available at www.sciencedirect.com

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

Article

Ho-modified Mn–Ce/TiO₂ for low-temperature SCR of NO_x with NH₃: Evaluation and characterization

Wei Li, Cheng Zhang *, Xin Li, Peng Tan, Anli Zhou, Qingyan Fang, Gang Chen #

State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan 430074, Hubei, China

ARTICLE INFO

Article history:

Received 4 April 2018

Accepted 8 May 2018

Published 5 October 2018

*Keywords:*Mn–Ce–Ho/TiO₂

Low-temperature selective catalytic reduction

Catalyst

Holmium

SO₂

ABSTRACT

Low-temperature selective catalytic reduction (SCR) of NO with NH₃ was tested over Ho-doped Mn–Ce/TiO₂ catalysts prepared by the impregnation method. The obtained catalysts with different Ho doping ratios were characterized by Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), temperature-programmed reduction (H₂-TPR), temperature-programmed desorption of NH₃ (NH₃-TPD), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). The catalytic activities were tested on a fixed bed. Their results indicated that the proper doping amount of Ho could effectively improve the low-temperature denitrification performance and the SO₂ resistance of Mn–Ce/TiO₂ catalyst. The catalyst with Ho/Ti of 0.1 presented excellent catalytic activity, with a conversion of more than 90% in the temperature window of 140–220 °C. The characterization results showed that the improved SCR activity of the Mn–Ce/TiO₂ catalyst caused by Ho doping was due to the increase of the specific surface area, higher concentration of chemisorbed oxygen, higher surface Mn⁴⁺/Mn³⁺ ratio, and higher acidity. The SO₂ resistance test showed that the deactivating influence of SO₂ on the catalyst was irreversible. The XRD and XPS results showed that the main reason for the catalyst deactivation was sulfates that had formed on the catalyst surface and that Ho doping could inhibit the sulfation to some extent.

© 2018, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Nitrogen oxide (NO_x) emitted from mobile sources and stationary sources can lead to ozone depletion, acid rain, photochemical smog, and global warming [1,2]. Nearly 46% of NO_x emission comes from coal-fired power plants [3]. Low-temperature selective catalytic reduction (SCR) is believed to be a promising technique for treatment of NO_x from stationary sources because the device can be located downstream from the precipitator and desulfurizer. As the key component of the SCR process, the low-temperature catalyst should have better performance and durability at low temperature [4,5].

Recently, researchers have focused on the preparation of new catalysts and the modification of catalysts to obtain high-performance low-temperature SCR [1]. Among these strategies, improving the preparation method, selecting high-quality raw materials, and doping elements have often been used in the modification of low-temperature catalysts [6–11]. Elements such as Sn, Ni, Co, Zr, Cr, Ni, and others already have been used to dope Mn-based catalysts, and the low-temperature SCR activity was improved in all experimental studies [12–16]. Among the widely studied catalysts, Mn and Ce containing catalysts such as Mn–Ce [17,18], Mn–Ce–Ti [19], and Mn–Ti [20] catalysts have been investigated extensively. Man-

* Corresponding author. Tel: +86-27-87542417; Fax: +86-27-87545526; E-mail: chengzhang@mail.hust.edu.cn

Corresponding author. Tel: +86-27-87542417; Fax: +86-27-87545526; E-mail: gangchen@mail.hust.edu.cn

DOI: 10.1016/S1872-2067(18)63099-2 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 10, October 2018

ganese oxides contain various types of labile oxygen, which have been considered to play an important role in the SCR catalytic circle, and ceria can store and release oxygen, which can effectively improve NO_x removal efficiency [20–22].

Holmium has been used commonly in the field of photocatalysis, and it has been reported that Ho doping can effectively improve the photocatalytic activity of TiO₂. Wu et al. [23] prepared Ho-doped TiO₂ nanoparticles and found that the phase transformation from anatase to rutile could be inhibited and that the growth of TiO₂ grains could be suppressed by Ho doping. Shi et al. [24] found that Ho³⁺ doping restrained the increase of grain size leading to crystal expansion. Additionally, Ho₂O₃ oxide can provide Lewis acid sites, which promote the SCR reaction. It has also been proven that Ho-modified Fe–Mn/TiO₂ catalyst has a broad operating temperature window and superior resistance to sulfur poisoning [25].

It is very important to study the performance of catalysts containing Mn, Ce, and Ho further. However, there are few reports about the performance of Ho-doped Mn–Ce/TiO₂ catalysts in low-temperature SCR. Hence, research pertaining to the performance of Mn–Ce–Ho/TiO₂ catalysts is very valuable. In this study, Mn–Ce–Ho/TiO₂ catalysts with different amounts of Ho were prepared to identify the effect of the introduction of Ho on catalytic performance. The activity, structural, redox, and acidic properties of the Ho-doped catalysts were investigated and the optimal Ho doping amount was identified.

2. Experimental

2.1. Catalyst preparation

The Mn–Ce–Ho/TiO₂ catalysts were prepared by the impregnation method. TiO₂ powder and specific amounts of manganese nitrate, ceria nitrate, and holmium nitrate were mixed together. Purified water was utilized as a solvent to be added to the aqueous solution. Then, the solution was stirred steadily in a magnetic stirring machine at room temperature for 6 h. The mixture was dried overnight at 105 °C, followed by a calcination at 450 °C for 4 h in a muffle furnace. The solid samples were crushed and sieved to 60–100 mesh sizes and were denoted as Mn_{0.4}Ce_{0.07}Ho_x/TiO₂, where *x* represents the molar ratio of Ho/Ti. The molar ratio of other components used for preparing the catalyst was Mn:Ce:Ti = 0.4:0.07:1.

2.2. Catalytic activity determination

Catalytic activities were measured over a fixed bed, as shown in Fig. 1, with a gas hourly space velocity (GHSV) of 10,000 h^{−1} at 80–220 °C. The reaction gases typically consisted of 0.08% NO, 0.08% NH₃, 5% O₂, and the balance N₂ to simulate the flue gas. In all tests, the total mass flow rate was maintained at 1000 mL/min. The concentrations of NO, NO_x, and N₂O were measured by OPTIMA7 flue gas analyzer (MRU GmbH, Germany). To assure the accuracy of the measurement, the reaction gas was accessed to the reactor until the inlet NO_x concentration was the same as that at the outlet to avoid absorption of the catalyst in the tube. The N₂ selectivity was calculated from

Fig. 1. Flow process diagram of the device used in the experiment. (1–4) N₂, NH₃, NO, and O₂ reaction gas, (5–8) flowmeters, (9) flue gas mixer, (10) temperature control device, (11) reaction tube, (12) heating furnace, (13) flue gas analyzer, (14) exhaust absorption.

