxidation. The temperature of oxygen activation can be lowered ca. 100 °C by the CeO_2 catalyst and thus the combustion rate of soot is increased.

Instead of using ceria alone as the catalyst for diesel soot oxidation, more researchers focus on modification of CeO_2 with different ions to increase the activity and thermal stability. The substitution of Ce^{4+} by Zr^{4+} or La^{3+} favors the creation of structural defects, accelerates oxygen diffusion and induces more surface active oxygen species which further promote the soot oxidation [8–11]. Doping with other rare earth elements (La, Pr, Sm, Y) also improves the activity and stability of ceria due to the increase of meso/macro-pore volume and stabilization of surface area after aging treatment [6]. Compared with rare earth metals, transition metals usually exhibit several oxidation states and better redox properties. Good redox properties and strong interaction between transition metals and ceria make the transition metal–Ce mixed oxides as candidate catalysts for diesel soot oxidation. Recent reports have shown the activity of ceria in complete oxidation reactions can be largely enhanced by transition metals in general. Tikhomirov et al. [12] have found that the incorporation of Mn into the ceria lattice favors the soot oxidation activity of the catalyst. The onset temperature of MnO_x–CeO_2 mixed oxides for the NO-free oxidation lies around 400 °C under loose contact conditions, while that for NO assisted oxidation starts at around 100 °C lower temperature. Our previous studies have also shown that copper modification increases the activity and selectivity of CeO_2. Cu_xO–CeO_2 mixed oxides exhibit the maximum oxidation rate at 496 °C under loose contact conditions for the NO-free oxidation and at 419 °C for NO-assisted oxidation. And this advantage is maintained after aging at 800 °C for 20 h [13,14].

Structural and redox properties of catalysts are always important factors for catalytic reactions. In this paper, the Cu- and Mn-doped CeO_2, which have different morphological states of doping elements and oxygen activation performances, were synthesized by the sol–gel method, and the influence of these structural and redox properties on soot oxidation activities were investigated. As demonstrated by lots of results, the activity of soot catalytic oxidation is mostly influent by the contact mode between soot and catalysts [15,16]. Here, the effect of active oxygen species on the activity of the catalysts under different contact conditions was especially discussed.

2. Experimental

2.1. Catalyst preparation

All the samples were prepared by the sol–gel method. The nitrates $Ce(NO_3)_3{\cdot}6H_2O$ (99.0 wt.%, Beijing Yili) and $Cu(NO_3)_2{\cdot}3H_2O$

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(99.5 wt.%, Yili) were mixed in deionized water according to the molar ratio of Cu:Ce = 1:9. The citric acid was used as the complexing agent with a 1.3:1 ratio of the acid to metal ions including Ce^{3+} and Cu^{2+}. Appropriate polyglycol was followed with the weight of 10% citric acid added. The blended solution was sufficiently mixed in a magnetic stirrer and heated at 80 °C till transparent gel was formed. The resulting gel was dried at 110 °C overnight. The received powders were submitted to decomposition at 300 °C for 1 h and calcination at 500 °C for 3 h under static air in a muffle. The powders were cooled to room temperature (RT) in the furnace to obtain the Cu–Ce mixed oxides. The Mn–Ce mixed oxides (the molar ratio of Mn:Ce = 1:9) and ceria were prepared by the same method with $Mn(NO_3)_2$ (50% water solution, Yili) and $Ce(NO_3)_3{\cdot}6H_2O$ as the precursors.

2.2. Catalyst characterization

The powder X-ray diffraction (XRD) experiments were performed on a Japan Science D/max-RB diffractometer employing Cu Kα radiation (λ = 1.5418 Å). The X-ray tube was operated at 40 kV and 120 mA. The X-ray powder diffractogram was recorded at 0.02° intervals in the range of $20^\circ \leq 2\theta \leq 80^\circ$ with a scanning velocity of 6°/min.

The specific surface areas of the samples were measured using the N_2 adsorption isotherm at −196 °C by the one-point Brunauer–Emmett–Teller (BET) method using an automatic surface analyzer (Quantachrome NOVA 4000). The samples were degassed in flowing N_2 at 200 °C for 2 h.

Temperature programmed desorption (TPD) of O_2 was performed in a fixed-bed reactor with the effluent gases monitored using a quadrupole mass spectrometer (MS) (Omnistar 200). Prior to O_2-TPD experiment, 100 mg sample was treated with O_2 with a total flow rate of 50 ml/min at 500 °C for 30 min, then cooled down to RT under the same atmosphere, and subsequently flushed by 50 ml/min He for 30 min to remove the physisorbed molecules. Finally, the reactor temperature was raised up to 800 °C at a constant heating rate of 10 °C/min. O_2 desorbed during the experiment was simultaneously monitored by MS.

