Density function theoretical and experimental study of $NH_3 + NO_x$ adsorptions on MnO_x/TiO_2 surface

Liangjing Zhang, Suping Cui *, Hongxia Guo, Xiaoyu Ma, Lu Wei

College of Materials Science and Engineering, Beijing University of Technology, Beijing 100124, PR China

ABSTRACT

The adsorption of NO and NH_3 gaseous molecules on Mn_3O_4/TiO_2 catalysts is studied based on density function theory and the corresponding experiments for low-temperature SCR of NO_x by ammonia. The SCR performances of the Mn_3O_4/TiO_2 catalysts prepared by joint precipitation method were systematically carried out in the temperature range of 90–300 °C. The results show that nitrogen oxide can first adsorb on the manganese-terminal to form nitrates species, and then NH_3 are more inclined to adsorb on Brønsted acid sites. Bridging nitrate and bidentate nitrate can be turned into monodentate nitrates, and NH_4^+ was formed when there is ammonia and water molecules because the adsorption and dissociation of the water on the surface of the catalyst is the main source of hydroxyl groups. It is indicated that L-H mechanism plays a major role in NH_3-SCR process.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Selective catalytic reduction (SCR) of nitrogen oxide with ammonia has already been applied for removing NO_x from stationary sources [1] in a cement kiln recently. Commercial SCR catalysts is mainly based on vanadium-based/TiO_2 [2]. This kind of catalyst generally shows a high catalytic activity in the high temperature range. However, SCR reactor is usually placed downstream of dust removal and desulfurization device where the gas temperature is lower than the optimum temperature in catalytic reaction [3]. Therefore, it is necessary to develop a catalyst which shows high SCR activity in low temperature range.

Manganese oxide has been demonstrated to contain a mass of lattice oxygen, which is the key to the catalytic reaction [4]. Donovan made a series of catalytic activity experiments to compare the influence on different component through trying to add different transition metals on titanium dioxide support [5]. It turned out that manganese shows superior low-temperature performance among the most of the transition metal. There have been a lot of experimental and theoretical studies of the adsorption of small molecules on different TiO_2 phases. In recent years, in-depth study indicated that catalytic activity of (0 0 1) surface is the highest in other surfaces and it plays a key role in chemical reaction [6–8].

Many theoretical researchers have investigated V_2O_5/TiO_2 catalysts by the DFT method. Zhang aimed at elucidating the SCR catalytic activity when F or W species doping on V_2O_5/TiO_2 catalyst [9,10]. The interaction of different molecules, such as water [11,12], gas molecules [13,14], alkali metal [15], Hg oxidation [16] and formaldehyde [17] on V_2O_5/TiO_2 catalyst has been investigated. Fang [18] studied NH_3 adsorptions on the Mn_2O_3 (2 2 2), Mn_3O_4 (2 1 1) and MnO_2 (1 1 0) surfaces. Alkali poisoning on Mn doping on TiO_2 catalyst based on experimental and theoretical study was reported by Guo et al. [19]. However, little attention was paid to manganese-base/TiO_2 catalyst until recently. In this study, based on density functional theory (DFT) and DRIFTS method, the change of the catalyst properties were investigated when NH_3 and NOx molecules adsorbed on the Mn_3O_4/TiO_2 catalyst. The analysis of adsorption distance, adsorption energy and density of states were investigated, in order to provide the theoretical foundation over manganese-base catalyst on low temperature in further study.

2. Computational models and methods

2.1. Catalysts preparation

The catalysts were prepared by joint precipitation method. Specifically, urea solution, ammonia (25 wt.%) and hydrogen peroxide as precipitant were added to the mixture of manganese acetate and titanyl sulfate (donated as Mn/TiO_2). The MnOx catalyst was adopted the same method that we added the same precipitant mixture to manganese acetate. The mixture was collected after

cleaning in ethanol for four times and the samples was dried at 105 °C for 12 h. Finally, the catalysts were calcined at 300 °C for 3 h.

2.2. Catalyst characterization

The crystallographic structures of the as-prepared catalytic materials were characterized by X-ray diffraction method on a Shimadzu XRD-7000 diffractometer, (Shimadzu, Japan) using Cu Kα (λ = 1.5406 Å) radiation source. Temperature programmed desorption (TPD) is performed by ChemBET Pulsar TPR/TPD (Quantachrome, American) chemical adsorption analyzer. The samples for TPD analysis first pretreated in high purity He at 550 °C for 1 h, and then cooled to 120 °C with high purity NH$_3$ for half an hour. NH$_3$–TPD was analyzed after raised up to 700 °C at a heating rate of 10 °C min^{-1}.

In-situ DRIFTS was measured by a VERTEX 70 (Bruker, Germany) spectrometers at 4 cm^{-1} resolution with 8000–50 cm^{-1} spectral range. The reaction temperature was controlled by a Pike temperature controller. The reaction conditions were controlled as follows: 500 ppm NO, 500 ppm NH$_3$ and N$_2$ balance.

2.3. Calculation details

All DFT calculations were carried out using modeling DMol^3 from Material Studio [20]. Double-numerical quality basis set with polarization functions (DNP) and GGA-PW91 was used. Comparable to the 6-31G** Gaussian basis set [21], a more accurate double-numerical quality basis set with polarization functions (DNP) was used. [22]. The Perdew–Wang 91 (PW91) form was used for the generalized gradient approximation (GGA) for the exchange and correlation potential [23].

