



Mechanism study of the promotional effect of O₂ on low-temperature SCR reaction on Fe–Mn/TiO₂ by DRIFT

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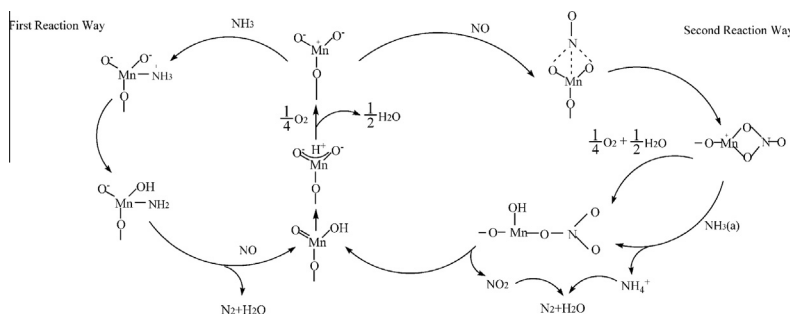
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HIGHLIGHTS

- O₂ promotes the dehydration reaction of the manganese oxides to produce active oxygen.
- O₂ enhances the amount of NO complexes and improves NO removal through two reaction ways.
- Active oxygen abstracts H from coordinated NH₃ to form amide species to react with NO.
- NO₂ reacts with NH₄⁺ produced by the transformation of bidentate nitrates to monodentate nitrates.

GRAPHICAL ABSTRACT



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ABSTRACT

In this manuscript, the low-temperature SCR catalyst Fe–Mn/TiO₂ was prepared by sol–gel method, and in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) was used for revealing the mechanism of the promotional effect of O₂ on low-temperature SCR reaction on Fe–Mn/TiO₂. The experiments showed that surface OH species were consumed during NO adsorption, indicating that O₂ could promote the dehydration reaction of the manganese oxides to produce active oxygen, and greatly enhance the amount of NO complexes on the catalyst. NO removal was influenced by O₂ through two reaction ways. In the first reaction way, with the active oxygen obtained, coordinated NH₃ was easier to be activated. Active oxygen could abstract H from coordinated NH₃, giving amide species to react with NO. In the second reaction way, with the active oxygen, much more bidentate nitrate could be formed from nitrosyl, and transformed to monodentate nitrate, producing new Brønsted acid sites to form NH₄⁺. With more NO₂ obtained from the decomposition of monodentate nitrate in the presence of O₂, NO could be removed effectively by the reaction between NH₄⁺ and NO₂.

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1. Introduction

Selective catalytic reduction (SCR) of nitrogen oxides (NO_x) with ammonia is one of the processes for cleaning the flue gas, and V₂O₅–WO₃ (or MoO₃)/TiO₂ was the most widely used catalyst. However, the narrow temperature window (573–673 K) of the

reactivity is the main obstacle for its real application, since high concentration of sulfur dioxide and dust would deactivate the catalyst. Therefore, there is an interest in developing a potential low-temperature (353–523 K) SCR catalyst in recent years, and then the catalyst bed can be moved to downstream of the desulfurization scrubber and/or particulate control device, where most of sulfur dioxide and dust is removed and the deactivation effect is weakened [1,2]. Among the low-temperature SCR catalysts, Fe–Mn/TiO₂ prepared by sol–gel method was proved to get high catalytic

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activity at low temperature, and more than 90% of NO could be removed at 361 K [3].

In previous literature, it has been proved that O₂ could promote NO removal, and the transient-state and steady-state effect of O₂ on the reaction has been investigated before [4,5]. It was known that O₂ promoted NO removal at different reaction conditions, and the NO conversion would decrease to less than 10% when O₂ was not included. O₂ was considered only as an operation parameter in these studies. And in some manuscripts, isotopic labeling experiments were performed to reveal the mechanism, and the transmission of oxygen was also included [6,7]. However, the role of O₂ in the whole catalytic cycle was still ambiguous. In recent years, in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) became widespread in applications for surface group identification and mechanism research [8–10]. Therefore, the mechanism of the promoting effect of O₂ on the low-temperature SCR reaction was investigated by DRIFT in this manuscript.

2. Materials and methods

2.1. Materials

Butyl titanate and acetic acid were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ethanol, manganese nitrate and ferric nitrate were provided by Shanghai Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals used were of analytical grade.

2.2. Preparation of Fe–Mn/TiO₂

The catalyst was prepared by sol–gel method [3]. Butyl titanate (0.1–0.3 mol), ethanol (0.8 mol), water (0.6 mol), acetic acid (0.3 mol), manganese nitrate (0.04–0.12 mol) and ferric nitrate (0.01–0.03 mol). The solution was mixed under vigorous stirring, formed transparent red sol. After being stable at room temperature for several days, the sol transformed to gel. The gel was dried at 378 K and transform to a porous solid. Then the solid was crushed and sieved to 60–100 mesh. After that the solid was calcined at 773 K for 6 h in air in a tubular furnace. The catalyst was denoted as Fe(0.1)–Mn(0.4)/TiO₂, which meant that the molar ratio of Fe to Ti was 0.1, and the molar ratio of Mn to Ti was 0.4.

