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In-situ DRIFTS for the mechanistic studies of NO oxidation over α-MnO_2, β-MnO_2 and γ-MnO_2 catalysts

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HIGHLIGHTS

- α-, β-, and γ-MnO_2 catalysts with different tunnel structures were synthesized for NO oxidation.
- γ-MnO_2 has outstanding catalytic activities due to the stacking faults for active oxygen species.
- The surface area was not the limiting factor for NO oxidation over MnO_2 catalyst.
- Bridged nitrate as intermediate profited from active oxygens was decomposed to NO_2 and new Mn-O-Mn.
- The reaction pathways of α-, β-, and γ-MnO_2 catalysts for NO oxidation were proposed.

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ABSTRACT

In this article, α-MnO_2 and β-MnO_2 nanorods, and urchin-like γ-MnO_2 catalysts with different tunnel structures were synthesized by a hydrothermal synthesis method and evaluated for the catalytic oxidation of nitric oxide (NO). The experimental results showed the γ-MnO_2 catalyst has the best catalytic activity among the three catalysts, with more than 80% NO conversion at 250 °C. The catalytic oxidation activities decreased in the order: γ- > β- ≈ α-MnO_2. The XPS results implied that main manganese in all the catalysts was Mn^{4+} and the activity was in close correlation with the surface concentration of O_α species. The BET results showed that the surface area was not the suppression factor for NO oxidation. O_2-TPO/TPD and *In-situ* DRIFTS experiments showed the catalytic activity of α-MnO_2 with [2 × 2] tunnels was benefit from the chemisorbed oxygen species while not the lattice oxygens or Mn cations. For β-MnO_2 with [1 × 1] tunnels and γ-MnO_2 with [2 × 1] tunnels, both chemisorbed oxygen and lattice oxygen or Mn cations were the influencing factors on the catalytic oxidation activity, and the chemisorbed oxygens were the major. The main intermediate active species were monodentate nitrites at low temperature, while were bridged nitrates mainly profited from chemisorbed oxygen over three catalysts at high temperature, and further decomposed to NO_2 and produced new Mn-O-Mn. The stacking faults of γ-MnO_2 with the random intergrowth of ramsdellite and pyrolusite structures resulted in the main sources of active oxygen species, which were beneficial to the catalytic activity. The reaction pathways over α-, β-, and γ-MnO_2 catalysts for NO oxidation were proposed.

1. Introduction

Nitrogen oxides (NOx) are mainly from the stationary and transportation sectors, which are regarded as one of the major contributions to the acid rain, photo-chemical smog, ozone depletion and greenhouse effects, etc. [1–3]. In the stationary sources, above 90% of total NOx emissions are in the form of NO. Selective catalytic reduction by NH_3 (NH_3-SCR) technique has been widely used for NOx purification from coal-fired power plants due to the outstanding-efficiency and strong-stability performances, with more than 95% NOx conversion in the temperature range of 300–400 °C. However, in the cases of steel, cement, glass and other industries, the traditional SCR is not applicable due to the burdensome operating costs for heating low-temperature flue gas (100–200 °C). Compared to SCR technology, the combination technique of NO oxidation to NO_2 and further sorption is an alternative method. Thus, many researchers are dedicated to developing the high-efficiency catalysts for NO catalytic oxidation.

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MnOx catalysts are the major targets on account of the excellent redox ability at low temperature due to its rich variable valence states (MnO, Mn_3O_4, Mn_5O_8, Mn_2O_3, and MnO_2). In recent years, Mn-containing catalysts, such as Mn-based composite oxide [4–6], perovskites [7,8] and supported catalysts [9,10], showed good performance for NO oxidation. It has been a consensus that Mn ions are the reactive sites and Mn^{4+} is more active for NO oxidation [7,8,11]. However, it is difficult to choose MnO_2 as a model catalyst due to the different crystal structure, such as α-MnO_2, β-MnO_2 and γ-MnO_2 with tunnel structure and δ-MnO_2 with layer structure. Xie et al. [12] found the catalytic activities of the MnO_2 catalysts for deep oxidation of propane decreased in the order: α- ≈ γ- > β- > δ-MnO_2. Dong et al. [13] synthesized MnO_2 catalysts for investigating the relationship between the structure and catalytic ozonation activity, and reported that the activities followed the order: α- > γ- > β-MnO_2. Li et al. [14] found α-MnO_2 was superior to β-MnO_2 and γ-MnO_2 for VOCs degradation with respect to the removal efficiency, the CO_2 selectivity and O_3 suppression. Liang et al. [15] reported the activities of the catalysts decreased in the order of α- ≈ δ- > γ- > β-MnO_2 for CO oxidation, concluding the activity was mainly predominated by the crystal phase and channel structure of the MnO_2 catalysts. Thus, it can be accepted that the structures have an important role in the activity of catalytic oxidation.

However, there is little literatures for discussing the relationship between catalytic performance and crystal phase or channel structure of MnO_2 for NO oxidation. On the basis of BET, XPS, H_2-TPR and Raman results, Chen et al. [16] found the tunnel structure and surface chemisorbed oxygen of γ-MnO_2 were proposed to be the main factors that contributed to the excellent performance in NO oxidation. Unfortunately, the reaction mechanisms over different MnO_2 catalysts were not investigated. Zhao et al. [17] investigated phase structures, morphologies, and NO catalytic oxidation activities of single-phase MnO_2 catalysts and pointed out the NO catalytic oxidation activities decreased in the order γ-MnO_2 > α-MnO_2 > β-MnO_2 > δ-MnO_2. Unfortunately, the reaction pathways over α-MnO_2 and β-MnO_2 catalysts were not discussed. Thus, it is a deficiency to investigate the otherness of reaction mechanisms between different structures of MnO_2 catalysts, and need be further discussed.

