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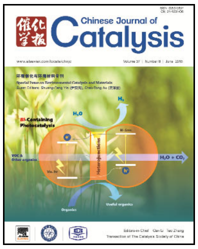

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Resistance to SO_2 poisoning of V_2O_5/TiO_2-PILC catalyst for the selective catalytic reduction of NO by NH_3

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ABSTRACT

A titania pillared interlayered clay (Ti-PILC) supported vanadia catalyst (V_2O_5/TiO_2-PILC) was prepared by wet impregnation for the selective catalytic reduction (SCR) of NO with ammonia. Compared to the traditional V_2O_5/TiO_2 and V_2O_5-MoO_3/TiO_2 catalysts, the V_2O_5/TiO_2-PILC catalyst exhibited a higher activity and better SO_2 and H_2O resistance in the NH_3-SCR reaction. Characterization using TPD, *in situ* DRIFT and XPS showed that surface sulfate and/or sulfite species and ionic SO_4^{2-} species were formed on the catalyst in the presence of SO_2. The ionic SO_4^{2-} species on the catalyst surface was one reason for deactivation of the catalyst in SCR. The formation of the ionic SO_4^{2-} species was correlated with the amount of surface adsorbed oxygen species. Less adsorbed oxygen species gave less ionic SO_4^{2-} species on the catalyst.

1. Introduction

Nitrogen oxides (NO_x) from the combustion of fossil fuels in vehicles or coke in the electrical power plants have resulted in serious environmental problems due to their promotion of acid rain, photochemical smog, ozone depletion, and greenhouse gases. The selective catalytic reduction (SCR) of NO_x with NH_3 is the most effective method for the removal of NO_x from stationary sources and diesel engines [1–3]. V_2O_5/TiO_2-based catalysts have been widely used in industry to eliminate NO_x for their high NO_x removal efficiency and strong resistance to poisoning by SO_2 that is common in flue gases [3–5]. Nevertheless, these catalysts still suffer from the high activity for SO_2 oxidation to SO_3, which cause corrosion and plugging of the reactor [6], and the high operating temperatures (300–400 °C) that cause high energy consumption. Low temperature SCR has aroused great interest in the past two decades [7–10]. Transition metal oxides like Fe_2O_3 [11], MnO_x [12–14], CuO [15] and V_2O_5 [16,17] have shown good activity for low temperature SCR reaction. However, these catalysts are easily deactivated in the presence of SO_2 and H_2O by the blocking of the active sites. Therefore, a high resistance to SO_2 and H_2O poisoning is of concern for low temperature SCR catalysts for NO_x removal.

Pillared interlayer clays (PILCs) are unique two dimensional zeolite-like materials prepared by intercalation of inorganic cationic clusters into clay layers followed by heating. Researchers have paid much attention to PILCs because of their large specific surface area, high surface acidity and good thermal stability. A series of PILCs were synthesized and used as catalysts for the SCR reaction of NO_x with NH_3 by Yang et al.

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[18,19]. These showed high activity in the SCR reaction that was better than the traditional V_2O_5-based catalysts. TiO_2-PILC has a large surface area and pore size, high thermal and hydrothermal stability as well as high resistance to SO_2 [20]. The activity of V_2O_5/TiO_2-PILC [21] and Fe/TiO_2-PILC [22] catalysts can be improved by the presence of H_2O and SO_2. Although PILCs-based catalysts showed high sulfur resistance in the NH_3-SCR reaction, there are no reports on the mechanisms of the resistance to SO_2 over the V_2O_5/TiO_2-PILC catalysts. Even the investigations of SO_2 interaction with vanadia/titania catalysts are not comprehensive. Orsenigo et al. [23] studied the role of sulfates in NO_x reduction and SO_2 oxidation, and suggested that the buildup of sulfates at the catalyst surface likely occurred first at or near the vanadyl sites and increased both the Brönsted and Lewis acidity of the catalyst and enhanced the reactivity in the de-NO_x reaction. However, their work did not include confirming experimental evidence from surface science methods. Baxter's group [24] used *in situ* FTIR and XPS to prove that a stable sulfate species was formed on titania but not on vanadia. In summary, there was no exact determination on the interaction between SO_2 and the vanadia/titania catalysts.

Understanding the effects of SO_2 on SCR activity over PILCs catalysts is important for the development and application of the appropriate catalysts. In this study, the effects of SO_2 on the NH_3-SCR reaction over a V_2O_5/TiO_2-PILC catalyst were investigated. X-ray fluorescence (XRF), X-ray diffraction (XRD), N_2 adsorption-desorption measurements, temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), and *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) were used to characterize the catalysts and identify the interaction between SO_2 and the catalysts.

