Applied Catalysis A: General 505 (2015) 235–242

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Synthesis, characterization and catalytic performance of $FeMnTiO_x$ mixed oxides catalyst prepared by a CTAB-assisted process for mid-low temperature NH_3-SCR

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ARTICLE INFO

Article history:
Received 23 June 2015
Received in revised form 2 August 2015
Accepted 5 August 2015
Available online 7 August 2015

Keywords:
NH_3-SCR
$FeMnTiO_x$ mixed oxides
CTAB-assisted
Calcination temperature
Operating temperature window

ABSTRACT

A series of $FeMnTiO_x$ mixed oxides catalysts, which were synthesized by a CTAB-assisted co-precipitation process and calcined at different temperatures, were investigated for selective catalytic reduction of NO with NH_3 in the presence of excess O_2. The samples were characterized by means of N_2-physisorption, XRD, TEM, H_2-TPR, XPS, NH_3-TPD, and *in situ* DRIFTS technologies. The results indicated that the activities of samples were not predominately determined by BET specific surface area. Compared with amorphous TiO_2, the anatase TiO_2 crystalline phase was more conducive to enhance the electron interaction between manganese species and support: $Mn^{4+} + Ti^{3+} \leftrightarrow Mn^{3+} + Ti^{4+}$. NH_3 was easier to be activated on the surface of samples which had lower binding energy of lattice oxygen in selective catalytic reduction of NO with NH_3. The addition of CTAB not only promoted the formation of anatase TiO_2 crystalline phase and Lewis acid sites, but also improved the dispersion extent of active phase on the surface of samples. Thus, it enhanced the catalytic performance of samples. In addition, calcination temperature had an important influence on the valence state of manganese species, as well as the dispersion extent of active phase and the crystal phase structure of support. The sample calcined at 400 °C showed excellent low-temperature activity and mid-temperature N_2 selectivity. The NO conversion and N_2 selectivity of this sample were above 90% in the range of 150–350 °C at a space velocity of 30,000 mL g^{-1} h^{-1}. Furthermore, it exhibited sulfur tolerance and water resistance to a certain extent.

1. Introduction

Atmospheric contaminant elimination have been an important research topic in recent years. Nitrogen oxide (NO_x), which is emitted from stationary sources (e.g., flue gases from coal-fired power plants) and mobile sources (e.g., vehicle exhausts), is one of the major air pollutants. It can cause photochemical smog, acid rain, ozone depletion and greenhouse effect [1]. Stationary sources emissions are the significant source of NO_x, and many methods and technology have been carried out in applied and fundamental researches on denitrification ($deNO_x$) in this field [2]. Among them, selective catalytic reduction of NO_x with NH_3 in the presence of excess O_2 (NH_3-SCR) is to date the most effective and widely used method for $deNO_x$ from stationary sources. And the general NH_3-SCR reaction is: $4NO + 4NH_3 + O_2 = 4N_2 + 6H_2O$ [3]. Commercial $deNO_x$ technology, which employed $V_2O_5 - WO_3(MoO_3)/TiO_2$ as catalyst, have exhibited excellent catalytic performance in NH_3-SCR reaction in the temperature range of 300–400 °C [4]. However, some disadvantages still need to be solved. Among them, narrow operating temperature window is one of the main disadvantage for its practical application, especially the mid-temperature N_2 selectivity and the low-temperature activity are unsatisfactory. Furthermore, V_2O_5 is easy to sublimate in the operating process, and further generate biological toxicity when it entered into the environment [5,6]. Hence, many efforts have been made to develop novel non-vanadium-based catalysts, which should have merits of excellent low-temperature catalytic performance, wide operation temperature window and environment friendly.

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http://dx.doi.org/10.1016/j.apcata.2015.08.009
0926-860X/

In recent years, manganese-based catalysts have attracted more attention for its excellent low-temperature activity in NH_3-SCR reaction. However, it is difficult to be applied in mid-temperature deNO$_x$, because of narrow operating temperature window and poor selectivity especially in medium temperature zone. Many groups modified the manganese-based catalysts by metal oxides (such as iron, cerium, copper and the like), and the low-temperature activity and/or mid-temperature selectivity could be improved greatly [7–11]. In present work, a different method was used to prepare catalysts and improve the mid-low temperature catalytic performance in NH_3-SCR.

Cationic surfactant cetyltrimethyl ammonium bromide (CTAB) can release cations in aqueous solution. In our previous work, FeMnTiO$_x$ mixed oxides catalyst, which was synthesized by a CTAB-assisted co-precipitation process and calcined at 500 °C, showed excellent low-temperature performance in NH_3-SCR reaction [12]. However, the N_2 selectivity at medium temperature could not meet the requirements of deNO$_x$. It was reported that the structure and valence state of the active phase, which could be adjusted by changing the calcination temperature, had a great influence on the catalytic performance [13–15]. Thus, different calcination temperatures were employed to prepare samples and investigate catalytic performance in NH_3-SCR reaction. In order to further investigate the effect of CTAB on the catalytic properties, the sample prepared without CTAB was used to compare. The obtained sample, which had been synthesized by a CTAB-assisted co-precipitation process and calcined in 400 °C, further improved the selectivity in mid-temperature and the activity in low-temperature. It not only expanded the operating temperature window, but also avoided the use of vanadium-based catalysts. These samples were characterized by means of N_2-physisorption, XRD, TEM, H_2-TPR, XPS, NH_3-TPD, and *in situ* DRIFTS technologies to reveal the mechanism of its excellent catalytic properties.

