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Improved activity of W-modified MnO_x–TiO_2 catalysts for the selective catalytic reduction of NO with NH_3

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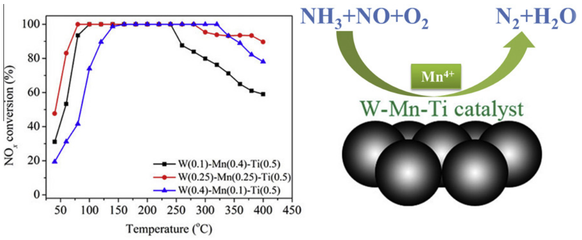
HIGHLIGHTS

- The W(0.25)–Mn(0.25)–Ti(0.5) catalyst showed the best SCR activity.
- The W(0.25)–Mn(0.25)–Ti(0.5) catalyst had a wide temperature window of 60–400 °C.
- The W(0.25)–Mn(0.25)–Ti(0.5) catalyst can tolerate the impact of a high GHSV.
- The mechanism of the SCR reaction was proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

The performances of a series of W-modified MnO_x–TiO_2 catalysts were investigated for selective catalytic reduction (SCR) of NO_x with NH_3. The catalyst prepared by one-pot co-precipitation method with an elementary ratio of W:Mn:Ti = 0.25:0.25:0.5 in raw materials showed a highest activity and a widest operation temperature window with 100% NO_x conversion within 80–280 °C. We suggest that the enhancement in reducibility of manganese and dominant active Mn^{4+} species is likely one predominant factor accounting for the excellent SCR performance of the best catalyst. *In situ* FTIR studies revealed that after W doping, more Brønsted and Lewis acid sites formed on the catalyst surface, as well as more active intermediates (monodentate nitrate) during reaction, are also responsible for the high activity both at low and medium temperatures.

1. Introduction

As a major air pollutant, nitrogen oxides (NO_x) have caused serious environmental problems such as ozone depletion, acid rain and photochemical smog. The selective catalytic reduction (SCR) with NH_3, as a well established technique, has been widely applied in the control of NO_x emissions from stationary sources for its high efficiency and low cost. The most commonly used commercial V_2O_5–WO_3/Mo_2O_3–TiO_2 catalyst shows good activity and selectivity at high temperatures (300–400 °C) [1–5]. However, owing to its narrow temperature window and poor activity in the low temperature range, the SCR reactor has to be placed upstream of particle removal and desulfurization devices. As a result, the catalyst is easily deactivated by SO_2 and alkaline metals from dust during practical operation. Therefore, the developing desire of catalysts which perform well in the region of low temperature has grown increasingly urgent recently.

Generally, composites of transition metal oxides present good SCR activity at low temperatures, and manganese-containing catalysts are regarded as a most active one [6–9]. The pure manganese oxides without any supports were reported to show high activity at

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relatively low temperature by Kapteijn et al. for the first time in 1994 [6]. Kang et al. investigated the effect of precipitants on the low-temperature activity of manganese oxide in NH_3–SCR reaction, and interpreted that carbonate is beneficial to the adsorptive property of catalyst with NH_3 [7]. Recently, Wan et al. found that bimetallic oxide of Ni–Mn catalyst showed 100% NO conversion from 120 to 240 °C, owning to the high surface concentration of Mn^{4+} and Lewis acid sites [10]. Additionally, it has been noticed by Liu et al. that molecular tailoring of surface chemisorbed oxygen over $Fe_aMn_{1-a}TiO_x$ catalyst could also improve the activity by facilitating oxidation of NO to NO_2, and thus leads to the so-called "fast SCR process" [11].

Tungsten has been proven to be a promoter to raise the activity and stabilize the active phase, and it has been widely reported that W could help stabilize the anatase phase of TiO_2 in the V_2O_5–WO_3–TiO_2 catalyst [12–14]. In addition, tungsten could also increase the surface acidity and the amount of active sites. Shan et al. reported that due to the increase of the amount of Brønsted and Lewis acid sites caused by the introduction of W, Ce–W–Ti catalyst exhibited excellent NH_3–SCR activity with broad operation temperature window [15]. Si et al. found that the formation of mixed bonds of Cu^{n+}–O_2–W^{n+} helped create more nitrite and enhance the Brønsted acidity, thus further raising the activity of the catalyst for NH_3–SCR reactions [16].

Considering that doping metals could facilitate NO_x conversion of the manganese oxide-based catalysts [17], with the aim of obtaining more efficient NH_3–SCR catalyst working at low temperatures, we developed a novel catalyst of W(0.25)–Mn(0.25)–Ti(0.5) mixed oxide in this work by employing one-pot co-precipitation strategy. The obtained catalyst featured favorably high activity and relatively wider temperature window. The physic-chemical properties, phase structures and surface properties of the catalysts were investigated by N_2 adsorption–desorption, XRD, H_2-TPR and XPS to reveal the role of W additive. In addition, *in situ* FTIR technique was also employed to identify the adsorption acid sites and reaction mechanisms.