[18]:

$$S_{N_2} = 1 - \frac{2C_{(N_2O)_{out}}}{C_{(NO_x)_{in}} - C_{(NO_x)_{out}}} \times 100\%$$

2.3. Catalyst characterization

The specific surface area and pore volume of the catalysts were determined by N₂ absorption at −196 °C using a Micromeritics ASAP 2020 system and were calculated by the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halend (BJH) methods. Powder X-ray diffraction (XRD) measurement was used to analyze the crystal structure of the catalysts and the metal oxide crystalline phases on the supports, and they were performed on an X'pert3 Powder X-ray diffractometer (PANalytical, Inc., Netherlands) with an angle of 10° to 90°.

Scanning electron microscopy (SEM) to examine the surface of the catalyst and obtain additional information was performed with a TESCAN MIRA3 system (TESCAN, Ltd.).

The characterizations of the valences of the surface elements and the atomic surface concentrations of the catalysts were examined using X-ray photoelectron spectroscopy (XPS) (AXIS-ULTRA DLD-600W; Shimadzu Kratos Corporation, Japan). The C 1s peak (284.6 eV) was used for calibration to obtain the precise binding energies of O 1s, Mn 2p, Ce 3d, and Ho 4d. During the measurement, the normal operating pressure used in the analysis was 10^{−9} Pa.

Temperature-programmed reduction (H₂-TPR) was carried out to study the redox behavior of the catalysts using a Chem-BET pulsar TPR/TPD (Quantachrome, Inc., USA). Before the characterization, the samples were pretreated at 300 °C for 1 h in He gas and then cooled to room temperature. The temperature was raised to 600 °C at a heating rate of 10 °C/min.

Temperature-programmed desorption of NH₃ (NH₃-TPD) experiments were carried out to study the acidity properties on a Chem BET pulsar TPR/TPD (Quantachrome, Inc., America) using 0.1 g catalysts. The sample was pretreated in pure N₂ at 300 °C for 1 h, cooled to room temperature, and then saturated for 30 min with NH₃. Next, the catalyst was flushed in a pure N₂ flow for 30 min at 120 °C. Finally, the TPD of NH₃ was carried

out by heating the catalysts in pure N₂ (10 °C/min) from 50 to 450 °C.

3. Results and discussion

3.1. Catalytic activity

The activities of five different Mn_{0.4}Ce_{0.07}Ho_x/TiO₂ catalysts ($x = 0, 0.01, 0.05, 0.1, 0.15$) are presented in Fig. 2. The results showed that the catalytic activities of the five catalysts increased with increasing temperature in the temperature range of 80 to 220 °C. Among all catalysts, Mn_{0.4}Ce_{0.07}Ho_{0.1}/TiO₂ performed most effectively and had the broadest temperature window, with more than 90% NO conversion obtained at 140–220 °C and 95.36% NO conversion obtained at 180 °C. The raw Mn–Ce/TiO₂ catalyst without Ho doping had a NO conversion rate of more than 80% at 180–220 °C. When the doping ratio Ho/Ti was 0.01, NO conversion decreased obviously. After that, the catalytic performance improved with increasing doping amount until Ho/Ti reached 0.1. Additionally, a wider NO reduction temperature window was observed under the optimum Ho doping amount. However, with increase of Ho/Ti to 0.15, the catalytic performance decreased. Therefore, the results indicated that Ho was an effective element for modifying Mn–Ce/TiO₂ catalysts and that there is an optimal doping ratio for catalytic efficiency. In this study, the optimal Ho doping ratio was found to be Ho/Ti = 0.1.

Fig. 3 shows the N₂ selectivity of the Mn_{0.4}Ce_{0.07}Ho_{0.1}/TiO₂ and Mn_{0.4}Ce_{0.07}/TiO₂ catalysts in the temperature range of 80–220 °C. The results show that the N₂ selectivity of both catalysts decreased with increasing temperature. This might indicate that more NH₃ will be oxidized to generate N₂O with increase of reaction temperature [26]. Also, Ho doping had a positive effect on the N₂ selectivity of the catalyst.

3.2. BET analysis

The specific surface areas and pore volumes of the different Ho-doped catalysts are shown in Table 1. The Mn_{0.4}Ce_{0.07}Ho_{0.1}/TiO₂ catalyst had the highest specific surface area among all the samples and the Mn_{0.4}Ce_{0.07}Ho_{0.01}/TiO₂ had

Fig. 2. Comparison of catalytic performance of different catalysts.

Fig. 3. N₂ selectivity of Mn_{0.4}Ce_{0.07}Ho_{0.1}/TiO₂ and Mn_{0.4}Ce_{0.07}/TiO₂ catalysts.

the lowest, indicating that only a proper amount of Ho could increase the specific surface area. The specific surface area of the raw catalyst Mn_{0.4}Ce_{0.07}/TiO₂ was 43.03 m²/g, and the Mn_{0.4}Ce_{0.07}Ho_{0.01}/TiO₂ catalyst (Ho/Ti = 0.01) showed a decrease to 39.34 m²/g. The BET surface area of the catalysts increased with increasing doping amount of Ho from 0.01 to 0.1 and reached its maximum at the Ho/Ti doping ratio of 0.1, which indicates that Ho doping has a positive effect for increase of the specific surface area of the catalyst. Higher BET surface area results in higher catalyst activity [26]. The improvement of the catalyst performance should be a result of many factors. We believed that the increase of specific surface area was one of these factors, but not the main contributing factor affecting catalyst performance. Therefore, other characterizations were conducted.