2. Experimental

2.1. Catalysts synthesis

FeMnTiO$_x$(S) mixed oxides catalysts were prepared by inverse co-precipitation method. 3.64 g CTAB was added to 330 ml distilled water, then the solution was heated to 35 °C to ensure that the CTAB was dissolved. $Fe(NO_3)_3\cdot 9H_2O$, $Mn(AC)_2\cdot 4H_2O$, $Ti(SO_4)_2$ with suitable amount (mole ratio = 0.1:0.1:1.0) were dissolved in CTAB solution with subsequently stirring for 30 min. After that, the mixture was added dropwise to an ammonia solution (25 wt%) and the pH value of the final solution was maintained at 11. During the reaction, the system was continuously stirred at 300 rpm. 3 h later, the precipitate was separated by filtrating and washing with distilled water and absolute ethanol for 3 times atleast, respectively. Then the precipitate was collected and dried in an oven for 12 h at 110 °C. After that, the samples were calcined in muffle furnace in air condition at different temperatures for 6 h, and the heating rate was kept at 2 °C min^{-1}. Subsequently, the calcined samples were crushed and sieved to 40–60 mesh for characterization and activity test. For simplicity, the synthesized samples by CTAB-assisted were denoted as FMT(S)-*t* (*t* = 400, 500, 600). Likewise, FeTiO$_x$(S) (mole ratio = 0.1:1.0) and MnTiO$_x$ (mole ratio = 0.1:1.0) samples were also prepared by the same way at 500 °C. And they were denoted as FT(S)-500 and MT(S)-500. As a comparison, FeMnTiO$_x$ mixed oxides catalyst was prepared by the same way just without CTAB during preparation, and other steps were the same as FMT(S)-*t* sample. This sample was calcined in muffle furnace in air condition at 400 °C, for simplicity, it was denoted as FMT-400.

2.2. Catalytic performance measurements

The catalytic performance of these samples were measured under the following conditions: 500 ppm NO, 500 ppm NH_3, 5% O_2, 100 ppm SO_2 (when used), 3.5% H_2O (when used), and N_2 balance. In order to remove adsorbed water and carbon dioxide on samples, the samples (200 mg) were fitted in a quartz tube and pretreated in a high purified N_2 stream at 300 °C for 1 h. After that, the sample was cooled down to room temperature. Then the feed gases (O_2, NO and NH_3) were introduced and the sample adsorbed feed gases until it got saturated. Subsequently, the catalytic performance of samples were tested at different temperatures: increased to the aimed temperature at the rate of 10 °C min^{-1} and held the temperature for 15 min to get steady state; followed by recording data at aimed temperature, and tested per 25 °C until 375 °C. The whole process was done stepwise, and the reactions were carried out with a space velocity of 30,000 mL g^{-1} h^{-1}. The concentrations of NO, NH_3, NO_2, and N_2O were measured at 150 °C by a Thermofisher IS10 FTIR spectrometer which equipped with 250 mL volume gas cell. The gas path from the reactor to FTIR spectrometer was kept at 150 °C by heating to avoid the deposition of nitrite/nitrate and the dissolution of NH_3 in liquid H_2O. The NO conversion and N_2 selectivity were calculated as the following equations:

$$\text{NOconversion}(\%) = \frac{[\text{NO}]\text{in} - [\text{NO}]\text{out}}{[\text{NO}]\text{in}} \times 100.$$

$$\text{N}_2\text{selectivity}(\%) = \frac{[\text{NO}]\text{in} - [\text{NO}]\text{out} + [\text{NH}_3]\text{in} - [\text{NH}_3]\text{out} - [\text{NO}_2]\text{out} - 2[\text{N}_2\text{O}]\text{out}}{[\text{NO}]\text{in} - [\text{NO}]\text{out} + [\text{NH}_3]\text{in} - [\text{NH}_3]\text{out}} \times 100$$

2.3. Catalysts characterization

Textural characteristic of these samples were measured by N_2-physisorption at −196 °C on a Micromeritics ASAP-2020 analyzer, using the Brunauer–Emmet–Teller (BET) method to determine their specific surface area. The pore size distributions were calculated from the desorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) algorithm. Measured samples were degassed under vacuum at 90 °C for 1 h and 300 °C for 4 h before analyzing.

X-ray diffraction (XRD) patterns were measured on a Philips X'pert Pro diffractometer using Ni-filtered Cu Kα radiation (l = 0.15418 nm). The X-ray tube was operated at 40 kV and 40 mA. The intensity data were collected over a 2q range of 10–80°. The scan speed was set at 10° min^{-1} with a step size of 0.02°.

H_2-temperature programmed reduction (H_2-TPR) experiments were carried out in a quartz U-type reactor that connected to a thermal conductivity detector (TCD) with Ar–H_2 mixture (7.0% of H_2 by volume, 70 ml min^{-1}) as a reductant. Prior to the reduction, samples (50 mg) were pretreated in a high purified N_2 stream at 300 °C for 60 min and then cooled to room temperature. Then, the TPR profiles were recorded from 50 °C to target temperature at a rate of 10 °C min^{-1}.

X-ray photoelectron spectroscopy (XPS) analysis was performed on a PHI 5000 Versa Probe system, using monochromatic Al Kα radiation (1486.6 eV) operating at an accelerating power of 15 kW. Samples were outgassed at room temperature in a UHV chamber ($<5 \times 10^{-7}$ Pa) before the measurement. The charge effect of samples were compensated by calibrating all binding energies (BE) with the adventitious C1s peak at 284.6 eV. This reference gave BE values with accuracy at ±0.1 eV.