2. Experimental

2.1. Catalyst preparation

A series of W–Mn–Ti mixed oxide catalysts with different molar ratios were prepared by one-pot co-precipitation method. $Mn(CH_3COO)_2{\cdot}4H_2O$, $(NH_4)_6H_2W_{12}O_{40}{\cdot}5H_2O$ and $Ti(SO_4)_2{\cdot}2H_2O$ were used as precursors and dissolved in distilled water under stirring for half an hour. $(NH_4)_2CO_3$ was used as the precipitator, which is prepared in advance with the concentration of 1 mol/L. The aqueous solution of $Mn(CH_3COO)_2{\cdot}4H_2O$, $(NH_4)_6H_2W_{12}O_{40}{\cdot}5H_2O$ and $Ti(SO_4)_2{\cdot}2H_2O$ accompanied with the solution of $(NH_4)_2CO_3$ were added simultaneously to a beaker with continuously stirring at room temperature, keeping the pH at 10 during the whole dripping process. The suspension obtained from precipitation was centrifuged and washed with deionized water, followed by drying overnight at 80 °C and then calcined at 400 °C for 6 h in static air. The obtained catalysts were denoted as W(x)–Mn(y)–Ti(z), where x, y and z stands for the molar ratio of W/(W + Mn + Ti), Mn/(W + Mn + Ti) and Ti/(W + Mn + Ti) in the raw materials. W–Ti and Mn–Ti catalysts were also prepared by the same preparation method as described above for comparison. Their mechanical mixture was obtained according to the exact composition of the sample W(0.25)–Mn(0.25)–Ti(0.5).

2.2. Catalyst characterizations

Physical adsorption of N_2 was performed on an NOVA 1200 (Quanta Chrome) instrument at −196 °C. All samples were degassed at 300 °C for 4 h prior to the measurement. The Brunauer–Emmett–Teller (BET) surface areas of the catalysts were calculated by using the BET method. Pore volume and average pore diameters were determined from desorption branch of the isotherms by the BJH method. XRD analysis were carried out on a Rigaku D/Max2550VB/PC X-ray powder diffractometer equipped with Cu Kα radiation ($\lambda = 0.154056$ nm) scanned between 20° and 80° with the step size of 0.02°. Hydrogen temperature programmed reduction (H_2-TPR) was conducted on a Chembet PULSAR TPR/TPD (p/n 02139-1) in order to study the reducibility of catalysts. Prior to the measurement, the samples (50 mg) were pretreated at 350 °C in a flow of He stream for 30 min and cooled down to the room temperature. Afterward, the temperature was raised linearly to 900 °C at a heating rate of 10 °C/min in a stream of 10 vol.% H_2/Ar. H_2 consumption was monitored online by TCD detector. X-ray photoelectron spectra (XPS) were collected on a Multilab 2000 electron spectrometer using a monochromatic Al Kα X-ray source ($h\nu = 1486.6$ eV). Binding energies of Mn2p, and O1s were calibrated using C1s (BE = 284.8 eV) as a standard. The obtained spectra were deconvolved using Lorentzian–Gaussian functions with a Shirley background.

The *in situ* FT-IR experiments over W(x)–Mn(y)–Ti(z) catalysts were performed on an FTIR spectrometer (VERTEX 70-FT-IR, Bruker). In a typical experiment, the samples (20 mg) were pretreated in a He stream at 350 °C for 30 min and cooled down to the desired temperature. The background spectrum was collected in flowing He and was automatically subtracted from the sample spectra. Then $NH_3/(NO + O_2)$ was introduced to the cell with a total flow of 50 ml/l (with He as balance) for 30 min at different temperatures followed by He purging for another 30 min until the spectra were unchanged. Finally, $(NO + O_2)/NH_3$ was introduced to react with pre-adsorbed NH_3/NO_x species. The reaction conditions were set as follows: 1000 ppm NH_3, 1000 ppm NO, 5 vol.% O_2 and He as the balance. All spectra were recorded by accumulating 64 scans with 4 cm^{-1} resolution, in the wavenumber range of 4000–400 cm^{-1}.

2.3. Catalyst activity test

The SCR activities of the catalyst samples were measured using a U-shaped quartz fixed-bed reactor at 40–400 °C with catalyst sieved to 20–40 mesh. The reaction conditions were set as follows: 50–200 mg of catalyst, 1000 ppm NH_3, 1000 ppm NO, 5 vol.% O_2, 100 ppm SO_2 (when used), 10 vol.% H_2O (when used), and He as balance, the total gas flow rate was 100 ml/min, and the corresponding gas hourly space velocity (GHSV) was 25,000–100,000 h^{-1}. The concentrations of NO and NO_2 were measured using a chemiluminescence gas analyzer (Testo 350). All data were collected after 20–60 min at the desired temperature in order to achieve a steady-state reaction condition. The NO_x conversion was calculated by the following equation:

$$NO_x\ \text{conversion}\ (\%) = \frac{[NO_x]_{in} - [NO_x]_{out}}{[NO_x]_{in}}$$

where NO_x was the sum of NO and NO_2, and the subscripts "in" and "out" denoted the inlet and outlet gas concentrations of NO_x, respectively.

3. Results and discussion

3.1. NH_3–SCR performance

Fig. 1 shows the activity of the prepared catalysts during NH_3–SCR reaction depending on temperatures, and the GHSV was controlled under the condition of 25,000 h^{-1}. As presented in Fig. 1a,