Article (Special Issue on Environmental and Energy Catalysis)

Synthesis of novel MnOₓ@TiO₂ core-shell nanorod catalyst for low-temperature NH₃-selective catalytic reduction of NOₓ with enhanced SO₂ tolerance

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ARTICLE INFO

ABSTRACT

In this study, a MnOₓ@TiO₂ core-shell catalyst prepared by a two-step method was used for the low-temperature selective catalytic reduction of NOₓ with NH₃. The catalyst exhibits high activity, high stability, and excellent N₂ selectivity. Furthermore, it displays better SO₂ and H₂O tolerance than its MnOₓ, TiO₂, and MnOₓ/TiO₂ counterparts. The prepared catalyst was characterized systematically by transmission electron microscopy, high-resolution transmission electron microscopy, X-ray diffraction, Raman, BET, X-ray photoelectron spectroscopy, NH₃ temperature-programmed desorption and H₂ temperature-programmed reduction analyses. The optimized MnOₓ@TiO₂ catalyst exhibits an obvious core-shell structure, where the TiO₂ shell is evenly distributed over the MnOₓ nanorod core. The catalyst also presents abundant mesopores, Lewis-acid sites, and high redox capability, all of which enhance its catalytic performance. According to the XPS results, the decrease in the number of Mn^{4+} active centers after SO₂ poisoning is significantly lower in MnOₓ@TiO₂ than in MnOₓ/TiO₂. The core-shell structure is hence able to protect the catalytic active sites from H₂O and SO₂ poisoning.

1. Introduction

Selective catalytic reduction (SCR) processes are the state-of-the-art for NOₓ abatement in coal-fired power plants [1–3]. However, the commercial catalytic (V₂O₅-WO₃ (MoO₃)/TiO₂) system exhibits some typical disadvantages [4], such as the need for a high starting temperature, narrow reactive temperature window (280–350 °C), and the decay of the N₂

selectivity at high temperatures [5–7]. Therefore, the development of novel catalysts for low-temperature NH₃-SCR remains a challenging task for industrial application. Recently, manganese oxide-based catalysts have attracted much attention for their superior activity in low-temperature SCR reactions [8–16]. However, they always suffer from severe SO₂ poisoning. Jin et al. [17] have reported that the NO conversion by Mn/TiO₂ catalysts decreases rapidly in the presence of SO₂, although an

enhancement of the SO_2 tolerance during low-temperature SCR was achieved after Ce doping. Sheng et al. [18] have also proposed that the presence of high concentrations of SO_2 in the flue gas leads to prominent deactivation of a Mn-Ce/TiO_2 catalyst prepared by a co-precipitation method for low-temperature SCR of NO_x with NH_3. Therefore, many researchers are working toward the development of superior SCR catalysts with high activity and good SO_2 tolerance [19–22].

Core-shell nanostructures have been widely studied for their unique structure, which can effectively protect the active components from migrating and sintering [23,24]. Therefore, the design of a catalyst with a core-shell structure seems a promising approach to protect the active sites from SO_2 poisoning. It has been reported that ceria supported on titania nanotubes shows high activity for intermediate- and high-temperature NH_3-SCR [25–27]. Pappas et al. [28] designed a series of manganese oxide-confined titania nanotube catalysts with different morphological features and found that their remarkable low-temperature SCR activity was due to the abundance of surface Mn^{4+} species. However, most of the literature so far regarding core-shell nanostructures for SCR reactions have reported titania nanotubes or carbon nanotubes (CNTs) as the shell [29,30], while granular metal oxide@TiO_2 has seldom been used.

In this work, a novel MnO_x@TiO_2 core-shell nanorod catalyst was prepared by a two-step method, as shown in Fig. 1. MnO_x nanorods were first prepared by a hydrothermal method [31], and then a versatile kinetics-controlled coating method [32] was used to fabricate a series of MnO_x@TiO_2 nanorod catalysts, one of which presented a core-shell structure. The influence of the presence of SO_2 in the flue gas on the SCR activity of the core-shell catalyst was also investigated.