3.3. XRD analysis

Fig. 4 shows the XRD patterns of the catalysts with different Ho doping amounts. The peaks at 2θ values of 25.33°, 37.88°, 48.09°, 54.02°, 55.11°, 62.79°, 68.89°, and 75.11° were consistent with the diffraction peaks of anatase TiO₂, indicating that the TiO₂ did not transform from the anatase phase to the rutile phase at 450 °C. Anatase TiO₂ has abundant active sites that can improve the activity of the catalyst during the SCR process [27]. The XRD patterns of all of the different Ho doping amount catalysts remained similar, and the peaks of all catalysts corresponded with anatase TiO₂. No peaks corresponding to HoO_x, CeO₂, or MnO₂ were observed for any catalyst, indicat-

Table 1
BET results of Ce_{0.3}Ho_xMn_{0.4}/TiO₂ catalysts.

Sample	BET surface area (m ² /g)	Total pore volume (cm ³ /g)
Mn _{0.4} Ce _{0.07} /TiO ₂	43.03	0.2224
Mn _{0.4} Ce _{0.07} Ho _{0.01} /TiO ₂	39.34	0.2190
Mn _{0.4} Ce _{0.07} Ho _{0.05} /TiO ₂	43.56	0.2139
Mn _{0.4} Ce _{0.07} Ho _{0.1} /TiO ₂	46.57	0.2009
Mn _{0.4} Ce _{0.07} Ho _{0.15} /TiO ₂	43.40	0.1997

Fig. 4. XRD patterns of $\text{Mn}_{0.4}\text{Ce}_{0.3}\text{Hox}/\text{TiO}_2$ catalysts. (1) $\text{Mn}_{0.4}\text{Ce}_{0.07}/\text{TiO}_2$, (2) $\text{Mn}_{0.4}\text{Ce}_{0.07}\text{Ho}_{0.01}/\text{TiO}_2$, (3) $\text{Mn}_{0.4}\text{Ce}_{0.07}\text{Ho}_{0.05}/\text{TiO}_2$, (4) $\text{Mn}_{0.4}\text{Ce}_{0.07}\text{Ho}_{0.1}/\text{TiO}_2$, (5) $\text{Mn}_{0.4}\text{Ce}_{0.07}\text{Ho}_{0.15}/\text{TiO}_2$.

ing that these elements were highly dispersed and in an amorphous form, which would contribute to the denitration reaction [28].

3.4. SEM analysis

SEM analysis was performed to acquire additional surface information of the catalysts. Fig. 5 shows SEM images of the raw and optimally Ho-doped catalyst. Fig. 5(a) and (b) show SEM images of the catalysts at a magnification of 250,000. A particle agglomeration phenomenon was observed in the SEM image of the raw catalyst without Ho doping, but this phenomenon was alleviated after Ho doping, indicating that Ho doping can inhibit particle agglomeration [29]. Fig. 5(c) and (d) show SEM images of the two catalysts at the lower magnification of 20,000. The surface of the raw catalyst without Ho doping was relatively smooth, but after Ho doping, the surface became rougher, which could increase the specific surface area of the catalyst and provide more reaction sites.

Fig. 5. SEM images of two catalysts. (a) $\text{Mn}_{0.4}\text{Ce}_{0.07}\text{Ho}_{0.1}/\text{TiO}_2$, (b) $\text{Mn}_{0.4}\text{Ce}_{0.07}/\text{TiO}_2$, (c) $\text{Mn}_{0.4}\text{Ce}_{0.07}\text{Ho}_{0.1}/\text{TiO}_2$, (d) $\text{Mn}_{0.4}\text{Ce}_{0.07}/\text{TiO}_2$.

3.5. XPS analysis

XPS spectroscopy was used to identify the valence of the surface elements of the catalysts. Fig. 6 shows the photoelectron spectra of Mn 2p, Ce 3d, and O 1s, and Table 2 shows the surface atomic ratios of the raw catalyst and the Ho-doped catalyst. The Mn 2p spectra of the raw and Ho-doped catalysts are displayed in Fig. 6(a). The Mn 2p region consisted of two peaks,

Fig. 6. Illustration of the working principle of multi-wavelength Raman spectroscopy of supported metal oxide. λ_{RR} and λ_{NR} refer to excitations resulting in resonance and non-resonance Raman, respectively.

Table 2

Surface atomic ratios for the catalysts determined by XPS spectra.

Catalyst	Ce ⁴⁺ /(Ce ⁴⁺ +Ce ³⁺)	Mn ⁴⁺ /(Mn ⁴⁺ +Mn ³⁺)	O _α /(O _α +O _β)
Mn _{0.4} Ce _{0.07} /TiO ₂	0.7	0.74	0.47
Mn _{0.4} Ce _{0.07} Ho _{0.1} /TiO ₂	0.71	0.76	0.79

Mn 2p_{3/2} with a binding energy (BE) of about 641.7 eV and Mn 2p_{1/2} with a BE of about 653.3 eV, which are consisted with Mn⁴⁺ and Mn³⁺, indicating that the Mn was in the mixed-valence state (Mn³⁺ and Mn⁴⁺) [13,21]. From the area of the peaks of the catalyst, the content ratio of Mn³⁺: Mn⁴⁺ was 0.179, which indicates that Mn⁴⁺ was the main valence of the catalyst and that the reduction process of Mn⁴⁺ played an important role in the high efficiency in the low-temperature SCR reaction. A high concentration of Mn⁴⁺ could promote the transformation of NO to NO₂ and contribute to the rapidity of the SCR reaction [30]. The peaks of Mn 2p_{3/2} and Mn 2p_{1/2} became broader after Ho doping, which implied that Ho doping made the Mn well-dispersed on the catalyst.

Fig. 6(b) shows the Ce 3d XPS spectra of the catalysts with and without Ho doping. The XPS peaks denoted as u''' (916.7 eV), u'' (907.5 eV), u (901.0 eV) and v''' (898.4 eV), v'' (888.8 eV), and v (882.5 eV) were attributed to Ce⁴⁺ species, but u' (903.5 eV) and v' (884.9 eV) were assigned to Ce³⁺ species, which indicated that Ce⁴⁺ and Ce³⁺ coexisted on the surface of the catalysts [13,21]. A comparison of the peak area of Ce⁴⁺ and Ce³⁺ indicated that Ce⁴⁺ was the main valence of the catalyst. After Ho doping, the Ce⁴⁺ peaks became broader, which represented an increase in the concentration of Ce⁴⁺. The redox cycle between Ce⁴⁺ and Ce³⁺ led to oxygen storage and release and generated oxygen vacancies. The generated oxygen vacancies enhanced oxygen mobility and reduction/oxidation capability, especially for the oxidation of NO to NO₂, which was beneficial to SCR reaction [31].

