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Comparative study of nanometric Co-, Mn- and Fe-based perovskite-type complex oxide catalysts for the simultaneous elimination of soot and NO_x from diesel engine exhaust

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ABSTRACT

In this feature article, the effects of the intrinsic factors including structure, nanometric size effect, nature of B-site ions, A-site ion substitution, redox properties of three systems of nanometric $La_{1-x}M_xCoO_3$, $La_{1-x}M_xMnO_3$, $La_{1-x}K_xFeO_3$ perovskite-type oxide catalysts, and the external factors containing contacting model of catalyst and soot, the content of O_2 or NO, the ratio of catalyst and the gas flow rate on their catalytic performances for the simultaneous elimination of soot particles and NO were systematically investigated. The catalysts were characterized by means of XRD, FT-IR, SEM, XPS and H_2-TPR, and the catalytic performances for the simultaneous removal of nitrogen oxides and diesel soot were evaluated by temperature-programmed oxidation reactions. All the prepared samples had the perovskite structure, possessed nano-sizes and gave high activities for the simultaneous elimination of soot particles and NO. On the one hand, the number of surface atoms is much greater than the normal bulk catalysts and the size of nanoparticle is small. These characters are favorable for the adsorption and activation of reactant molecules including the O_2 or NO, even soot particle. On the other hand, the surface atoms of small nanoparticles formed on the surface of the nanometric perovskite oxide samples possess high free energy, which improves the mobility of catalyst, and thus it favors the contact between the catalysts and soot. Besides the intrinsic factors, the external factors of reaction conditions containing contact model of soot and catalyst, the content of O_2 or NO, the ratio of catalyst to soot and gas flow rate also play important roles in affecting the catalytic performances for the simultaneous removal of NO and soot. The reaction mechanisms for soot oxidation and the simultaneous removal of soot particles and NO over $La_{1-x}K_xMnO_3$ were also briefly discussed.

1. Introduction

Diesel engines have attracted much attention owing to their low fuel consumption, low maintenance cost, and low CO_2 emission. Their development, however, is limited by the fact that their exhaust gases still seriously pollute atmosphere and cause human health risks [1–3]. Diesel engine exhaust gases mainly contain the air pollutants like nitrogen oxides (NO_x), soot particulate, hydrocarbons (HC) and carbon monoxide (CO). The latter two components can be simply removed by the oxidation over platinum-containing catalysts. In contrast to that, it is very difficult to remove NO_x from the oxygen-rich exhaust gases of diesel engines and it is also more problematic to oxidize the soot to CO_2 due to the low temperature of the exhaust gases emitted from the diesel engines. Therefore, the development of the catalytic purifying technology for the simultaneous elimination of soot and NO_x from diesel engine exhaust should have significant importance for the environmental protection.

Yoshida et al. [4] firstly proposed a catalytic process for the simultaneous elimination of NO_x and soot under oxidizing conditions, and the possibility of reaction among the three components of soot–NO–O_2 was explored. Results showed that the oxidation of soot and the reduction of NO_x can be carried out within the same temperature range, and NO_x can decrease the activation energy for the soot combustion. Then the metal composite oxides for the simultaneous removal of soot and NO_x from diesel engine exhaust have attracted much interest. Shangguan et al. have done many explorative and pioneering works using perovskite and spinel oxides, and they compared a mixed oxide with a spinel-type oxide in terms of their activities for the simultaneous eliminating of nitrogen oxides and soot [5,6]. When soot and catalyst were tight-contact, the spinel-type oxide ($CuFe_2O_4$), compared with the simple mixture of CuO and Fe_2O_3, leads to a similar ignition temperature of soot, while resulting in a higher selectivity for the reduction of

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NO_x. With respect to the spinel-type $CuFe_2O_4$ catalysts where some of A-site cations were partially replaced by alkali metal ions except Li, their activities were enhanced to different extent, with excellent effect achieved by K replacement. The catalyst $Cu_{0.95}K_{0.05}Fe_2O_4$ serves as an ideal material for eliminating soot–NO, with a high selectivity for producing N_2 and a low ignition temperature of soot. It is also reported that KCo/C catalyst significantly improves the reduction rate of NO with soot and the combustion rate of soot, and that the catalyst Pt/Al_2O_3 exhibits catalytic activity in eliminating both NO_x and soot in the presence of oxygen [7]. For example, NO and soot can be eliminated entirely in the presence of 1–8% of O_2 at a temperature higher than 400 °C. Nejar et al. [8] reported that the catalysts loaded bi-metals on activated carbon efficiently decreased the combustion temperature of soot in a soot–NO–O_2 reaction system. More researches [9–12] were reported that the catalysts in which K and Ba were loaded over La_2O_3 and CeO_2 display good performances in trapping nitrogen oxides and oxidizing soot, and thus they were capable of simultaneously eliminating NO_x and soot.

