Study on the role of Mn species in low temperature SCR on MnO$_x$/TiO$_2$ through experiment and DFT calculation

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ABSTRACT

The reaction mechanism of selective catalytic reduction of NO with ammonia (SCR) on MnO$_x$/TiO$_2$ catalysts was investigated through experiments and density functional theory (DFT) calculation. Firstly, the catalytic performance of catalyst with different molar ratios of MnO$_x$/TiO$_2$ was investigated and then was analyzed by NH$_3$ temperature programmed desorption (NH$_3$-TPD). The crystalline structure and the valence state of the MnO$_x$/TiO$_2$ catalyst were characterized by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). According to the results, the model of MnO$_x$/TiO$_2$ was established. Secondly, the different active sites of catalyst surface and adsorption characteristics of reacting gases during the SCR reaction based on in-situ DRIFT was investigated. Finally, the energy of different elemental reaction and isomerization of intermediate was calculated by MS Dmol^3. It was found that the main active substance of catalyst was Mn^{4+} species which distributed dispersedly on the catalyst surface. The introduction of MnO$_x$ dopant can promote the adsorption of gas and reduce the formation energy of oxygen vacancy. The complete catalytic cycle goes in three steps: (a) Lewis acid site reaction follows Eley-Rideal mechanism; (b) Brønsted acid site reaction follows Langmuir-Hinshelwood mechanism; (c) Regeneration of catalyst.

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1. Introduction

Nitrogen oxides have many adverse impacts on human health, environment and biological [1]. 90% of NO$_x$ emission comes from stationary sources, motor vehicle's exhausts and fossil fuel vapors [2]. Short-term exposure of NO$_x$ leads to respiratory morbidity, including impaired host defense systems, increased lung inflammation and decreased lung function and growth [1]. NO$_x$ also reacts instantly with common organic chemicals to form various toxic products such as nitrated and nitrosamines, which results in acid rains [3]. Selective catalytic reduction (SCR) of NO$_x$ to N$_2$ with NH$_3$ have been considered to be an effective process for removal of NO$_x$ from stationary sources and the general reaction occurring is 4NO + 4NH$_3$ + O$_2$ = 4N$_2$ + 6H$_2$O [4]. The commercial V$_2$O$_5$ based catalyst has been widely used and exhibited a better catalytic activity for eliminating NO$_x$ where the temperature window of exhaust is 300 °C–400 °C [5]. For some plant such as cement industry of which the exhaust contains much dust and SO$_2$ gas, the deNO$_x$ reactor has to be placed downstream of the desulfurization device where dust controller was used to keep from the deactivation of SCR cat-

alyst. However, the temperature of downstream in the technology process is no more than 200 °C. Thus, a catalyst which can maintain relatively high activity in low temperature SCR reaction attract much attention.

Smirniotis et al. has studied transition metal oxides supported on Hombikat TiO$_2$, which showed substantial performance and higher selectivity of N$_2$ for low-temperature SCR of NO with NH$_3$, and found that Mn showed the best activity among transition metal [6]. The same group had researched the catalytic of different oxidation states of Mn oxide and demonstrated the activity of MnO$_x$ maintained a positive correlation with the valence of Mn, and MnO$_2$ was the most active among several kinds of MnO$_x$ [7]. Manganese oxides have caused extensive concern with their superior SCR activity at low-temperature. Many scholars characterized the surface of Mn-based catalyst and studied the reaction mechanism through experimental methods such as XPS, isotopic labeled, they found the lattice oxygen was critical on activity and selectivity in both ammonia oxidation and SCR reaction [8,9]. The activity of Mn-based catalyst is mainly dependent on the valence state of Mn species, the specific surface area and crystallinity of MnO$_x$. Boningari et al. supposed that the main reason that Mn-based catalyst showed preferable NO conversions with NH$_3$ was MnO$_2$ evenly distributed on TiO$_2$ support with a higher surface coverage [7]. Despite extensive experimental and theoretical studies,

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some fundamental questions for the SCR reaction under the effect of Mn-based catalyst, such as (a) the interaction between gas and active sites of the catalyst, (b) the underlying elucidation of the full catalysis process, still remain unclear.

Furthermore, a number of scholars have carried out numerous experiments to study the elucidation of reaction mechanism which gave guidance and inspiration in designing and developing highly active catalysts [10]. Donovan et al. elucidate the reaction mechanism of SCR reaction on MnO_x/TiO_2 catalyst through In-situ FT-IR spectroscopy, and got the conclusion that the azoxy species formed by NH_3 adsorbed onto the Lewis acid sites of Mn^{4+} combined with moderately strong monodentate and bidentate nitrate species, which was important for high activity and selectivity for low-temperature SCR. Smirniotis indicated that active intermediates are mianly due to a coupling of one nitrogen from ammonia adsorbed on the catalyst and other on from gaseous nitric oxide, lattice oxygen participated in the SCR reaction by filling oxygen gaps. Kapteijn et al. researched the NH_3-SCR reaction on the surface of MnO_x/Al_2O_3 by isotope labeling and further proved the existence of [-NH_2] as the intermediate. In addition, they suggested the NH^{4+} adsorbed on the Brønsted acid sites hardly participated in the main reaction. By comparison, the active [-NH_2], dehydrogenation on the Lewis acid sites, can react with NO_x through both ER-mechanism and LH-mechanism [11,12].