There were two peaks in the O 1s spectra, as shown in Fig. 6(c), the lattice oxygen at 529.3–530.0 eV, denoted as O_β, and the chemisorbed oxygen at 531.3–531.9 eV, denoted as O_α [13,21]. The chemisorbed oxygen O_α had a larger peak area after Ho doping than the raw catalyst. Proper loading of Ho³⁺ could separate the electron-hole pairs effectively and cause more charge imbalances and vacancies, which accounts for the increase of chemisorbed oxygen [29,32]. It has been reported that O_α is the most active oxygen and that it is helpful in the oxidation of NO to NO₂. The conversion of NO to NO₂ by Mn_{0.4}Ce_{0.07}Ho_{0.1}/TiO₂ and Mn_{0.4}Ce_{0.07}/TiO₂ is shown in Fig. 7. The results clearly show that the conversion of NO to NO₂ of both catalysts increased with increasing temperature. Additionally, Mn_{0.4}Ce_{0.07}Ho_{0.1}/TiO₂ showed an obvious enhancement compared with the raw catalyst, which proved that O_α was conducive to the oxidation of NO to NO₂. The enhancement of the oxidation of NO to NO₂ was favorable to the low-temperature SCR process [33]. Therefore, Ho doping can increase the chemisorbed oxygen of the catalyst and promote the SCR reaction.

3.6. H₂-TPR analysis

Fig. 7. Oxidation of NO to NO₂ over Mn_{0.4}Ce_{0.07}Ho_{0.1}/TiO₂ and Mn_{0.4}Ce_{0.07}/TiO₂.

Fig. 8. H₂-TPR profiles of Mn_{0.4}Ce_{0.07}Ho_{0.1}/TiO₂ (1) and Mn_{0.4}Ce_{0.07}/TiO₂ (2) catalysts.

Fig. 8 shows the H₂-TPR curves of the raw catalyst and the optimal Ho-doped catalyst. Mn_{0.4}Ce_{0.07}Ho_{0.1}/TiO₂ had three peaks within the temperature range of 300–570 °C, which appeared at 370, 443, and 528 °C, respectively. The three peaks might account for the successive reduction steps of MnO₂ → Mn₂O₃ → Mn₃O₄ → MnO [21,34]. The peaks at 420–450 °C may have been due to overlapping of the reduction peaks of both Mn₂O₃ and CeO₂ [35]. All peaks of the catalyst without Ho doping were shifted toward higher temperature, suggesting that Ho doping can lower the reduction temperature and that the reduction reaction occurs more easily on the Ho-doped catalyst. The peak area (below 500 °C) representing the number of reductive species of the Mn_{0.4}Ce_{0.07}Ho_{0.1}/TiO₂ catalyst was larger than that of the raw catalyst, which indicates that Ho doping can increase the reductive species of the catalyst and thus improve SCR activity [36].

3.7. NH₃-TPD analysis

NH₃-TPD was used to analyze the acidity properties of the catalysts in the temperature range of 50–450 °C, and the results are presented in Fig. 9. The Mn_{0.4}Ce_{0.07}/TiO₂ catalyst had two

Fig. 9. NH_3 -TPD profiles of two catalysts. (1) $\text{Mn}_{0.4}\text{Ce}_{0.07}\text{Ho}_{0.1}/\text{TiO}_2$, (2) $\text{Mn}_{0.4}\text{Ce}_{0.07}/\text{TiO}_2$.

peaks in the temperature range of 200–500 °C, which showed that NH_3 was desorbed mainly by weak and medium acid sites. After Ho doping, three peaks were observed, including a new peak representing a strong acid site at around 425 °C. A larger area of desorption peaks was observed in the $\text{Mn}_{0.4}\text{Ce}_{0.07}\text{Ho}_{0.1}/\text{TiO}_2$ catalyst, which indicates the strong acidity of the catalyst. The strong acidity would lead to a significant increase in the adsorption capacity of NH_3 , and the adsorbed NH_3 could be used more easily in the SCR process. Thus, Ho doping can lead to higher surface acidity and good adsorption capacity of NH_3 , which are believed to be conducive to SCR reaction [37].

3.8. Effect of sulfation

3.8.1. Effect of SO_2 and H_2O on NH_3 -SCR performance

Residual SO_2 in the flue gas can poison the catalyst and shorten its lifetime, so good resistance to SO_2 is an important evaluation index for the low-temperature SCR reaction. Therefore, the SO_2 resistance experiment testing the raw and the optimal Ho-doped catalyst was conducted under the circumstance of 0.03% SO_2 . Fig. 10(a) shows the NO conversion over

$\text{Mn}_{0.4}\text{Ce}_{0.07}\text{Ho}_{0.1}/\text{TiO}_2$ and $\text{Mn}_{0.4}\text{Ce}_{0.07}/\text{TiO}_2$ when 0.03% SO_2 was added into the reaction gas at 180 °C. The SCR reaction was stable for more than 1 h before SO_2 was added. The results indicated that SO_2 had a poisoning effect on both catalysts. When SO_2 was added, the NO conversion of both catalysts began to decrease. The conversion of the $\text{Mn}_{0.4}\text{Ce}_{0.07}\text{Ho}_{0.1}/\text{TiO}_2$ catalyst decreased from 95.01% to 88.29%, but the $\text{Mn}_{0.4}\text{Ce}_{0.07}/\text{TiO}_2$ catalyst showed a relatively faster deactivation, with an NO conversion decrease of from 81.34% to 60.1%. The results showed that the $\text{Mn}_{0.4}\text{Ce}_{0.07}\text{Ho}_{0.1}/\text{TiO}_2$ catalyst performed better for sulfur resistance. After cutting off the addition of SO_2 , the NO conversion of both catalysts did not recover to its original level, suggesting that the SO_2 poisoning effect is irreversible and that SO_2 acts as a deactivator during the low-temperature SCR reaction. Fig. 10(b) shows the effect of coexistence of SO_2 and H_2O for NO conversion over $\text{Mn}_{0.4}\text{Ce}_{0.07}\text{Ho}_{0.1}/\text{TiO}_2$ and $\text{Mn}_{0.4}\text{Ce}_{0.07}/\text{TiO}_2$. The activity of both catalysts started to decrease after 0.03% SO_2 and 10% H_2O were fed into the reactor, and the catalytic activity decreased more than that shown in Fig. 10(a), suggesting that the effect of H_2O and SO_2 on the activity of the catalyst is greater than that only SO_2 . The activities of the $\text{Mn}_{0.4}\text{Ce}_{0.07}\text{Ho}_{0.1}/\text{TiO}_2$ and $\text{Mn}_{0.4}\text{Ce}_{0.07}/\text{TiO}_2$ catalysts decreased by about 19.41% and 30.97%, respectively, indicating that the Ho-modified catalyst had better resistance to SO_2 and H_2O .

