Research article

Eu-Mn-Ti mixed oxides for the SCR of NO_x with NH_3: The effects of Eu-modification on catalytic performance and mechanism

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ABSTRACT

A series of highly active de-no_x catalysts, Eu-modified MnO_x-TiO_2 (MnTiEu), was prepared by an inverse co-precipitation method. Their physiochemical properties were investigated by XRD, TEM, EDS, BET, XPS and H_2-TPR in detail, and their catalytic activities were evaluated by the selective catalytic reduction (SCR) of NO with NH_3. The results showed that the introduction of Eu with proper amount into MnO_x-TiO_2 can effectively restrain the crystallization process of MnO_x and TiO_2, enhance specific surface area, increase the concentration of both surface Mn^{4+} and chemisorbed oxygen species, improve the stability of Mn^{4+} and Mn^{3+}, reduce the amount of surface acid sites, enhance the strength of surface acid sites. The obtained MnTiEu-0.3 catalyst (the molar rate of Eu/Mn was 0.3 and the mole rate of Mn/Ti was 0.1) exhibited a 100% NO_x conversion activity in a wide temperature window from 180 to 390 °C and a 100% N_2 selectivity from 120 to 390 °C under a high space velocity of 36,000 h^{-1}. Furthermore, MnTiEu-0.3 catalyst presented stronger resistance to concurrent H_2O and SO_2 poison in comparison with MnO_x-TiO_2 catalyst without Eu addition. *In-situ* DRIFT spectra suggested that NH_3 can be adsorbed on both Lewis and Brønsted acid sites. For MnO_x-TiO_2 catalyst, both coordinated NH_3 species on Lewis acid sites and NH_4^+ species on Brønsted acid sites can react with gas-phase NO following E-R mechanism. As regards MnTiEu-0.3, the NH_3-SCR of NO follows both Eley-Rideal and Langmuir-Hinshelwood mechanisms, in which the Eley-Rideal mechanism is predominated.

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1. Introduction

Nitrogen oxides (NO_x, x = 1, 2), emission by high temperature combustion from power stations, industrial heaters, and diesel engines are one of the serious environmental issues. NO_x are harmful to human health, and can lead to a series of environmental problems, such as acid rain, photochemical smog, greenhouse effects and ozone depletion [1]. The selective catalytic reduction (SCR) with NH_3 has been proven to be the most effective and economic method for controlling NO_x emissions from stationary source [2], and V_2O_5-$WO_3(MoO_3)/TiO_2$ has been most popular commercial SCR catalyst used since 1970s [3]. Nevertheless, V_2O_5-based catalysts suffer from several problems, such as toxicity of vanadium, SO_2 oxidation to SO_3, over-oxidation of NH_3 to N_2O, high working temperature [4]. Because of the high working temperature, the catalysts have to be placed upstream of the dust removal system and desulfurization units to avoid costly heating the catalyst where the catalysts are susceptible to deactivation by dust accumulation and SO_2 poison [5,6]. Therefore, it is highly desired to develop SCR catalysts which are environmentally benign and can work at low temperature (<250 °C) with a wide working temperature window (150–450 °C) [7–9].

Due to its high low-temperature catalytic activity, manganese oxides (MnO_x) have been intensively studied for low temperature de-NO_x [10]. However, several problems, including thermal instability and poor resistance to H_2O and SO_2 poison remain to overcome [11]. Several strategies, such as modification by mixing with other metal oxides, doping with other ions [8,12], and dispersion on a high surface area support [13,14], have been employed to improve the de-NO_x activity of MnO_x catalyst. Rare earth metals with incompletely occupied 4f and empty 5d orbitals are often used as active catalyst component or catalyst promoters [15]. It has been demonstrated that, by mixing CeO_2 with MnO_x, the de-NO_x performance of MnO_x, including catalytic activity, thermal stability and resistance to H_2O and SO_2 poison can be greatly enhanced [16–18]. Recently, Meng et al. showed that, by addition of small amount Sm to MnO_x (Sm/Mn = 0.1) [19], low temperature activity of MnO_x can be further improved, and more importantly, the modification by Sm also increased the stability of the MnO_x catalyst against H_2O and SO_2 poison. TiO_2 is a key component of commercial V_2O_5 class catalyst [20]. A new class of low temperature catalyst based on MnO_x and TiO_2 mixture oxides or TiO_2 supported MnO_x is emerging