2.3. Activity test of the catalyst

The SCR activity measurement was carried out in a fixed-bed, quartz flow reactor. The experiments were performed under atmospheric pressure at 353–523 K. The reactor (i.d. 1 cm) consisted of a quartz tube in which 2 ml of catalyst was placed. The typical reactant gas composition was: NO of 1000 ppm, NH₃ of 1000 ppm, O₂ of 0–6%, and balanced N₂. And the total flow rate was 1000 ml min⁻¹. The tubing of the reactor system was heat traced to prevent formation and deposition of ammonium nitrate. NO, NO₂, and O₂ concentration were monitored by a flue gas analyzer (KM9006 Quintox Kane International Limited).

2.4. Temperature programmed desorption (TPD) experiments

The TPD experiments were carried out on Quantachrome Chembet TPR/TPD (p/n 02138-1) with Hiden HAL 201 RC mass spectrometer as a detector. 50 mg sample was put in the quartz reactor, and the balance gas was He. When the experiment was performed with O₂, the catalyst was exposed to 1% NO + 5% O₂ at 323 K for 60 min (80 min for 1% NH₃ + 5% O₂) at 423 K, flushed with He for 30 min and finally the temperature was linearly increased to 773 K in He with a speed of 10 K min⁻¹. A corresponding experiment without

O₂ was performed, where the sample was exposed to 1% NO for 60 min (80 min for 1% NH₃) at 323 K. This was followed by flushing the sample with He for 30 min and finally a temperature ramp to 773 K was conducted, with a speed of 10 K min⁻¹, while exposing the catalyst to He only.

2.5. Transient DRIFT experiments

FTIR spectra were acquired using in situ DRIFT cell (high temperature chamber with ZnSe window) equipped with gas flow system. The DRIFT measurements were performed with Nicolet 6700 FTIR spectrometers at 4 cm⁻¹ resolution with 64 co-added scans. The balance gas was He, and the gas flow rate was 30 ml min⁻¹.

When desorption of reactant gas at different temperature was investigated, the catalyst was treated at 773 K in He environment for 2 h, then cooled to temperature desired. The background spectrum was recorded with the flow of He and was subtracted from the sample spectrum. When it has been cooled to 353 K, the reaction gas (1000 ppm NO/1000 ppm NO + 3% O₂/1000 ppm NH₃/1000 ppm NH₃ + 3% O₂) was introduced to the cell, and flushed for 30 min. And then the sample was purged with He for 30 min. After that, temperature was raised up to 373 K, 393 K, 423 K, 453 K, 493 K and 523 K. At each temperature, the sample was treated with He flushing for 30 min, and the spectra was recorded.

Since 423 K was the most commonly used temperature at which SCR was performed, the reaction between NO and NH₃ with and without O₂ was performed at 423 K. In these experiments, the catalyst was treated at 773 K in He environment for 2 h, then cooled to 423 K. The background spectrum was recorded with the flowing of He and was subtracted from the sample spectrum. 1000 ppm NO/1000 ppm NH₃ was introduced with (or without) 3% O₂, and then the sample was flushed with He for 30 min. After that, 1000 ppm NH₃/1000 ppm NO was introduced with (or without) 3% O₂, and the spectra were recorded with time. When the in situ reaction of NO and NH₃ was investigated, 1000 ppm NO + 1000 ppm NH₃ was introduced with 3% O₂, and the spectra were recorded with time.

3. Results

3.1. The effect of O₂ concentration on NO removal

The catalytic reduction of NO by NH₃ over Fe(0.1)–Mn(0.4)/TiO₂ significantly depended on both O₂ concentration and temperature. As shown in Fig. 1, when there was no O₂ existed in the system, NO conversion was low and almost the same at around 10% at each temperature. When O₂ concentration was between 0% and 2.5%, NO conversion increased quickly with the increase of O₂ concentration. And it became stable when O₂ concentration was higher than 2.5%. The final NO conversion at high O₂ concentration was also affected by temperature. At 353 K, NO conversion was about 60%. At 423 K, 453, 493 and 523 K (not shown), NO conversion was almost the same, higher than 95%.

3.2. TPD study

The NO-TPD experiment was conducted over the catalyst. In Fig. 2, it showed that the results were different with and without O₂. In the adsorption process, when the experiment was conducted with O₂, the increase of the NO concentration at the tail gas was slower, and the adsorption equilibrium time was longer. And during the desorption process, there were two desorption peaks, the first one was around 433 K, assigned to the decomposition of weakly bound nitrite species [11,12], and the second one was around 533 K, which was always due to the decomposition of

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