To understand the mechanism of SO_2 resistance over the Ho-modified Mn–Ce/TiO₂ catalyst further, XRD and XPS characterizations were conducted to analyze the crystal structure of the two catalysts, the valences of the surface elements, and the atomic surface concentration of the catalysts following the SO_2 and H_2O resistance test.

3.8.2. XRD analysis

Fig. 11 shows the XRD patterns of the catalysts before and after the SO_2 and H_2O resistance test. As shown in Fig. 11, the three catalysts had peaks consistent with anatase TiO₂. However, for the poisoned $\text{Mn}_{0.4}\text{Ce}_{0.07}/\text{TiO}_2$ catalyst, a peak consistent with $(\text{NH}_4)_2\text{SO}_4$ was observed [22]. The weak intensity of this peak might indicate that the reaction time was not long enough to form sufficient $(\text{NH}_4)_2\text{SO}_4$ on the surface of the cata-

Fig. 10. Effect of SO_2 (a) and $\text{SO}_2+\text{H}_2\text{O}$ (b) on NO conversion over $\text{Mn}_{0.4}\text{Ce}_{0.07}/\text{TiO}_2$ and $\text{Mn}_{0.4}\text{Ce}_{0.07}\text{Ho}_{0.1}/\text{TiO}_2$ catalysts.

Fig. 11. XRD results of the catalysts before and after the reaction in the presence of $\text{SO}_2 + \text{H}_2\text{O}$. (1) Poisoned $\text{Mn}_{0.4}\text{Ce}_{0.07}\text{Ho}_{0.1}/\text{TiO}_2$ catalyst; (2) Poisoned $\text{Mn}_{0.4}\text{Ce}_{0.07}/\text{TiO}_2$ catalyst; (3) Fresh $\text{Mn}_{0.4}\text{Ce}_{0.07}\text{Ho}_{0.1}/\text{TiO}_2$ catalyst.

lyst. The same $(\text{NH}_4)_2\text{SO}_4$ diffraction peak did not appear for the $\text{Mn}_{0.4}\text{Ce}_{0.07}\text{Ho}_{0.1}/\text{TiO}_2$ catalyst after the test, which might

indicate that $(\text{NH}_4)_2\text{SO}_4$ generation was inhibited by Ho doping, or the amount of $(\text{NH}_4)_2\text{SO}_4$ that formed was too small to be detected by XRD. $(\text{NH}_4)_2\text{SO}_4$ on the catalyst could block and occupy active sites on the surface of the catalyst, thereby reducing the activity of the catalyst [38].

3.8.3. XPS analysis

Fig. 12 shows the photoelectron spectra of S 2p, Mn 2p, Ce 3d, and O 1s before and after the SO_2 and H_2O resistance test, respectively.

The XPS spectra of S 2p is shown in Fig. 12(a). The fresh catalyst is not shown here because it had no S 2p spectra. The S 2p spectra consisted of three peaks at 169.8, 166.9, and 163.8 eV, respectively. The peaks of 169.8 and 163.8 eV belonged to SO_4^{2-} and the peak at 166.9 eV belonged to SO_3^{2-} [39]. This result confirmed the $(\text{NH}_4)_2\text{SO}_4$ diffraction peak detected in XRD. In addition, the contents of each element on the surface of the two catalysts after the SO_2 and H_2O resistance test are shown in Table 3. As can be seen from the table, the S content of the $\text{Mn}_{0.4}\text{Ce}_{0.07}\text{Ho}_{0.1}/\text{TiO}_2$ catalyst was lower than that of the $\text{Mn}_{0.4}\text{Ce}_{0.07}/\text{TiO}_2$ catalyst.

Fig. 12(b) shows the XPS spectra of Mn 2p. The binding energy of the $\text{Mn}_{0.4}\text{Ce}_{0.07}/\text{TiO}_2$ catalyst shifted higher by about 1

Fig. 12. XPS spectra of catalysts before and after the reaction in the presence of $\text{SO}_2 + \text{H}_2\text{O}$ (a–d). (1) Poisoned $\text{Mn}_{0.4}\text{Ce}_{0.07}\text{Ho}_{0.1}/\text{TiO}_2$ catalyst, (2) poisoned $\text{Mn}_{0.4}\text{Ce}_{0.07}/\text{TiO}_2$ catalyst, (3) fresh $\text{Mn}_{0.4}\text{Ce}_{0.07}\text{Ho}_{0.1}/\text{TiO}_2$ catalyst.

Table 3Surface atomic ratios for the catalysts after SO₂ and H₂O resistance test.

Catalyst	Surface atomic concentrations (%)						
	Ho	Ti	O	Ce	Mn	S	C
Mn _{0.4} Ce _{0.07} /TiO ₂	—	12.77	51.79	1.98	9.31	1.58	22.57
Mn _{0.4} Ce _{0.07} Ho _{0.1} /TiO ₂	0.62	11.86	52.27	2.62	10.58	0.74	21.31

eV after the test, indicating that a substance other than manganese oxide had formed [10]. Based on the results of the S 2p spectrum in the XPS spectrum and XRD analysis results, the substance might be Mn contained in sulfates. However, the spectra of the Ho-modified Mn–Ce/TiO₂ catalyst did not change significantly. This might indicate that Ho doping can inhibit the formation of sulfate.