CO temperature programmed reduction (TPR) was performed in a fixed-bed reactor with the effluent gases monitored using a quadrupole MS (Omnistar 200). Prior to CO-TPR experiment, 50 mg sample was treated with O_2 (2 vol%)/He with a total flow rate of 50 ml/min at 500 °C for 30 min, then cooled down to RT in the same atmosphere. It was subsequently flushed by 50 ml/min He for 30 min to remove the physisorbed molecules. Finally, the reactor temperature was raised up to 600 °C at a heating rate of 10 °C/min in CO (4 vol%)/He with a flow rate of 75 ml/min. CO_2 and CO production during the experiment was simultaneously monitored by MS.

CO reduction test was performed in a flow reactor system under isothermal conditions (300, 350, 400, 450 and 500 °C). Typically, 25 mg powders were loaded into a 1.0-cm i.d. quartz tube reactor. The sample was first heated in O_2 for at least 20 min at the desired temperature, purged in He for 10 min to remove oxygen from the system and then exposed constantly to 4% CO/He. A total gas flow rate of 300 ml/min was employed. Instantaneous CO_2 concentration in the outlet gas in the first 50 s was detected by an on-line quadrupole mass spectrometer (Omnistar 200).

2.3. Activity measurement

Printex-U (Degussa) was used a model soot. Its particle size was 25 nm and specific surface was 100 m^2/g. The catalytic activity was evaluated by a temperature programmed oxidation (TPO) reaction apparatus. Before the reaction, the soot–catalyst mixture, in a 1/10 weight ratio, were milled in an agate mortar for "tight contact" or mixed carefully by a spatula for "loose contact". 110 mg catalyst–soot mixture was placed in the tubular quartz reactor (i.d. = 10 mm), and the oxidation test was carried out in the temperature range from RT to 700 °C at a heating rate of 10 °C/min. The inlet gas mixture was 10% O_2 in nitrogen with a flow rate of 500 ml/min. The concentrations of CO_2 and CO in the outlet gases were determined on-line by a five-component analyzer FGA4015 with infrared sensor.

Table 1
The lattice constant and specific surface area of the samples

Samples	Lattice constant (Å)	Crystallite size (Å)	BET surface area (m^2/g)
CeO_2	5.410	78	61.8
Cu–Ce	5.411	59	68.4
Mn–Ce	5.406	47	72.5

3. Results and discussion

3.1. XRD and BET

The XRD patterns of the samples are shown in Fig. 1. All the samples present the characteristic peaks of a fluorite-like cubic phase. No diffraction peaks of copper or manganese oxides are found in the diffraction patterns of the Cu- and Mn-doped samples. Table 1 summarizes the lattice constants of the samples. It is found that the doping of Mn induces the contraction of the cell volume of the ceria lattice, while the lattice constant of the Cu–Ce mixed oxides keeps unchanged. The ionic radii of Mn^{4+}, Mn^{3+}, Cu^{2+} and Cu^{+} are 0.56, 0.62, 0.73 and 0.77 Å, respectively, which are all smaller than that of Ce^{4+} (0.97 Å). The decrease in lattice constant of the Mn-doped ceria indicates the formation of MnO_x–CeO_2 solid solutions which have been widely verified in the literature [12,17,18]. On the other hand, the precise state of copper oxide in CuO_x–CeO_2 catalyst is still in debate [19]. Although substitution of Ce^{4+} by Cu^{+} at the interface of Cu–Ce was proposed [20], according to the similarity of lattice constants of Cu–Ce and CeO_2 in this paper, the copper oxides are more probably in the form of well dispersion or amorphous state in strong contact with the surface of ceria [21].

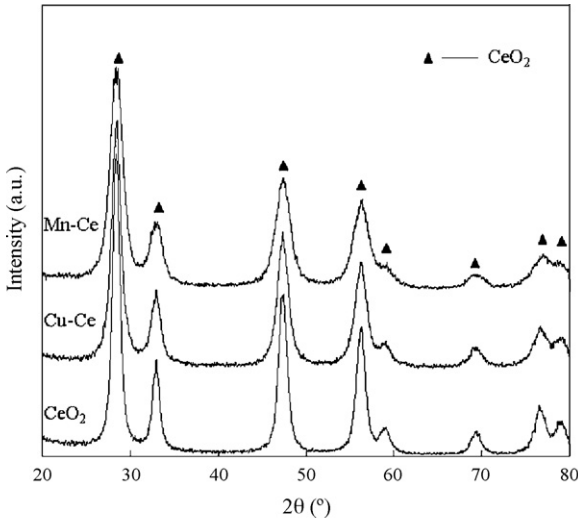

Fig. 1. XRD patterns of the samples.