De-reducibility mechanism of titanium on maghemite catalysts for the SCR reaction: An *in situ* DRIFTS and quantitative kinetics study

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ABSTRACT

An environmental benign TiO_2 doped maghemite catalyst, the γ-$Fe_{95}Ti_5$, was prepared via the precipitation microwave pyrolysis method for the NO_x removal. The γ-$Fe_{95}Ti_5$ exhibited significantly higher catalytic activity and better N_2 selectivity than the pure maghemite, γ-$Fe_{100}Ti_0$. The SCR active window of the catalyst is broadened and the resistances to H_2O and SO_2 are also preserved. Ti^{4+} cations could enter the lattice of γ-$Fe_{100}Ti_0$, forming the partial solid solution on the catalyst surface, as γ-$Fe_{2-\zeta}Ti_\zeta O_{3+\xi}$. This structure improves the quantity and stability of both Lewis and Brönsted acid sites compared with the γ-$Fe_{100}Ti_0$. Meanwhile, the dopant cations suppress the reduction of Fe^{3+} and the percentage of active oxygen on the catalyst surface. These could suppress the N_2O formation from NH_3 oxidation and NO_x reduction. By the combination of both DRIFTS and kinetic methods, the rate constants of the γ-$Fe_{95}Ti_5$ catalyst via the Eley-Rideal and Langmuir-Hinshelwood mechanisms increase simultaneously, while the rate constant via the catalytic oxidation of NH_3 decreases compared with the γ-$Fe_{100}Ti_0$.

1. Introduction

The removal of NO_x has attracted the world-wide attentions due to the serious threat to human health and environment [1–3]. The selective catalytic reduction (SCR) of NO_x by NH_3 is one of the most efficient methods that has been widely applied in coal-fired power plant. Commercial V_2O_5-$WO_3(MoO_3)/TiO_2$ catalyst exhibits high activity at standard working temperatures (350–420 °C) [4–6]. However, there are still some inevitable disadvantages, such as the toxicity of V_2O_5 and secondary pollution caused by fly ash at high temperatures [7]. Furthermore, the relative narrow active window restricts its utilization in the industry boilers and waste incineration. Thus, it is necessary to develop the SCR catalyst with high activity in a wider temperature window.

A series of transitional and rare-earth metals have been adopted as active components and/or additions during the catalyst design because of their appropriate reducibility and surface acidity [8–13]. Iron exhibits great potentials for the SCR catalyst due to its accessibility and good activity. Maghemite, as a non-stoichiometric iron oxide, was used in catalytic oxidation for its excellent reducibility and oxygen storage-release ability. It can be considered as an Fe(II)-deficient magnetite with formula $(Fe_8^{III})_A[Fe_{40/3}^{III}\circ_{8/3}]_BO_{32}$ where $\circ$ represents a cations vacancy, A and B indicates tetrahedral and octahedral positioning respectively. Part of Fe^{3+} (convert from Fe^{2+} in magnetite) are metastable, which are easily reduced to Fe^{2+} [14,15]. However, it was not an appropriate iron-based catalyst for the SCR reaction due to its excessive reducibility and unstable surface acidity. Therefore, many researchers tried to modify the stability and acidity of this catalyst by cations doping method.

The stability of metastable iron cations can be improved by depressing the electronegativity around them. Donor dopants (dopants with higher valence) can decrease the electronegativity around cations and enrich cation vacancies simultaneously [16,17]. It is predictable that when higher valence ions with larger ionic radius are incorporated into the lattice, at least two positive effects will be produced: (1) increasing the stability of adjacent ions; (2) emerging more cation vacancies. Titanium is a perfect donor dopants and has a high valence stability in the SCR reaction. Moreover, Ti^{4+} cations exhibit great surface acidity and are independent of the redox cycle. The ionic radius of 6 coordinated Ti^{4+} (0.745 Å) is close to that of Fe^{3+} (0.69 Å). Thus, Ti^{4+} is supposed to be a good dopant for balance the reducibility and surface acidity of maghemite.