The XPS spectrum of the Ce 3d orbit is shown in Fig. 12(c). Compared with the XPS spectra of the fresh catalyst, the Ce⁴⁺ concentrations of the two catalysts after the SO₂ and H₂O resistance test were reduced, but the Ce⁴⁺ concentration of Mn_{0.4}Ce_{0.07}Ho_{0.1}/TiO₂ catalyst was higher than that of the Mn_{0.4}Ce_{0.07}/TiO₂ catalyst. The reason for the reduction of Ce⁴⁺ concentration in the catalysts might be that SO₂ could function a reductant promoting the conversion of Ce⁴⁺ to Ce³⁺ [40]. The main role of CeO₂ in the catalyst was to store oxygen. The Ho-modified catalyst had a higher concentration of Ce⁴⁺ after the water and sulfur resistance test, which contributed to the storage of active oxygen and thus improved catalyst activity [41].

Fig. 12(d) shows the O 1s XPS spectra. The chemical absorbed oxygen concentration of the two catalysts after the SO₂ and H₂O resistance test showed an activity decrease compared with the activity of the fresh catalyst, but the Ho-modified Mn–Ce/TiO₂ catalyst had higher chemical absorbed oxygen concentration than the Mn_{0.4}Ce_{0.07}/TiO₂ catalyst. High chemical absorbed oxygen concentration is conducive to improvement of catalytic activity, which is consistent with the result of the catalyst activity after the SO₂ and H₂O resistance test. During the reaction, active oxygen on the surface of the catalyst adsorbed and oxidized SO₂ to SO₃, converted Mn⁴⁺ to lower valence state, and converted Ce⁴⁺ to Ce³⁺, thus poor activity Mn₂(SO₄)₃ and Ce₂(SO₄)₃ formed, resulting in irreversible valence reduction of Mn⁴⁺ and Ce⁴⁺. The oxidized SO₃ further reacted with ammonium ions and metal ions to form sulfates. As shown in Fig. 12(b) and 12(c), the Ho-doped catalyst had a higher concentration of Mn⁴⁺ and Ce⁴⁺ after the water and sulfur resistance test. The reason for this difference might be that Ho doping inhibits the irreversible valence reduction of Mn⁴⁺ and Ce⁴⁺ and thus affects the SO₂ oxidation. The amount of SO₃ generated was reduced, which thereby reduced sulfate production.

3.8.4. Regeneration of deactivated catalysts

To study the mechanism of the poisoning process of SO₂ further, regeneration of the deactivated Mn_{0.4}Ce_{0.07}Ho_{0.1}/TiO₂ and Mn_{0.4}Ce_{0.07}/TiO₂ catalysts was necessary. Thus, regeneration of the deactivated catalysts was carried out in the reactor tube at 400 °C with 5% NH₃/N₂ at a flow rate of 100 mL/min [42]. Fig. 13 shows the NO conversion of both recovered cata-

Fig. 13. SCR activities of regenerated catalysts.

lysts after the heating treatment. The result showed that the NO conversion of the regenerated catalysts was increased by regeneration, but neither of these catalysts recovered to its original level. Fig. 14(a) shows the XRD patterns of the regenerated Mn_{0.4}Ce_{0.07}Ho_{0.1}/TiO₂ and Mn_{0.4}Ce_{0.07}/TiO₂ catalysts. After regeneration, the peak consistent with (NH₄)₂SO₄ had disappeared compared with the result shown in Fig. 11, indicating that the ammonium sulfate decomposed or that the amount was too small to detect by XRD. XPS was also conducted to identify the effect of regeneration over the Ho-doped catalyst as there was no peak consistent with (NH₄)₂SO₄ before and after the SO₂ resistance test. The N 1s XPS spectra of the regenerated catalysts are shown in Fig. 14(b). The peak at 407.0 eV was attributed to NO₃⁻ and the peak at 399.6 eV was attributed to NH₄⁺ [43,44]. After regeneration, Mn_{0.4}Ce_{0.07}/TiO₂ had a very weak NH₄⁺ peak, which suggested that few ammonium sulfates existed after regeneration and that the heating treatment could effectively decompose the ammonium sulfates. Moreover, the Ho-doped catalyst had no NH₄⁺ peak. Considering the result that SCR performance did not recover to its original level after regeneration, other inactive and stable sulfate species, which decreased the catalytic activity, must have formed during the SO₂ resistance test. Based on the analysis of the XPS spectra of the O 1s in Fig. 12(d), manganese sulfate and cerium sulfate could be the species preventing the catalyst from returning to its original activity after regeneration [45]. Because the SCR performance of both catalysts recovered mostly after regeneration, the ammonium sulfates formed during the SO₂ resistance test must have been the main deactivator of the catalysts.

4. Conclusions

The Mn_{0.4}Ce_{0.07}Ho_{0.1}/TiO₂ catalyst synthesized by the impregnation method showed high activity for low-temperature SCR of NO with NH₃. Ho was effectively for modification of the Mn–Ce/TiO₂ catalyst and could effectively improve the low-temperature denitrification performance and SO₂ resistance. A more than 90% NO conversion was obtained at the temperature range of 150–220 °C with a GHSV of 10,000 h⁻¹. The catalysts were characterized by BET, XRD, H₂-TPR,

Fig. 14. XRD (a) and XPS (b) results of $\text{Mn}_{0.4}\text{Ce}_{0.07}\text{Ho}_{0.1}/\text{TiO}_2$ (1) and $\text{Mn}_{0.4}\text{Ce}_{0.07}/\text{TiO}_2$ (2) catalysts after regeneration.

NH_3 -TPD, XPS, and SEM. The Ho-doped catalysts exhibited highly dispersed active components, such as manganese and cerium, and had the positive effect of increased specific surface area of the catalyst. The XPS results indicated that Ho doping could elevate the $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio and result in amounts of chemisorbed oxygen conducive to the SCR process. Additionally, more reductive species and higher acidity were achieved due to Ho doping. All of these were beneficial to SCR activity.

