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A highly efficient and porous catalyst for simultaneous removal of NOx and diesel soot

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Abstract

A highly efficient and porous catalyst ($La_{0.8}K_{0.2}Cu_{0.05}Mn_{0.95}O_3$) for simultaneous removal of nitrogen oxides (NOx) and diesel soot was synthesized and the sample was characterized by XRD, BET, SEM–EDS, XRF, and XPS. The results indicate that this catalyst is perovskite and it possesses the very good characteristics for multiphase catalytic reactions. The catalytic properties were appraised under simulated diesel engine exhaust by temperature programmed reaction (TPR). TPR results indicate that this catalyst is a promising candidate for simultaneous removal of NOx and diesel soot. The maximum NO conversion into N_2 and the ignition temperature of soot are 54.8% and 260 °C, respectively. Comparing with those in previous reports, the comprehensive performance of this catalyst is greatly improved by partial substitution of La with K and Mn with Cu at the same time.

Keywords: Simultaneous removal; Nitrogen oxides; Diesel soot; Perovskite-type oxides; Catalysts

1. Introduction

Spark-ignition (gasoline) and compression–ignition (diesel) engines are major sources of urban air pollution. Because of the oxygen abundance in compression–ignition combustion, the CO and hydrocarbons (HC) emissions of diesel engines are insignificant. NOx and soot particulate matters (PM) are the main pollutants from diesel engine. Recently the regulations on diesel engine emissions become more and more stringent, especially with respect to NOx and PM. To solve these problems, both the internal combustion techniques and the exhaust after treatment are needed. As a promising process, the simultaneously catalytic removal of NOx and soot was proposed [1].

Commonly used catalysts in diesel engine exhaust after treatment are precious metals [2,3], single metal oxides [4–7], mixed metal oxides [8–16], and zeolites [17]. Results prove that these catalysts can be used for the simultaneous removal of NOx and soot and that manganese based perovskites have received great attention due to their high catalytic activity for this reaction [10,11]. To meet the request of real diesel engine exhaust after treatment, the performance of catalysts still need to be improved. Furthermore, most of the previous studies adopt tight contact between catalysts and soot. But in fact, the contact between catalysts and soot is loose. Teraoka pointed out that the optimal substitution level of K in $La_{1-x}K_xMnO_3$ is $0.2 \sim 0.25$ [10] for this reaction. The purpose of this paper is to develop a new active catalyst and study its performance under loose contact condition.

2. Experimental

2.1. Catalyst preparation

The precursors were weighed according to the stoichiometric ratio of desired catalyst and then dissolved into

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non-ion water with a beaker. The starting materials used in this study were salts of different metals, including nitrates of La and Mn, acetate of Cu, and citrate of K. Aqueous solution was heated and stirred to let the water evaporate. The residual solid composition was dried at 110 °C for 2 h, followed by decomposition at 500 °C for 2 h in air and calcination at 750 °C for 8 h in air. After grinding, the catalyst powder was obtained.

2.2. Catalyst characterization

X-ray diffraction (XRD, BRUKER-AXS) with CuKα2*θ* was used to detect the crystal structure of catalysts. BET surface area (multipoint analysis) and porosity parameters were measured with nitrogen as adsorbate at −196 °C using NOVA-1000 (Quantachrome). Scanning electron microscope (SEM) and associated energy-dispersive X-ray spectroscopy (EDS) (JEOL, JSM-5600), along with X-ray diffraction (XRF, Rigaku RIX 2100), were used to observe the microstructures of catalysts and measure the composition of catalysts. X-ray photoelectron spectra (XPS) spectra was obtained by using ESCA-3300KM spectrometer which was equipped with a concentric hemispherical analyzer. Mg Kα (1253.6 eV) X-ray source was used for excitation and the binding energy (BE) was calibrated with respect to the C1s value (284.5 eV) of a contaminated carbon.

2.3. Activity measurement

A kind of carbon black was used to substitute the real diesel soot, with 120.6 m^2/g specific surface area, less than 0.4% heating loss and less than 0.3% ash content. The simultaneous removal reaction between NO*x* and soot was carried out by temperature programmed reaction (TPR). Catalysts and soot are blended using agate mortar and then placed into the center of a quartz reactor. The weight ratio of catalysts to soot is 20:1. The simulated exhaust consists of 0.25% NO, 5% O_2 with He as the base gas and the total flow rate is 80 ml/min. After reaction, the gas is automatically sampled and analyzed by a TCD gas chromatograph (modified Shimadzu GC-14B), which is equipped with column Porapak Q for separating CO_2 and N_2O, and column molecular sieve 5A for O_2, N_2, NO, and CO. During the test in this study, there was not detectable N_2O and CO.

The catalytic performance for catalysts is evaluated by two parameters obtained from the TPR results. One of them is the ignition temperature (T_{ig}) of soot, which can be estimated by extrapolating the steeply ascending portion of the carbon dioxide formation curve to zero carbon dioxide concentration, almost the same as that used in literatures [9,10]. The other is the maximum NO conversion into N_2, which can be calculated by $2[N_2]_o/[NO]_i$, where $[N_2]_o$ and $[NO]_i$ are concentrations of N_2 in the outlet gas and NO in the inlet gas, respectively.

3. Results and discussion

3.1. XRD

X-ray diffraction patterns of catalysts is shown in Fig. 1. It reveals that the crystal structure of these catalysts is perovskite. After adding some K and Cu, the crystal becomes more perfect.

3.2. BET

Fig. 2 is the nitrogen sorption isotherms of catalysts. They can be classified as type IV according to the IUPAC

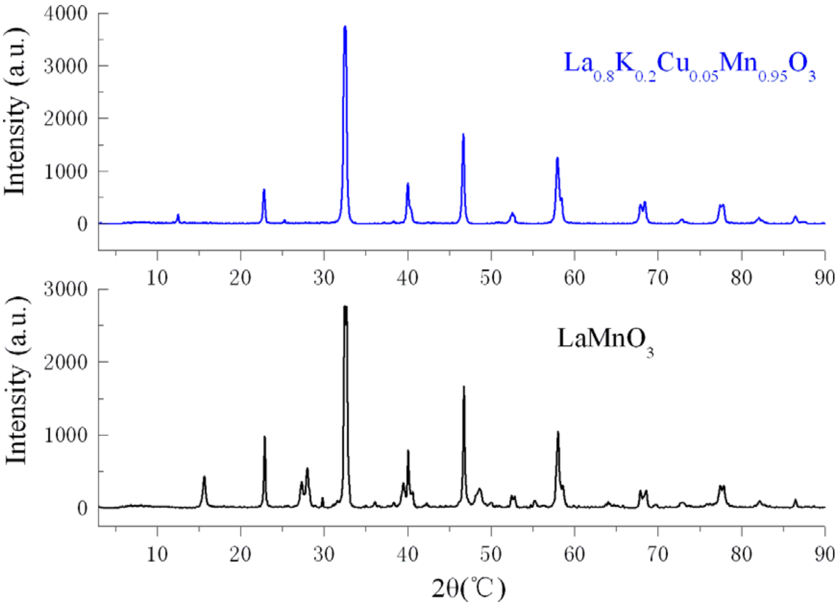

Fig. 1. X-ray diffraction patterns of catalyst.