



Short communication

Enhancement in oxidative property on amorphous rare earth doped Mn catalysts



Yuanyuan Sun, Shifa Zhong, Hongchuan Xin*, Feng Zhang, Lei Chen, Xuebing Li*

Key Laboratory of Biofuels, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China

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ABSTRACT

Rare earth metal (Ce, La, or Pr) doped Mn-based catalysts were prepared to obtain amorphous Mn–Ce–O_x, Mn–La–O_x and Mn–Pr–O_x. Promotional effects of NO conversion at low temperature were observed after rare earth metal doping. The Mn–Ce–O_x catalyst had the best oxidation performance and the maximum NO oxidation conversion was 94.0% at the reaction temperature of 239 °C. Among the reported Mn-based catalysts for NO oxidation, the Mn–Ce–O_x catalyst showed superior low-temperature activity. The SEM, XRD, BET and XPS analyses further confirmed that the amorphous structure of the catalyst contributed a lot to the enhancement of activity.

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1. Introduction

Nitrogen oxides (NO_x: 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 → 2 N₂ + 3H₂O. The rate of this reaction is maximized (fast SCR) when the NO:NO₂ ratio approaches unity. An alternative route for removing NO_x is oxidizing NO into NO₂, which is then captured by alkali liquor as useful resources-nitrate, also an NO₂:NO ratio of 1:1 is the most effective. However, lean burn exhaust gas typically contains less than 10% NO₂. Hence, an effective catalyst is required to convert NO to NO₂ in order to improve the after-treatment efficiency.

Platinum-based catalysts have been investigated for NO oxidation [5–6], but the high cost limited their commercial application. Manganese-based materials are able to operate environmentally soundly 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 MnO_x 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,

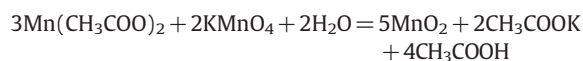
and reduced surface areas, while the effect of amorphous forms on catalytic properties has not been reported yet. Moreover, except cerium, other rare earth metals have not been fully studied.

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:



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 Mn_{0.85}RE_{0.15}O₂ (RE = rare earth). The three catalysts doping with rare earth element were labeled as Mn–Ce–O_x, Mn–La–O_x and Mn–Pr–O_x, and the catalyst without rare earth element was labeled as Mn–O_x. The detailed information is in the Supplementary material.

* Corresponding authors.

E-mail addresses: xinhc@qibebt.ac.cn (H. Xin), lixb@qibebt.ac.cn (X. Li).

2.2. Characterization

N₂ adsorption/desorption measurements were carried out at –196 °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 K α radiation (wavelength $\lambda = 1.5406 \text{ \AA}$) at the scanning rate of 4°/min. X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo ESCALAB 250XI spectrometer equipped with a Al K α 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 H₂-temperature-programmed reduction (H₂-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% O₂, and balance N₂ 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 O₂ in the oxidation

process, the mixed gas without O₂ was also charged with the same operation conditions. The NO conversion was calculated according to the following formula:

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

where [NO]_{inlet} and [NO]_{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 MnO₂ crystallization. The characteristic peaks corresponding to cerium oxide, lanthanum oxide, praseodymium oxide or MnO₂ 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,

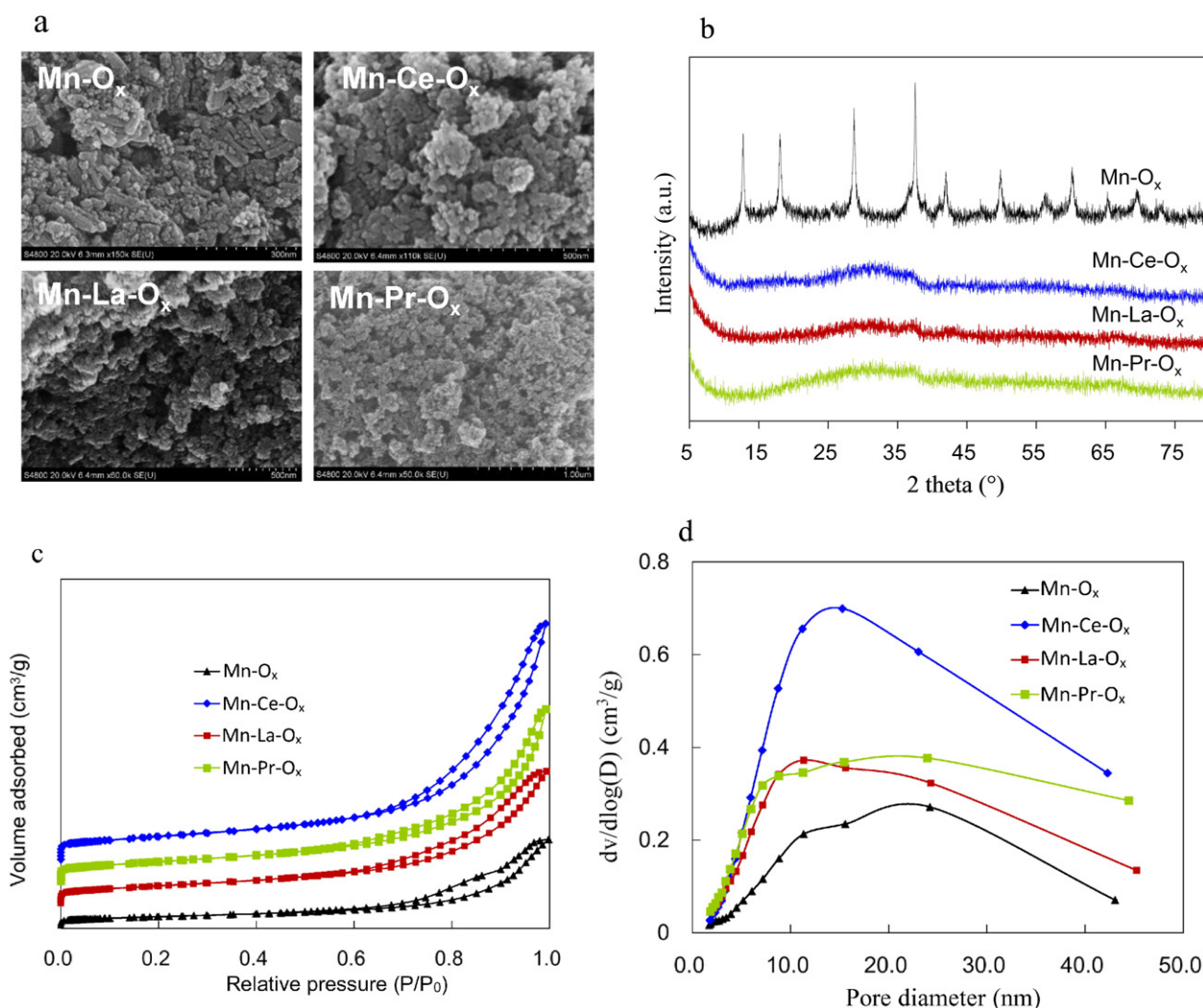


Fig. 1. (a) SEM images, (b) XRD patterns, (c) Nitrogen adsorption/desorption isotherms, (d) BJH size distributions of the catalysts.

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