Acknowledgments

This work was supported by the National Key Research and

Development Program of China (NO. 2018YFB0605105); the technical support from the Analytical and Testing Center at the Huazhong University of Science and Technology is greatly appreciated.

References

- [1] G. Busca, L. Lietti, G. Ramis, F. Berti, *Appl. Catal. B*, **1998**, 18, 1–36.
- [2] M. Kang, E. D. Park, J. M. Kim, J. E. Yie, *Catal. Today*, **2006**, 111, 236–241.
- [3] G. S. Qi, R. T. Yang, R. Chang, *Appl. Catal. B*, **2004**, 51, 93–106.
- [4] L. L. Zhu, B. C. Huang, W. H. Wang, Z. L. Wei, D. Q. Ye, *Catal.*

Graphical Abstract

Chin. J. Catal., 2018, 39: 1653–1663 doi: 10.1016/S1872-2067(18)63099-2

Ho-modified Mn-Ce/TiO₂ for low-temperature SCR of NO_x with NH₃: Evaluation and characterization

Wei Li, Cheng Zhang*, Xin Li, Peng Tan, Anli Zhou, Qingyan Fang, Gang Chen*
Huazhong University of Science and Technology

Ho can be an effective doping element for improving the low-temperature SCR performance and the SO_2 resistance of Mn-Ce/TiO₂ catalyst.

- Commun.*, **2011**, 12, 394–398.
- [5] S. L. Zhang, H. Y. Li, Q. Zhong, *Appl. Catal. A*, **2012**, 435–436, 156–162.
 - [6] B. Q. Jiang, Y. Liu, Z. B. Wu, *J. Hazard. Mater.*, **2009**, 162, 1249–1254.
 - [7] X. L. Tang, J. M. Hao, W. G. Xu, J. H. Li, *Catal. Commun.*, **2007**, 8, 329–334.
 - [8] W. Li, R. T. Guo, S. X. Wang, W. G. Pan, Q. L. Chen, M. Y. Li, P. Sun, S. M. Liu, *Fuel Process. Technol.*, **2016**, 154, 235–242.
 - [9] L. S. Wang, B. C. Huang, Y. X. Su, G. Y. Zhou, K. L. Wang, H. C. Luo, D. Q. Ye, *Chem. Eng. J.*, **2012**, 192, 232–241.
 - [10] Z. B. Wu, R. B. Jin, H. Q. Wang, Y. Liu, *Catal. Commun.*, **2009**, 10, 935–939.
 - [11] J. W. Kan, L. Deng, B. Li, Q. Huang, S. M. Zhu, S. B. Shen, Y. W. Chen, *Appl. Catal. A*, **2017**, 530, 21–29.
 - [12] S. H. Jo, B. K. Shin, M. C. Shin, C. J. Van Tyne, H. Lee, *Catal. Commun.*, **2014**, 57, 134–137.
 - [13] H. Z. Chang, X. Y. Chen, J. H. Li, L. Ma, C. Z. Wang, C. X. Liu, J. W. Schwank, J. M. Hao, *Environ. Sci. Technol.*, **2013**, 47, 5294–5301.
 - [14] Y. P. Wan, W. R. Zhao, Y. Tang, L. Li, H. J. Wang, Y. L. Cui, J. L. Gu, Y. S. Li, J. L. Shi, *Appl. Catal. B*, **2014**, 148–149, 114–122.
 - [15] B. X. Shen, Y. Y. Wang, F. M. Wang, T. Liu, *Chem. Eng. J.*, **2014**, 236, 171–180.
 - [16] Z. H. Chen, Q. Yang, H. Li, X. H. Li, L. F. Wang, S. C. Tsang, *J. Catal.*, **2010**, 276, 56–65.
 - [17] F. Eigenmann, M. Maciejewski, A. Baiker, *Appl. Catal. B*, **2006**, 62, 311–318.
 - [18] Z. M. Liu, Y. Yi, S. X. Zhang, T. L. Zhu, J. Z. Zhu, J. G. Wang, *Catal. Today*, **2013**, 216, 76–81.
 - [19] Z. M. Liu, J. Z. Zhu, J. H. Li, L. L. Ma, S. I. Woo, *ACS Appl. Mater. Interfaces*, **2014**, 6, 14500–14508.
 - [20] B. Thirupathi, P. G. Smirniotis, *Appl. Catal. B*, **2011**, 110, 195–206.
 - [21] Z. B. Wu, R. B. Jin, Y. Liu, H. Q. Wang, *Catal. Commun.*, **2008**, 9, 2217–2220.
 - [22] Z. B. Wu, R. B. Jin, H. Q. Wang, Y. Liu, *Catal. Commun.*, **2009**, 10, 935–939.
 - [23] W. Y. Zhou, Y. C. He, *Chem. Eng. J.*, **2012**, 179, 412–416.
 - [24] J. W. Shi, J. T. Zheng, Y. Hu, Y. C. Zhao, *Mater. Chem. Phys.*, **2007**, 106, 247–249.
 - [25] Y. W. Zhu, Y. P. Zhang, R. Xiao, T. J. Huang, K. Shen, *Catal. Commun.*, **2017**, 88, 64–67.
 - [26] X. N. Lu, C. Y. Song, S. H. Jia, Z. S. Tong, X. L. Tang, Y. X. Teng, *Chem. Eng. J.*, **2015**, 260, 776–784.
 - [27] F. P. Liu, H. He, C. B. Zhang, *Chem. Commun.*, **2008**, 164, 2043–2045.
 - [28] S. M. Saqer, D. I. Kondarides, X. E. Verykios, *Appl. Catal. B*, **2011**, 103, 275–286.
 - [29] A. Khataee, S. Saadi, B. Vahid, S. W. Joo, *J. Ind. Eng. Chem.*, **2015**, 35, 167–176.
 - [30] F. P. Liu, H. He, Y. Ding, C. B. Zhang, *Appl. Catal. B*, **2009**, 93, 194–204.
 - [31] Z. Y. Pu, J. Q. Lu, M. F. Luo, Y. L. Xie, *J. Phys. Chem. C*, **2007**, 111, 18695–18702.
 - [32] J. W. Shi, J. T. Zheng, P. Wu, *J. Hazard. Mater.*, **2009**, 161, 416–422.
 - [33] L. Jing, Z. Xu, X. Sun, J. Shang, W. Cai, *Appl. Surf. Sci.*, **2001**, 180, 308–314.
 - [34] A. Gil, L. M. Gandía, S. A. Korili, *Appl. Catal. A*, **2004**, 274, 229–235.
 - [35] X. Y. Fan, F. M. Qiu, H. S. Yang, W. Tian, T. F. Hou, X. B. Zhang, *Catal. Commun.*, **2011**, 12, 1298–1301.
 - [36] G. Gao, J. W. Shi, C. Liu, C. Gao, Z. Fan, C. M. Niu, *Appl. Surf. Sci.*, **2017**, 411, 338–346.
 - [37] L. Lietti, I. Nova, G. Ramis, L. Dall’Acqua, G. Busca, E. Giamello, P. Forzatti, F. Bregani, *J. Catal.*, **1999**, 187, 419–435.
 - [38] C. L. Yu, B. C. Huang, L. F. Dong, F. Chen, Y. Yang, Y. M. Fan, Y. X. Yang, X. Q. Liu, X. N. Wang, *Chem. Eng. J.*, **2017**, 316, 1059–1068.
 - [39] S. M. Lee, K. H. Park, S. C. Hong, *Chem. Eng. J.*, **2012**, 195–196, 323–331.
 - [40] M. Waqif, P. Bazin, O. Saur, J. C. Lavalley, G. Blanchard, O. Touret, *Appl. Catal. B*, **1997**, 11, 193–205.
 - [41] D. J. Yan, Y. Yu, X. M. Huang, S. J. Liu, Y. H. Liu, *J. Fuel Chem. Technol.*, **2016**, 44, 232–238.
 - [42] Z. Y. Sheng, Y. F. Hu, J. M. Xue, X. M. Wang, W. P. Liao, *J. Rare Earths*, **2012**, 30, 676–682.
 - [43] X. J. Yao, K. L. Ma, W. X. Zou, S. G. He, J. B. An, F. M. Yang, L. Dong, *Chin. J. Catal.*, **2017**, 38, 146–159.
 - [44] X. J. Yao, L. Chen, T. T. Kong, S. M. Ding, Q. Luo, F. M. Yang, *Chin. J. Catal.*, **2017**, 38, 1423–1430.
 - [45] K. Zhuang, Y. P. Zhang, T. J. Huang, B. Lu, K. Shen, *J. Fuel Chem. Technol.*, **2017**, 45, 1356–1364.