Most of perovskite-type oxides, which have the size of 100–600 nm, meet the requirements for soot particle trapper and soot oxidation, and thus many kinds of bulk perovskite-type oxides have been prepared and studied in order to improve the performances for soot oxidation or trapping soot. The redox property of a perovskite-type oxide is closely related to the nature of B-site or A-site cations, the cations and their amount for partly replacing A-site or B-site ions. Some researchers [13–16] have proved that the perovskite-type oxide catalysts exhibit much better catalytic performances for the title reaction than that of simple oxide. Recently, we also reported that nanometric Mn- and Co-based perovskite type complex oxides are highly active catalysts for the diesel soot oxidation and/or for the simultaneous removal of soot and NO_x [17–19]. And the perovskite-like complex oxides, which are in a layered configuration, are also one kind of good catalysts for treating diesel engine exhaust [20,21]. In this feature article, the structures, physico-chemical properties and catalytic performances of Mn-, Co- and Fe-based perovskite-type complex oxide catalysts for the simultaneous removal of diesel soot and NO_x were comparatively and systematically studied. The effects of the intrinsic factors including nanometric size effect, nature of B-site ions, A-site ion substitution, redox properties of perovskite-type composite oxide catalysts, and the external factors containing contact model of catalyst and soot, the content of O_2 and NO, the ratio of catalyst to soot, and the gas flow rate on their catalytic performances for the simultaneous elimination of soot particles and NO were also investigated. Some of our recent works were summarized and some important conclusions were reached.

2. Experimental

2.1. Preparation of catalyst

A series of perovskite-type oxide catalysts were prepared by the complex combustion method [17–19].

2.2. Characterization of catalyst

The formed catalyst samples were characterized by using a SHIMADZU XRD-6000 X-ray powder diffraction, in order to confirm whether the catalyst possessed the perovskite-type structure. The test conditions were as follows: Cu Kα radiation, tube pressure 40 kV, tube current 30 mA, scanning angle from 5° to 80°, and scanning rate 4°/min. The morphologies of the catalysts were observed through a HITACHI S-4800 scanning electron microscope. The Fourier transform infrared spectrometer (FTIR) characterization was carried out by using a FTS-3000 made by the DIGILAB Inc., USA. The sample was mixed with KBr at a mass ratio of 1:100, and the resulting mixture was pressed into a wafer. Scanning range is from 6000 cm^{-1} to 400 cm^{-1}, and scanning resolution 2 cm^{-1}. The catalyst samples were analyzed by using an XSAM-800 multi-functional X-ray electron spectrometer from the KRATOS Inc., U.K., to obtain their X-ray photoelectron spectra (XPS). The excitation source was Mg Kα radiation (1254 eV), and the test mode was FAT (fixed analyzer transmission). The pressure in the vacuum chamber was $<10^{-7}$ mbar during the test. The C 1s element from the vacuum pump in the vacuum chamber was used for calibration. The C 1s binding energy determined was 284.6 eV.

A temperature-programmed reduction (TPR) of H_2 was carried out on a TP-5000 multi-purpose adsorption apparatus from the Tianjin Xianquan Instrument Inc., China [20,21].

2.3. Evaluation of catalytic activity

The catalytic performances of the prepared catalysts for the simultaneous elimination of soot particles and NO_x from diesel engine exhaust were evaluated with a temperature-programmed oxidation reaction (TPO) on a normal-pressure fixed-bed tubular quartz reactor ($\phi = 8$ mm). The soot in diesel engine exhaust was simulated with Printex U, commercial carbon black, produced by the DEGUSSA Inc. The catalyst and the soot particles were mixed with a sampling spoon so that they were in the loose-contact, which was similar to the actual circumstances. All the mixtures were in the loose-contact unless indicated otherwise. The mass ratio of the catalyst to the soot was 5:1, and the amount of the sample was 180 mg. The composition of the reaction gas was NO 2000 ppm, O_2 5 vol%, and the balance with He. Gas flow rate was 50 ml/min, and the heating rate was 2 °C/min. The reaction exhaust was measured online by using an SP-3420 gas chromatograph from the Beijing Analytical Instrument Factory, China. CO and CO_2 were separated from the reaction exhaust by using a Porapak N chromatographic column and detected by using the FID with a methanizer at 380 °C. O_2, N_2, CO and NO were separated by using a 5A molecular sieve chromatographic column and then detected by using the TCD [17–21].

The capability of the catalyst for the oxidation of soot was represented by the combustion temperatures of the soot, i.e. the ignition temperature T_{ig}, the temperature at the maximum combustion rate T_m, and the temperature at the end of combustion T_f. The capability of the catalyst for the reduction of NO_x by soot was evaluated by the maximal conversion of NO to N_2, X_{NO}%.

3. Results

3.1. Catalyst characterization results

3.1.1. XRD characterization results

Figs. 1–3 depict the XRD patterns of the Co-, Mn- and Fe-based catalyst samples, respectively. All the samples prepared by the complex combustion method had the perovskite structure. From Fig. 1, it can be seen that no other phases were detected in the $La_{1-x}M_xCoO_3$ catalysts, in which some La^{3+} were partly replaced by alkali metal ions (except Li) when x is 0.1. When x is 0.25, the characteristic peaks of the Co_3O_4 phase appeared at 2θ about 36.9° and 65.2°. With the increasing of the replacing K^+ ion amount, the peak intensity of Co_3O_4 was slightly enhanced, which indicates the increase in Co_3O_4 content in the sample. In order to systemically examine the effect of alkali metal dopants on the structures and the properties of perovskite-type oxides, Li^+ was also selected as one of the ions for replacing A-site cations in the samples. When the replacing ion was Li^+, a peak at about 18.9°, which may be attributable to Li_2O, was detected. Although tolerance factors (0.8864 and 0.8641) of the samples partly replaced by Li^+ can