2. Experimental

2.1. Catalysts preparation

MnO_x@TiO_2 nanorod catalysts were prepared by a new two-step method. $KMnO_4$ (2 mmol) and $MnSO_4 \cdot H_2O$ (3 mmol) were dissolved in deionized water (80 mL) at room temperature. After stirring ceaselessly for 20 min, the solution was transferred to a Teflon-lined stainless steel autoclave. The autoclave was maintained at 180 °C for 4 h and then cooled down
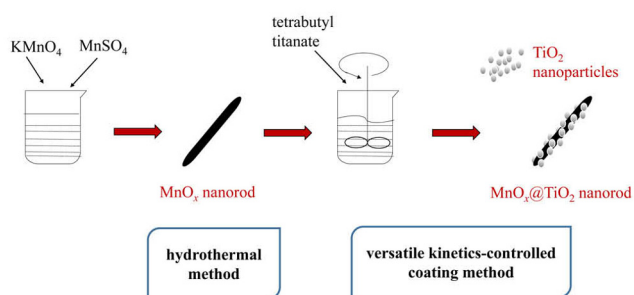

Fig. 1. Schematic illustration of the fabrication process of MnO_x@TiO_2 nanorods.

to ambient temperature. The resulting solid product was filtered, washed carefully with deionized water, and finally dried in an electric oven at 80 °C for 12 h [31]. The obtained powder was used as the MnO_x nanorod core. The TiO_2 shell material was prepared via a versatile kinetics-controlled coating method [32]. The MnO_x nanorod (0.5 mmol) core material was dispersed in ethanol (100 mL) and a concentrated ammonia solution (0.30 mL, 28 wt%) by ultrasonication for 30 min. Then, different molar amounts of tetrabutyl titanate were added dropwise and the reactions were allowed to proceed for 24 h at 45 °C under continuous mechanical stirring. The resultant products were separated, collected, and washed with deionized water and ethanol for several times. Finally, the obtained powders were dried in an electric oven at 100 °C for 12 h and calcined at 500 °C in air for 2 h [32]. The catalysts were denoted as MnO_x@$TiO_2(y)$, where y refers to the Mn:Ti molar ratio, which were 1:4, 1:2, and 1:1 in this study.

The counterpart MnO_x/TiO_2 nanomaterial was also prepared by a hydrothermal method. $KMnO_4$ (2 mmol), $MnSO_4 \cdot H_2O$ (3 mmol), and an appropriate amount of tetrabutyl titanate were mixed in deionized water. Then, the mixture was sealed in a Teflon-lined stainless steel autoclave at 180 °C for 4 h after further magnetic stirring. The sediment was then centrifuged, washed with deionized water and ethanol, dried at 100 °C for 12 h, and finally calcined in air at 500 °C for 2 h. The catalyst was denoted as MnO_x/TiO_2. MnO_x nanorods were prepared using the first step of the MnO_x@TiO_2 synthesis, and TiO_2 nanoparticles were prepared using a similar hydrothermal method as that employed for the MnO_x/TiO_2 catalyst.

2.2. Catalyst characterization

The morphological features of all the prepared catalysts were characterized by transmission electron microscopy (TEM), high-resolution TEM (HR-TEM), and element mapping using a FEI TECNAI G2 F20 instrument operated at 200 kV. The crystalline structure of the samples was examined by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer. Raman spectra were recorded on an SPEX-1403 Laser Raman Spectrometer at room temperature with a resolution of about 0.6 cm^{-1}. An Ar-ion laser with a wavelength of 514.5 nm in backscattering configuration was used to excite the crystals. The surface area and pore distribution of the catalysts were calculated with the Brunauer-Emmett-Teller (BET) equation using Micromeritics ASSP 2020 equipment at –196 °C by N_2 physisorption. The surface atomic states of the catalysts were analyzed by X-ray photoelectron spectroscopy (XPS) on a Thermo Escalab 250Xi instrument. H_2 temperature-programmed reduction (H_2-TPR) experiments were performed on a Tianjin XQ TP5080 auto adsorption apparatus. Prior to the H_2-TPR measurements, 50 mg of the catalysts were pretreated under N_2 at a total flow rate of 30 mL·min^{-1} at 300 °C for 0.5 h, and then cooled down to room temperature under N_2 atmosphere. The temperature was then raised to 600 °C at a constant heating rate of 10 °C·min^{-1} under H_2 (5 vol%)/N_2 flow (30 mL·min^{-1}). The H_2 consumption during the experiment was monitored by a thermal conductivity detector (TCD). NH_3 tem-