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[3,13,21]. For example, Wu et al. prepared a MnO_x/TiO_2 catalyst capable of removal of NO at an efficiency > 90% at 150 °C [22]. Recently, several papers reported that the catalytic activity of MnO_x/TiO_2 can be further improved by modification with the third ions, such as Ce, Fe, and Ni [23–25]. A report showed that, by modification with Ce, the catalytic activity of MnO_x/TiO_2 was significantly enhanced from 39% NO conversion to 84% at 80 °C at a GHSV of 40,000 h^{-1} [26]. Wu et al. prepared a Fe modified MnO_x/TiO_2 catalyst, which presented a NO conversion activity of nearly 100% from 100 to 350 °C with a N_2 selectivity of 80% from 75 to 200 °C [27]. Therefore, the modification of MnO_x/TiO_2 with the third component would be a promising strategy to obtain $deNO_x$ catalysts with high activity and N_2 selectivity.

Europium (Eu) is an important rare earth element, for many applications including laser materials, phosphors, magnetic materials, and catalysts [28]. Recently, it has been found that Eu doping greatly improved the photocatalytic efficiency of TiO_2 due to the fact that Eu doping leads to the formation of surface oxygen defects, which serve as trap states to minimize recombination of charge carriers [29]. We have prepared Eu and N-codoped TiO_2 microspheres with high visible-light photocatalytic activity and found that Eu could capture and redeliver photo-generated electrons via its 4f orbitals, which helps to inhibit the recombination of electrons and holes [30]. Recently, P. Sun et al. successfully prepared $MnEuO_x$ catalysts by a co-precipitation method and found the modification of MnO_x catalyst by Eu enhanced its activity for SCR of NOx with NH_3 [31]. In this work, we used Eu as a dopant to modify MnO_x-TiO_2 catalysts for NH_3-SCR de-NO_x. The effects of Eu-modification on the catalytic performance and mechanism of MnO_x-TiO_2 were investigated in detail.

2. Experimental section

2.1. Preparation of catalysts

The Eu-modified MnO_x-TiO_2 composite oxides were prepared by an inverse co-precipitation method. A certain amount of $Mn(AC)_2 \cdot 4H_2O$, $Eu(NO_3)_3 \cdot 6H_2O$ and $Ti(SO_4)_2$ were added into 50 mL of distilled water with a certain amount of Behenyltrimethylammonium chloride (BTAC), and then the solution was stirred for 30 min to ensure that the precursors were dissolved completely. Then the precursors solution was added dropwise to an ammonia (25 wt%) solution 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 products were separated by filtrate and washed with distilled water for 3 times at least. Then the products were collected and dried in an oven at 110 °C for 12 h. Finally, the products were calcined in a muffle furnace in air at 500 °C for 6 h. The catalysts were designated as MnTiEu-x, where x was the molar ratio of Eu and Mn (note: the molar ratio of Mn and Ti was maintained at 1:10). For comparison, pure TiO_2 and MnO_x-TiO_2 composite oxides were also prepared by using the same method, and Eu_2O_3 was prepared by the heat-treatment of $Eu(NO_3)_3 \cdot 6H_2O$ in air at 500 °C for 6 h.