We chose TiO$_2$ (001) supercell layer structure as the carrier model and select a repeating unit of Mn$_3$O$_4$ crystal cell molecular for active substances setting up Mn$_3$O$_4$/TiO$_2$ catalyst reaction model. The Mn$_3$O$_4$/TiO$_2$ model contains 39 atoms. A periodic boundary condition was employed to model this slab, and the area of the surface was 7.552 Å × 7.552 Å. Six atom layers were used to simulate the (001) surface. The vacuum region was set to 1.0 nm in order to avoid the interference between layer and layer. The whole support consists of three atomic layers to ensure that calculation will not too big on the premise of a certain accuracy, on top of which Mn$_3$O$_4$ is deposited. All of the atoms in the gas and adsorption substrate were allowed to relax during the optimization process, except for the bottom two layers. The adsorption energy (Eads) was calculated as follows:

$$Eads = E(Mn_3O_4/TiO_2\text{-gas}) - E(Mn_3O_4/TiO_2) - E(gas)$$

$E(Mn_3O_4/TiO_2\text{-gas})$ is the total energy of adsorption substrate and gas, while $E(MnOx)$ and $E(NH_3)$ are the energies of free gas and Mn$_3$O$_4$/TiO$_2$ surface, respectively. If Eads is negative values, indicating that there is strong interaction between adsorption substrate and gas.

2.4. Activity measurements

NH$_3$-SCR activity tests were carried out over 3 mL catalyst in a self-made fixed-bed quartz reactor. The reactant conditions were as follows: 1000 ppm NO, 1000 ppm NH$_3$, 5% O$_2$ and N$_2$ balance and gas hourly space velocity (GHSV) was 27,000 h^{-1}. The inlet and outlet concentrations of NO and NO$_2$was measured by the NO–NO$_2$–NO$_x$ Model 42i-HLinstrument (Thermo, USA). NOx conversion was calculated as follows:

$$X_{NOx} = 100\% \times (1 - [NOx]_{out}/[NOx]_{in})$$

$$[NOx] = [NO] + [NO_2]$$

3. Results and discussion

3.1. XRD and NH$_3$–TPD analysis

XRD patterns of Mn/TiO$_2$ catalyst shown in Fig. 1, indicated that the peaks attributed to Mn$_3$O$_4$ and anatase TiO$_2$ [24]. Comparing the two kinds of catalysts, we found that the diffraction peak strength of Mn/TiO$_2$ catalyst declined, which showed that the combination between Mn$_3$O$_4$ and TiO$_2$ is helpful to reduce the crystallinity. The partial MnOx distributed in the catalyst appeared as amorphous state, largely improved the dispersion of manganese. The type and amount of active sites of the catalyst surfaces play a vital role in the NO conversion of the catalysts. Fig. 2 shows NH$_3$–TPD and NO conversion curves for MnOx and Mn/TiO$_2$ catalysts. One broad desorption peak in 150–500 °C is attributed to MnOx and Mn/TiO$_2$, owing to NH$_3$ desorbed by weak acid sites and Brønsted acid sites. The peak in 600–700 °C is due to NH$_3$ molecules adsorbed by Lewis acid sites [25]. In contrast, MnO$_x$ catalyst of Fig. 2 showed a decreased activity first with the increase of temperature, which agrees well with the results of NH$_3$–TPD. Thus, we can infer that the reaction temperature range is related to weak acid and Brønsted acid sites.
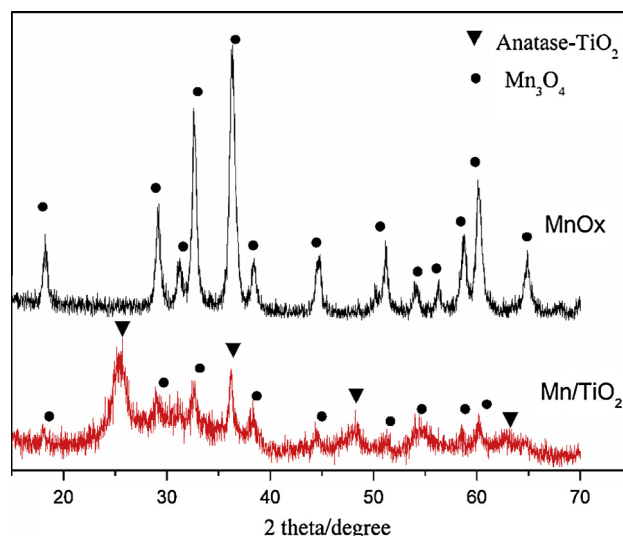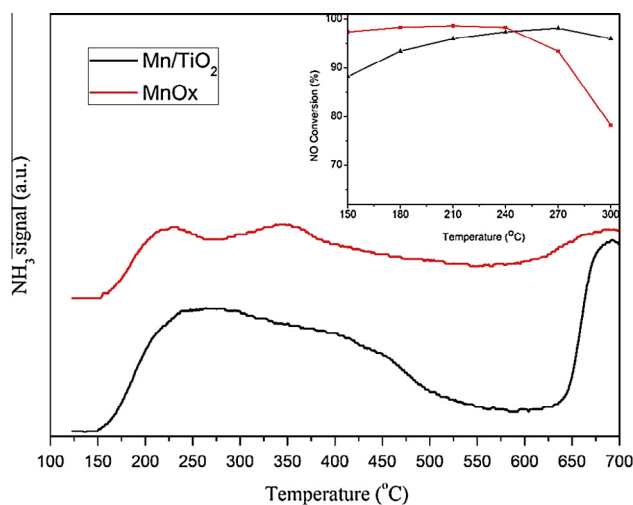

Fig. 1. XRD patterns of MnO$_x$ and Mn/TiO$_2$ catalyst.

Fig. 2. NH$_3$–TPD profiles and NO conversion of MnO$_x$ and Mn/TiO$_2$ catalyst.