Kinetic study is an important way to guide the design of catalysts. However, there is still a lack of rigorous demonstration for the exact path of the SCR reaction over maghemite [18,19]. The quantitative

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studies should solve the contributions, rate-determining steps and key factors of the Eley-Rideal mechanism (E-R mechanism, adsorbed NH_3 reacts with gaseous NO), Langmuir-Hinshelwood mechanism (L-H mechanism, adsorbed NH_3 reacts with adsorbed NO), and Catalytic-Oxidation reaction (C-O reaction). Nevertheless, the C-O reaction was not yet taken into account during the former kinetic study of NO reduction over iron-based catalysts [20–22].

This work attempts to investigate the SCR performance and intrinsic properties over maghemite catalysts. The novel γ-$Fe_{95}Ti_5$ catalyst has high SCR activity, N_2 selectivity, thermal stability and H_2O/SO_2 durability. A global quantitative kinetic study over maghemite catalysts was studied by the steady-state kinetic experiments.

2. Experimental

2.1. Catalyst preperation

Maghemite catalysts were prepared via precipitation microwave pyrolysis method using $FeSO_4 \cdot 7H_2O$ and $Ti(SO_4)_2$. NH_4OH was used as precipitator. The precursors were first dissolved into deionized water, in which the total concentration of cation was 0.1–0.5 $mol \cdot L^{-1}$. The mixed solution was stirred at 20 °C for 1 h. Then, NH_4OH was introduced into the mixed solution until the pH of the solution reached 9–10. Without aging, the precipitate was filtered washing with deionized water for certain times, followed by heat treatment with microwave assisted. After that, the precipitate was desiccated at 105 °C for 12 h and then calcined at 375–425 °C for 5 h under air atmosphere. The calcined samples were crushed and sieved to a size of 40–60 mesh for catalytic activity test. The maghemite catalysts were denoted as the γ-$Fe_{100}Ti_0$ and γ-$Fe_{95}Ti_5$, where the number represents the mole percent of the corresponding elements.

2.2. Catalyst characterization

The crystalline phase of catalysts was measured by powder X-ray diffraction (XRD) using a Rigaku D/MAC/max 2500 v/pc diffractometer (Japan, Cu K_α as radiation resource, λ = 0.15406 nm) with a nickel filter operating at 50 kV and 150 mA in the 2θ range of 10–90° at a scanning rate of 4°·min^{-1}. The diffraction lines were identified by matching with reference patterns in the JCPDS database.

N_2 adsorption-desorption isotherms over maghemite catalysts were obtained at −196 °C using Micromeritics ASAP2020 Surface Area and Porosity Analyzer. Prior to N_2 physisorption, the catalysts were degassed at 300 °C for 5 h. Average pore diameters, pore volumes and pore size distributions were determined by Barrett-Joyner-Halenda (BJH) method from the desorption branches of the isotherms. Surface areas were determined by Brunauer-Emmertt-Teller (BET) equation in 0.05–0.35 partial pressure range. Textural properties of micropores were calculated using t-plot model.

The chemical states of surface compositions were observed by X-ray photoelectron spectra (XPS) recorded using a Kratos' Axis Ultra DLD photoelectron spectrometer. Wide spectrum test conditions were Pass energy: 160 eV, Anode: Mono (Al, 112 W), Step (meV): 1000.0, Dwell Time (ms): 150. Fine spectrum test conditions were Pass energy: 40 eV, Anode: Mono (Al, 112 W), Step (meV): 100.0, Dwell Time (ms): 600. Binding energies were calibrated using C 1 s (BE = 184.8 eV) as a standard.

The thermal stability of maghemite catalysts was analyzed utilizing thermogravimetric-derivative thermogravimetric (TG-DTG) recorded on a TGA/SDTA 851e (Mettler-Toledo, Co., Ltd, Switzerland). The samples were weighted to 10 ± 0.1 mg in an aluminum oxide ceramic crucible with depth of 5 mm and inner diameter of 5 mm, and heated from 25 °C to 325 °C at 10 °C·min^{-1} under N_2 flow (with the concentration of 99.99%) of 40 mL·min^{-1}. The protection gas is 30 mL·min^{-1} of N_2, with the concentration of 99.99%.

