Short communication

Enhancement in oxidative property on amorphous rare earth doped Mn catalysts

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1. Introduction

Nitrogen oxides (NOx: NO, NO2, N2O), mainly emitted from the combustion of fossil fuels, can easily induce many environmental problems [1]. The extensively studied and widely implemented method of NO elimination is selective catalytic reduction with ammonia (NH3-SCR) [2–4] through the reaction: 2NH3 + NO + NO2 → N2 + 3H2O. The rate of this reaction is maximized (fast SCR) when the NO: NO2 ratio approaches unity. An alternative route for removing NOx is oxidizing NO into NO2, which is then captured by alkali liquor as useful resources. Efficiency on amorphous rare earth doped Mn catalysts

At low temperatures and show superior catalytic activity towards NO oxidation [1,5,7]. The composite oxides of Mn–Ce have drawn much attention due to their environmentally-friendly properties and high activity for catalytic oxidation of VOCs [8] and CO [9] or NH3-SCR [10]. For NO oxidation, Qi et al. [11] reported that the manganese–cerium oxides showed better performance than MnOx and CeO2, and low crystallinity should contribute to the high catalytic performance. However, in the work the catalysts were prepared at a higher temperature (550 °C), resulting in the crystalline phase of the catalysts. The existing methods generally result in poorly dispersed manganese oxide, large crystals, and reduced surface areas, while the effect of amorphous forms on catalyst properties has not been reported yet. Moreover, except cerium, other rare earth metals have not been fully studied.

Thus, this study aims to prepare amorphous catalysts through the interaction between Mn and rare earth metal by preventing the formation of crystal structure and diminishing the particle size. The roles of rare earth metal-doping in the oxidation mechanism of NO over the catalysts were fully examined.

2. Experiment

2.1. Material preparation

Mn-based catalysts were prepared mainly based on the following procedures. KMnO4-rare earth solution was prepared by dissolving KMnO4 and one nitrate of rare earth element (Ce(NO3)3·6H2O, La(NO3)3·6H2O, or Pr(NO3)3·6H2O) into deionized water. The above solution was gradually added to the Mn(CH3COO)2 solution with thorough stirring. The following reaction occurred:

3Mn(CH3COO)2 + 2KMnO4 + 2H2O = 5MnO2 + 2CH3COOK + 4CH3COOH

After being filtered and dried, the products were calcined at 400 °C. The theoretical composition of the final product can be written in the format of Mn0.85RE0.15O2 (RE = rare earth). The three catalysts doping with rare earth element were labeled as Mn–Ce–Ox, Mn–La–Ox, and Mn–Pr–Ox, and the catalyst without rare earth element was labeled as Mn–Ox. The detailed information is in the Supplementary material.

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2.2. Characterization

$N_2$ adsorption/desorption measurements were carried out at $-196\,^\circ C$ with a surface analyzer (Micrometrics, ASAP 2020). SEM images were acquired with a Hitachi S-4800 electronic microscope working at 20.0 kV. XRD pattern was collected on a Bruker D8 Advance diffractometer using Cu Kα radiation (wavelength $\lambda = 1.5406\,\text{Å}$) at the scanning rate of 4°/min. X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo ESCALAB 250XI spectrometer equipped with an Al Kα X-ray source ($h\nu = 1486.6\,\text{eV}$). The binding energies were corrected by the C 1s peak of carbon at 284.9 eV. The H$_2$-temperature-programmed reduction (H$_2$-TPR) was tested on a Micromeritics Autochem 2920 instrument in a quartz reactor with a TCD as detector.

2.3. Catalytic test

NO oxidation experiments were performed in a fixed bed reactor (Fig. S1) using a flue gas detector (VARIO PLUS, MRU, Germany) for NO$_x$ concentration analyzer. Prior to reaction, 1.0 g of the catalyst was pretreated at 400 °C under nitrogen atmosphere for 1 h. Then, a flowing gas containing 385 ppm of NO, 6% O$_2$, and balance N$_2$ were mixed in by pass. After steady state was achieved, NO oxidation experiment was performed by exposing the catalyst to the flowing mixed gas. NO oxidation capacity was recorded at different temperatures when steady state was achieved. The experiments were operated at a gas hourly space velocity (GHSV) of 51,000 h$^{-1}$. To test the role of O$_2$ in the oxidation process, the mixed gas without O$_2$ was also charged with the same operation conditions. The NO conversion was calculated according to the following formula:

$$\text{NO conversion} = \frac{[\text{NO}]_{\text{inlet}} - [\text{NO}]_{\text{effluent}}}{[\text{NO}]_{\text{inlet}}} \times 100\%$$

where $[\text{NO}]_{\text{inlet}}$ and $[\text{NO}]_{\text{effluent}}$ were the inlet and effluent concentrations of NO (ppm).

3. Results and discussion

3.1. Structure properties and BET results

Fig. 1a reveals that the Mn–O$_x$ sample is composed of slender crystals approximately 1 nm in size, while the other three catalysts present amorphous fine particles. The XRD patterns (Fig. 1b) of Mn–O$_x$ confirmed the presence of MnO$_2$ crystallization. The characteristic peaks corresponding to cerium oxide, lanthanum oxide, praseodymium oxide or MnO$_2$ were not distinct, indicating that the metal oxides were amorphous, highly dispersed and homogeneous. The obvious hysteresis loop for the isotherms (Type IV) at high relative pressure (Fig. 1c), indicated that the four samples were mesoporous materials, which was consistent with their pore size distribution (Fig. 1d). The average pore sizes ($D_p$) of the four catalysts were in the range of 13.0–14.4 nm (Table S1). Compared with rare earth metal doped catalysts,
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