In order to get more details about the low temperature activity of manganese-based catalysts, a series of theoretical researches have been carried out by applying a method of the first principles calculation. Gao et al. established the model of MnO_x/ZrO_2-CeO_2 and indicated that the Mn^{4+} species distributed evenly on the surface of support are the reason that this catalyst presented a better catalytic activity [13]. Maitarad et al. calculated the energy of oxygen vacancy formation, adsorption ability of NO and NH_3 for the model of CeO_2 (110) and Mn/CeO_2 (one lattice cerium atom was replaced by the manganese atom) [14]. They suggested that the oxygen adjusted Mn atom in the Mn/CeO_2 surface can easily escape to form a stronger nitrite intermediate with NO due to the less energy requirement for the oxygen vacancy distortion. At the same time, the H atom of NH_3 adsorbed on the catalyst surface migrated toward to the oxygen surface because of the hydrogen bond interactions between the H atom and surface oxygen. Finally, the nitrite intermediate can work as a stronger electrophilic site and react with the active state of [NH] rapidly following the LH-mechanism [17]. However, most of these works are just concentrated on establishment of catalyst model and investigated surface features. Up to now, the atomic-scale understanding of NH_3-SCR reaction on manganese-based catalyst has not been studied yet.

In this work, we investigated the reaction mechanism of NH_3-SCR on Mn-doped TiO_2 catalyst through experiment and density functional theory calculations (DFT). From experimental point, XRD and XPS were applied to confirm microstructure and oxidation state of the surface manganese in order to build the catalyst model and make it closer to actual system. What is more, the interaction between gas and active sites of the catalyst was studied by in-situ DFIFT, NH_3-TPD, which was crucial for searching the feasible paths of the reaction initially. Based on the results, the systematic process of reaction on Lewis acid sites and Brønsted acid sites, respectively, were derived. And the energy of intermediate and transient state was calculated. The results of this work could provide theoretical guidance for the design and development of new catalyst and modification of transition metal oxide catalyst.

2. Experimental section

2.1. Catalytic preparation

MnO_x/TiO_2 were prepared by the co-precipitation method similar to our previous [15]. Titanium sulphate and manganese acetate were used as the precursor of manganese and Ti, respectively. The required quantities of precursors with the Mn/Ti atomic ratio in the range of 0-0.4 were pre-mixed in with water of 60 °C. Then, to the mixture, the precipitating agents were added in the order of: carbamide solution, ammonia and hydrogen peroxide. After the sedimentation process completed, the precipitates were separated by centrifugation and washed by deionized water to remove basic ionic. Next, the precipitates were kept in a vacuum drying oven at 70 °C for 12 h. After throughout drying, the resulting powder was crushed and sieved (60–80 mesh) and calcined at 400 °C in a muffle furnace for 6 h to get MnO_x/TiO_2 catalyst.

2.2. Catalytic performance

The catalytic performance was evaluated in a fixed-bed quartz tube reactor. The weight of the catalyst was 40 mg. The gas flow rate and the gas hourly space velocity (GHSV) were 200 ml/min and 24 000 h^{-1}. The reaction gas condition was: 500 ppm NH_3, 500 ppm NO, 5% O_2 and N_2 balance. The temperature was controlled from 90 to 300 °C.The gas concentration in the outlet was continually monitored by a Fourier transform infrared spectrometer (FTIR, Thermo, Nicolet 6700 FT-IR). The rate of conversion was calculated from the equation

Y_{NO}-concentration of inlet, X_{NO}-concentration of outlet, V-the total flow rate, W-the mass of catalyst.

2.3. Catalyst characterizations

The power XRD patterns were performed on a Shimadzu XRD-7000 diffractometer using a Cu-Kα radiation source (wavelength 1.5406 Å) between 10° and 80° at a scan speed of 5°/min. An aluminum holder was used to support the catalyst simples. The X-ray photoelectron spectroscopy (XPS) were carried out on a Thermo ESCALAB 250 with Al Kα X-rays (1486.7 eV) to analyze the atomic surface concentration of the catalyst. Binding energies were measured for C1s, O1s, Ti2p, Mn2p. The concentrations of Mn, Ti and O on catalysts surface were calculated from the peak areas ratios of the samples. The overlapped peaks were deconvoluted and the fitting was performed by searching for the optimal combination of Guassian and Lorenzian curves. The temperature programmed desorption (NH_3-TPD) was performed on the ChemBET Pulsar TPR/TPD (Quantachrome, USA.). Prior to the NH_3-TPD experimental, the sample was initially pretreated at 200 °C in highly pure Helium environment (30 ml/min). After that, the catalyst was saturated with NH_3 (4% in He) at a flow rate of 30 ml/min for about 1 h. Desorption data was collected by heating the simple from 100 °C to 800 °C at a rate of 5 °C/min.

In situ Drift spectra were recorded using a VERTEX 70 (Bruke, Germany) spectrometers with KBr windows. For experimental purpose, the wafers consisting of 50 mg of catalyst were placed into gas flow cell and poured with high purity nitrogen at 400 °C for 3 h to remove any adsorbed impurities and then cooled to the desired temperature. The back ground spectrum was recorded simultaneously and then subtracted from the sample spectrum.

2.4. Models selection and computational details

According to the results of XPS and XRD analysis, the anatase TiO_2 was chosen as the dominate agent of the model. Since TiO_2 (110) was the most stable among low index surfaces, TiO_2 (110) was consequently cleaved with six layers and reconstructed as 3*3 surface supercell, which was composed of 117 atoms. It has a vacuum gap of 12 Å to avoid the interference between layer and layer. We have proved that the manganese atom replaced the titanium atom and incorporated into the lattice structure of TiO_2 Accord-