2.2. Characterizations

The XRD patterns were recorded with a Bruker D2 Phaser diffractometer with CuKα Radiation (λ = 0.154056 nm). Transmission electron microscope (TEM) and high resolution TEM (HR-TEM) were carried out on JEM-2100 HT. The elemental composition over the selected region was analyzed by an energy dispersive X-ray spectrometer (EDS) attached to the transmission electron microscope (TEM, JEM ARM200F). N_2 adsorption-desorption isotherms were conducted using a Quantachrome Analyzer at liquid N_2 temperature. The specific area was determined from the linear portion of the Brunauer-Emmett-Teller (BET) plot. The average pore diameter was calculated from the desorption branch of the N_2 adsorption isotherm using the Barrett-Joyner-Halenda (BJH) method. All samples were degassed in vacuum

at 200 °C for 4 h prior to analysis. X-ray photoelectron spectroscopy (XPS) analyses were carried out using a PHI5300 analyzer (Perkin Elmer, America) with aluminum K_α radiation. Temperature-programmed reduction (H_2-TPR) experiments were conducted with a chemisorption analyzer (Quantachrome, ChemBET Pulsar TPR/TPD) under a 10% H_2/Ar gas flow (20 mL min^{-1}) at a temperature rate of 10 °C min^{-1}.

2.3. In-situ DRIFT spectra experiments

In-situ DRIFT (diffuse reflectance infrared Fourier transform) spectra was performed on Bruker Vertex 70 infrared spectrometer (Bruker, Germany) with a mercury–cadmium–telluride (MCT) detector. Prior to each experiment, the catalysts were pretreated at 350 °C in a flow of N_2 for 30 min and cooled down to target temperature under N_2 flow. Background spectra were then recorded in the N_2 flow and automatically subtracted from the corresponding spectra. All spectra were recorded at a resolution of 4 cm^{-1} with 100 scans.

2.4. Catalytic activity testing

The activity measurements were carried out in an 8 mm (internal diameter) fixed-bed quartz reactor, using 600 mg catalyst (40–60 mesh) from 60 °C at a temperature step of 30 °C. The feed-gas mixture contained 500 ppm of NO, 500 ppm NH_3, 5% O_2, and N_2 as balance gas. The total flow rate of the feed gas was 600 cm^3 min^{-1}, corresponding to a gas hourly space velocity (GHSV) of 36,000 h^{-1}. The composition of the product gas was continually monitored by a NO/NO_2 flue gas analyzer (Testo 350) and N_2O detector (SKY2000). All data was collected when the catalytic reaction practically reached steady-state condition at each temperature. The NO_x conversion and N_2 selectivity were calculated according to the following equations [32,33]:

$$NO_x \text{ conversion } (\%) = \frac{[NO_x]_{in} - [NO_x]_{out}}{[NO_x]_{in}} \times 100\%$$

$$N_2 \text{ selectivity } (\%) = \left(1 - \frac{2[N_2O]_{out}}{[NO_x]_{in} - [NO_x]_{out}}\right) \times 100\%$$

where $[NO_x] = [NO_2] + [NO]$, and the subscripts "in" and "out" indicated the inlet concentration and outlet concentration of the gas at the steady state, respectively.

3. Results and discussion

3.1. NO_x conversion activity and N_2 selectivity of catalysts

Three catalysts denoted as MnTiEu-0.1, MnTiEu-0.3 and MnTiEu-0.5 were carried out the NH_3-SCR of NO reaction. For comparison, the data measured from MnO_x-TiO_2 (abbreviated to MnTi) and V_2O_5/WO_3-TiO_2 (abbreviated to VWTi, provided by Cormetech, Inc) are also plotted. As shown in Fig. 1A, MnTi exhibited a 100% NO_x conversion temperature window from 150 to 240 °C, and after 240 °C, the NO_x conversion quickly decreased with increasing temperature. After a small amount of Eu was added (MnTiEu-0.1), the de-NO_x activity was improved in the whole temperature region, especially at high temperature section, and the 100% NO_x conversion window expanded by about 30 °C (from 150 to 270 °C). When the mole ratio of Eu/Mn was increased from 0.1 to 0.3 (MnTiEu-0.3), the temperature window for 100% NO_x conversion was widened significantly for high temperature side (from 180 to 390 °C) while the NO_x conversion curve at low temperature side slightly shifted to higher temperature region in comparison with that for MnTi. More interesting, when the mole ratio of Eu/Mn was further increased to 0.5 (MnTiEu-0.5), the NO_x conversion curve was entirely shifted to higher temperature region, and a 100% NO_x conversion was showed from 270 to 480 °C (480 °C was the highest temperature we carried