In this paper, α-, β-, and γ-MnO_2 catalysts with different tunnel structures were synthesized for NO oxidation. The aims are to probe into the relationship between structure and catalytic activity, and expound the reaction mechanisms on different structure MnO_2, combining the main analysis of *in-situ* DRIFTS characterization.

2. Experimental

2.1. Catalyst preparation

α- and β-MnO_2 catalysts were prepared by a hydro-thermal synthesis method in a Teflon-sealed autoclave while γ-MnO_2 was synthesized under the normal pressure [17]. The preparation conditions of these catalysts were described as follows: For α-MnO_2, $KMnO_4$ (12.482 g, AR) and $MnCl_2·4H_2O$ (6.135 g, AR) were mixed in 400 ml de-ionized water and treated in a Teflon-sealed autoclave (500 ml) at 160 °C for 12 h. The preparation method of β-MnO_2 was same to that of α-MnO_2, with 19.494 g of $(NH_4)_2S_2O_8$ and 17.019 g of $MnCl_2·4H_2O$. γ-MnO_2 was synthesized via the reaction of $(NH_4)_2S_2O_8$ (9.006 g) and $MnCl_2·4H_2O$ (7.916 g) at 90 °C for 24 h under the normal pressure. All the above precipitates were filtered and washed with de-ionized to pH ≈ 7, and then, α- and β-MnO_2 samples were calcinated at 400 °C for 4 h while at 300 °C for γ-MnO_2.

2.2. Catalytic performance

The catalytic performances of three catalysts were tested in a fixed-bed quartz-tube reactor of 10 mm internal diameter. The reaction temperature was controlled by a K-type thermocouple in direct contact with the reactor loaded by samples. The inlet gas compositions were set as follows: 500 ppm NO, 5 vol% O_2 and N_2 to balance with a total flow rate of 250 ml/min. The typical gas hourly space velocity (GHSV) was set as 48000 h^{-1} or 24000 h^{-1} according to the loading amount of catalysts. The concentration of feed and effluent gas was performed using Flue Gas Analyzer (KM9106, Kane International LTD). NO conversion was obtained as follows:

$$\text{NO conversion } (\%) = ([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}})/[\text{NO}]_{\text{in}} \times 100$$

where, $[NO]_{in}$ and $[NO]_{out}$ indicates the inlet and outlet concentration of gaseous NO, respectively. Considering that MnO_2 shows NOx adsorption ability, the NO conversion was determined from the oxidation reaction after waiting long enough (1–2 h) to reach the steady state at each temperature points.

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) was obtained on a D8 ADVANCE diffractometer (Bruker, Germany) with Cu Kα radiation. Physisorption of N_2 measurements were performed on a surface area analyzer (ASAP 2020, USA) after pretreatment of samples at 300 °C for 2 h, respectively.

The morphology of the catalysts were inspected by a scanning electron microscope (SEM) by SU-8010 at 30 kV. Transmission electron microscopy (TEM) were characterized by JEM-1200EX at 120 kV after deposition in ethanol ultrasonically.

X-ray photoelectron spectra (XPS) were carried out on Thermo escalab 250Xi system with Al Kα radiation, and the spectra was calibrated against the standardized C1s peak at 284.6 eV. Raman spectra were measured on a Renishaw in Via Raman Microscope configuring with a 632.8 nm wavelength laser and a full-range grating.

O_2-temperature programming desorption (O_2-TPD) and O_2-temperature programming oxidation (O_2-TPO) experiments were performed on an analyzing instrument (PCA-140 TPD/TPR) with a thermal conductivity detector (TCD). About 0.1 g of typical sample was pre-treated in 50 ml/min N_2 at 300 °C for 1 h. In the case of O_2-TPD, the sample was treated in a flow of 8% O_2/N_2 (50 ml/min) at 30 °C for 30 min, and then heated from 30 to 800 °C in a flow of N_2 at a heating rate of 10 °C/min. For O_2-TPO there was no adsorption step while run in 8% O_2/N_2 from 30 to 800 °C.

The *in-situ* DRIFTS were acquired on IS50 spectrometer equipped with an MCT/A detector cooled by liquid nitrogen and an *in-situ* DRIFT reaction cell with ZnSe windows. Prior to each experiment, the sample was pretreated at 300 °C for 1 h with N_2. Reaction conditions were set selectively: 500 ppm NO, 5 vol% O_2 (when used), N_2 balance with 100 ml/min. All spectra were recorded from 600 to 4000 cm^{-1} by accumulating 100 scans with a resolution of 4 cm^{-1}.

3. Results and discussion

3.1. Structures and morphologies of catalysts

XRD measurements were obtained to search and confirm the crystal structure of three catalysts, as shown in Fig. 1(a–c). The sample (a) prepared by using $KMnO_4$ and $MnCl_2·4H_2O$ was assigned to α-MnO_2 (JCPDS 44-0141; *I*4/*m* space group; a = b = 0.9785 nm, c = 0.2863 nm) with the peaks at 2θ = 12.9°,