Hydrogen-temperature programmed reduction (H_2-TPR) was carried out on a Micromeritics' Chemisorb 2720 TPx Chemisorption Analyzer calibrated using Ag_2O. The catalyst samples (30–40 mg) were pretreated at 500 °C for 30 min in Ar gas (50 mL·min^{-1}) and then cooled down to 50 °C. The measurement was carried out at the temperature range of 50 − 1100 °C, in the steam of 10 vol.% H_2/Ar, with a heating rate of 10 °C·min^{-1}.

Temperature programmed desorption of ammonia (NH_3-TPD) was performed on the chemisorption analyzer of Micromeritics' AutoChem 2920. The catalyst samples (90 mg) were first pretreated at 300 °C for 1 h in Ar gas and then cooled down to 50 °C. After that, the samples were exposed to 10 vol.% NH_3/He for 30 min at 50 °C, followed by Ar purge for another 1 h at 100 °C. Finally, the temperature programed desorption was run to 700 °C in Ar flow with heating rate of 5 °C·min^{-1}.

In situ DRIFT spectra were recorded on a Fourier Transform Infrared Spectrometer (FTIR, Nicolet NEXUS 870) equipped with a liquid-nitrogen-cooled MCT detector, collecting 100 scans with a resolution of 4 cm^{-1}.

2.3. Catalyst acticity measurement

The SCR activity over the maghemite catalysts were measured in a fixed-bed quartz reactor. The test was carried out under atmospheric pressure at the temperature range of 100–350 °C. The total flow rate was 200 mL·min^{-1} responding to the GHSV of 60,000·mL·g^{-1}·h^{-1}. The typical reactant gas composition was as follows: 500 ppm NH_3, 500 ppm NO, 3 vol.% O_2, 200–800 ppm SO_2 (when used), 5/10 vol.% H_2O (when used) and balance N_2. The concentrations of the gases (NO, NO_2, N_2O, and NH_3) were continually monitored by an FTIR spectrometer (MultiGas TM 2030 FTIR Continuous Gas Analyzer). And the data was recorded only when the SCR reaction reached the steady state after 30 minutes of continuous and stable operation running at each measuring temperature. As the SCR reaction reached the steady state, the ratio of NO_x conversion (η), N_2O selectivity (S) and the pseudo-first order rate constant (τ) of the SCR reaction were calculated according to the following equations:

$$\eta = \frac{[NO_x]_{in} - [NO_x]_{out}}{[NO_x]_{in}} \times 100\% \tag{1}$$

$$S = \frac{2[N_2O]_{out}}{[NH_3]_{in} + [NO_x]_{in} - [NH_3]_{out} - [NO_x]_{out}} \times 100\% \tag{2}$$

$$\tau = -\frac{V}{W} \times \ln(1 - \eta) \tag{3}$$

where $[NO_x]_{in}$ and $[NO_x]_{out}$ were the concentrations of gaseous NO_x in the inlet and outlet, respectively; $[N_2O]_{out}$ was the concentration of gaseous N_2O in the outlet; V was the total flow rate; and W was the mass of catalyst (g).

3. Results and discussion

3.1. SCR performance

3.1.1. SCR activity

Fig. 1 shows that doping of 5% titanium has a considerable impact on the NH_3-SCR reaction over maghemite catalyst. The γ-$Fe_{95}Ti_5$ showed a good SCR activity in the range of 250–300 °C (NO_x conversion was higher than 80%). Whereas the NO_x conversion of the γ-$Fe_{100}Ti_0$ was only about 40% at 250 °C, and further decreased above 300 °C. The outlet NO_x concentration of the γ-$Fe_{100}Ti_0$ was even higher than the inlet data at 350 °C (shown in Fig. 1a), and the NO_x conversion was lower than the NH_3 conversion above 300 °C. The results suggest that part of NH_3 was directly oxidized to NO with O_2 on the γ-$Fe_{100}Ti_0$ catalyst. High percentage of N_2O formed on the γ-$Fe_{100}Ti_0$ above 150 °C. In contrast, the γ-$Fe_{95}Ti_5$ catalyst showed excellent N_2 selectivity (close to 100%) in the range of 250–300 °C. Compared with the