2. Experimental

2.1. Catalyst preparation

TiO_2-PILCs were synthesized by the established procedures [25,26]. The starting clay was a purified grade montmorillonite powder from Nanocor Company. The cation exchange capacity (CEC) of the clay was 145 meq/100 g. The pillaring agent, a solution of partially hydrolyzed Ti polycations, was prepared by adding $TiCl_4$ into HCl solution (2 mol/L). The mixture was then diluted by the slow addition of distilled water with stirring to reach a final Ti concentration of 0.82 mol/L. The amount of HCl solution corresponded to the final concentration of 0.11 mol/L. The solution was aged for 8 h at room temperature, which was the pillaring solution. Clay (10 g) was dispersed in 2.0 L of deionized water and the slurry was stirred for 24 h. The pillaring solution was then slowly added into the suspension of clay with vigorous stirring until the amount of pillaring solution reached the required Ti/clay ratio of 10 mmol/g. The product was left in the solution for 24 h. Subsequently, the mixture was separated by centrifugation and washed with deionized water until the liquid was free of chloride ions as indicated by the silver nitrate test. The samples were dried at 120 °C for 12 h and then calcined at 400 °C for 4 h.

The TiO_2-PILCs supported vanadia catalysts were prepared by the impregnation of TiO_2-PILCs with aqueous solutions of NH_4VO_3 in oxalic acid. The samples were dried at 105 °C for 4 h and then calcined at 250 °C for 1 h and 450 °C for 3 h. The obtained V_2O_5/TiO_2-PILC catalysts were labeled as nV/TiO_2-PILC, where n referred to the vanadium amount (mass fraction, %) on the support. Besides the pillared clay catalysts, V_2O_5/TiO_2 and V_2O_5-MoO_3/TiO_2 catalysts were also prepared using a similar method for comparison. These catalysts contained 4% V_2O_5 and 6% MoO_3 and were denoted as 4V/TiO_2 and 4V6Mo/TiO_2, respectively.

2.2. Catalytic activity measurement

The SCR activity measurement was carried out in a fixed bed quartz microreactor (i.d. = 8 mm) with 0.2 mL catalyst (40–60 mesh) at atmospheric pressure. The flue gas was simulated by blending different gaseous reactants that contained 0.1% NO, 0.1% NH_3, 8% O_2, 0.05% SO_2 (when used), 10% H_2O (when used), and balanced with He. The total flow was 100 mL/min with the GHSV of 30 000 h^{-1}. The gas mixtures in the reactor outlet that contained NO, NO_2, N_2O, and N_2 was analyzed by a gas chromatograph (GC-2014C, Shimadzu) equipped with a TCD detector and a Fourier transform infrared (FT-IR) spectrometer (Tensor 27, Bruker). The NO conversion (X) was calculated by

$$X = \frac{[\mathrm{NO}]_{\mathrm{in}} + [\mathrm{NO_2}]_{\mathrm{in}} - [\mathrm{NO}]_{\mathrm{out}} - [\mathrm{NO_2}]_{\mathrm{out}}}{[\mathrm{NO}]_{\mathrm{in}} + [\mathrm{NO_2}]_{\mathrm{in}}} \times 100\%$$

where "in" and "out" represented inlet and outlet of the reactor, respectively.

2.3. Characterization

Elemental analysis of the samples was carried out on an X-ray fluorescence spectrometer (Magix PW2403, PAN alytical). The XRD patterns were measured on a Bruker D8 Advance diffractometer operated at 50 kV and 40 mA using Cu K_α radiation (λ = 0.154 nm) for 2θ = 5°–80° with a step size of 7.2°/min. The specific surface areas, pore volumes and micropore volumes of the samples were measured by a physical adsorption instrument (Micromeritics ASAP 2020). Specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method. All the samples were degassed at 250 °C under vacuum for 12 h, and N_2 was adsorbed at –196 °C. *In situ* DRIFTs were carried out using an FT-IR spectrometer (Nicolet 6700, Thermo) equipped with an *in situ* diffuse reaction chamber and a high sensitivity mercury cadmium telluride (MCT) detector cooled by liquid nitrogen. The samples were first treated at 110 °C in N_2 flow for 30 min to remove water and impurities on the surface of the catalysts. All spectra were collected at a resolution of 4 cm^{-1} by an accumulation of 32 scans. The TPD spectra were obtained by a quantitative gas analysis (QGA) system (HIDEN analytical). For each experiment, the catalyst was preconditioned at 110 °C in N_2 at a flow rate of 30 mL/min and then cooled to 40 °C. The catalyst samples were then treated with 1% SO_2/N_2 or (1% SO_2+8% O_2)/N_2 at 40 °C for 1 h. The total flow rate was 30 mL/min. Subsequently, the samples were