Ho改性的Mn–Ce/TiO₂催化剂低温脱硝性能的评价和表征

李 伟, 张 成*, 李 鑫, 谭 鹏, 周安鹏, 方庆艳, 陈 刚[#]

华中科技大学, 能源与动力工程学院, 煤燃烧国家重点实验室, 湖北武汉430074

摘要: 作为引起酸雨、光化学烟雾、雾霾等大气污染问题的主要根源, 氮氧化物(NO_x)的防治已成为亟待解决的问题。选择性催化还原技术作为最成熟有效的脱硝技术, 目前已经被广泛应用于各燃煤电厂。低温脱硝催化剂具有优秀的低温活性, 使得脱硝装置可以安放在脱硫装置和除尘装置下游, 受到了学者广泛的研究。目前低温脱硝催化剂的研究主要是对催化剂进行改性以提高催化剂的性能, 已有许多研究报道了Sn、Ni、Co、Zr、Cr、Ni等对催化剂的改性影响。Ho作为一种改性元素被应用于光催化领域, 能提高TiO₂的光催化能力。但Ho应用于脱硝领域的研究鲜有报道, 其氧化物具有酸性位点有助于脱硝反应, 因此研究Ho对低温SCR催化剂的改性作用具有重要意义。

本文采用浸渍法制备Ho掺杂的Mn–Ce/TiO₂催化剂, 研究了Ho的掺杂对于Mn–Ce/TiO₂催化剂低温脱硝性能的影响, 同时还研究了烟气中的SO₂和H₂O对催化剂活性的影响, 并利用XPS、XRD、H₂-TPR、NH₃-TPD等表征方法从物理性质和化学性质两方面对Ho改性的影响机理进行了研究。研究发现, Ho的掺杂能提高Mn–Ce/TiO₂催化剂的脱硝能力, 有助于催化剂N₂选择性的提高。分析表明, Ho的掺杂有助于催化剂比表面积的提升, 且能提高催化剂的酸性, 有利于催化剂对NH₃的吸附, 从而提高催化剂的性能。XPS表征结果表明Ho掺杂后的催化剂具有更高的化学吸附氧浓度和较高的Mn⁴⁺/Mn³⁺比例,

使得脱硝反应更容易进行. 改性后催化剂的抗水抗硫实验结果表明, Ho的掺杂能够提高催化剂的抗水抗硫性能. XRD结果表明, 抗水抗硫实验后催化剂表面形成了硫酸铵盐, 硫酸铵盐的形成会堵塞催化剂表面的活性位, 限制脱硝反应的进行, 从而影响催化剂的脱硝活性. 同时, 400 °C下进行再生实验后的催化剂活性有所恢复, 但是未能达到抗水抗硫实验前的活性, 表明在抗水抗硫实验中催化剂表面形成了除硫酸铵盐以外的其他硫酸盐类. 结合XPS和XRD表征结果, 推断生成的盐类物质为硫酸锰和硫酸铈, 从而导致再生后的催化剂的脱硝活性无法恢复到最初的活性水平. 由此可以看出, 硫酸盐的形成是催化剂在含硫气氛中失活的主要原因.

关键词: Mn–Ce–Ho/TiO₂; 低温选择性催化还原; 催化剂; 钬; 二氧化硫

收稿日期: 2018-04-04. 接受日期: 2018-05-08. 出版日期: 2018-10-05.

*通讯联系人. 电话: (027)87542417; 传真: (027)87545526; 电子信箱: chengzhang@mail.hust.edu.cn

#通讯联系人. 电话: (027)87542417; 传真: (027)87545526; 电子信箱: gangchen@mail.hust.edu.cn

基金来源: 国家重点研发计划重点专项(2018YFB0605105).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).