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Research



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Sulfur resistance of Ce-Mn/TiO₂ catalysts for low-temperature NH₃-SCR

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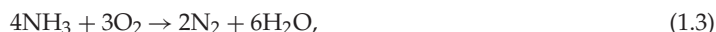
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Ce-Mn/TiO₂ catalyst prepared using a simple impregnation method demonstrated a better low-temperature selective catalytic reduction of NO with NH₃ (NH₃-SCR) activity in comparison with the sol-gel method. The Ce-Mn/TiO₂ catalyst loading with 20% Ce had the best low-temperature activity and achieved a NO conversion rate higher than 90% at 140–260°C with a 99.7% NO conversion rate at 180°C. The Ce-Mn/TiO₂ catalyst only had a 6% NO conversion rate decrease after 100 ppm of SO₂ was added to the stream. When SO₂ was removed from the stream, the catalyst was able to recover completely. The crystal structure, morphology, textural properties and valence state of the metals involving the novel catalysts were investigated using X-ray diffraction, N₂ adsorption and desorption analysis, X-ray photoelectron spectroscopy, scanning electron microscopy and energy dispersive spectroscopy, respectively. The decrease of NH₃-SCR performance in the presence of 100 ppm SO₂ was due to the decrease of the surface area, change of the pore structure, the decrease of Ce⁴⁺ and Mn⁴⁺ concentration and the formation of the sulfur phase chemicals which blocked the active sites and changed the valence status of the elements.

1. Introduction

Nitrogen oxides NO_x (NO, NO₂, N₂O) are global by-products of high-temperature combustion [1]. NO_x abatement from emissions is necessary because emitted nitrogen oxides cause severe adverse health effects, acid rain and ozone layer depletion [2–6]. Among the NO_x treatment approaches, the technology involving the selective catalytic reduction (SCR) of NO_x with NH₃ (NH₃-SCR) has been regarded as the most effective and widely

used method because of its high denitration efficiency and wide operable temperature range [7]. The SCR method refers to the process in which the reducing agent NH_3 reacts with NO_x with the assistance of catalyst, generating N_2 and H_2O [8]. The reactions involved in this process can be seen in the following equations



and



Reactions (1.1) and (1.2) are designated as the main reactions, and reaction (1.1) is often regarded as the standard SCR reaction. Elevated temperature may lead to the occurrence of NH_3 oxidation side effects, partly shown in equations (1.3) and (1.4). The coexistence of NH_3 , NO and NO_2 will lead to a rapid SCR reaction, shown in equation (1.5). Studies have shown that the reaction rate of equation (1.5) is faster than that of standard SCR reactions.

The fundamental goal of NH_3 -SCR technology is to develop a SCR catalyst that possesses a high activity at relatively low temperature ranges, strong anti-sulfur performance and vanadium-free to be environmentally friendly. Metal oxide catalyst groups that are Mn-based [9–11] and Ce-based [12–14] have high efficiencies at low temperature ranges because of the reduction of Mn^{4+} to Mn^{3+} in the Mn phase, and CeO_2 has a considerably large oxygen storage capacity and excellent redox properties. Composite catalysts prepared using these two kinds of active components have favourable low-temperature denitration activity and are stable when introduced to typical catalyst poisons. In addition, the vast surface area, developed pore structure and acid sites of TiO_2 are more conducive to the adsorption of NH_3 and can accelerate the reaction [15–17]. Qi *et al.* [18] prepared a non-load-type MnO_x - CeO_2 , low-temperature SCR catalyst using co-precipitation. The removal of NO was boosted by improving the ability of the redox catalyst by infusing Mn in the CeO_2 lattice. This generated a large number of oxygen vacancies. Lee *et al.* [19] prepared a $\text{MnO}_x/\text{CeO}_2$ - TiO_2 catalyst. They found that Ce doping increased the surface area of the catalyst, improved the Mn^{4+} concentration and increased the overall catalytic activity. Liu *et al.* [3] proved that the environmentally benign Mn-Ce-Ti catalyst had a high affinity for NO_x removal because of the dual redox properties and the amorphous structure of the catalyst. Moreover, the Mn-Ce-Ti catalyst displayed a high resistance towards H_2O and SO_2 .

The principal objective of this study involves determining how well the co-doped Ce-Mn/ TiO_2 catalyst can tolerate sulfur while undergoing low-temperature SCR. A series of Ce-Mn/ TiO_2 catalysts were prepared using a single impregnation (IP) method and investigated for their effectiveness of low-temperature SCR of NO_x with NH_3 . The possible mechanism of the best performing, low-temperature SCR catalyst in this work is discussed in detail using various characterization methods.

2. Material and methods

2.1. Catalyst preparation

Catalysts were prepared using previously discussed IP and sol-gel (SG) methods [20,21]. The IP method involved using a molar ratio of 2:3 manganese acetate to cerium nitrate. The components were dissolved in deionized water and stirred for 1 h. Subsequently, approximately 2.5 g of TiO_2 was added to the mixture and stirred for 2 h. The suspension was transferred to a rotary evaporator and heated at 55°C for 1 h to obtain the viscous liquid. This sample was dried at 105°C overnight in an oven. Subsequently, the sample was calcined at 550°C for 6 h and ground to a mesh size of 20–40. The mass ratio of Ce/ TiO_2 was tuned and recorded as Ce(wt%)-Mn/ TiO_2 . The molar ratio of Mn and Ce element maintains constant in each catalyst.

The SG method involved using 2.65 g of tetra-*n*-butyl titanate and 21.2 g of ethanol. The components were mixed and stirred for 50 min to form a yellow-tinted solution referred to as ‘solution A’. A separate solution of manganese nitrate and cerium nitrate was dissolved in deionized water, and then anhydrous ethanol and acetic acid were added. This solution was stirred for 1 h to obtain a red-tinted solution referred to as ‘solution B’. Subsequently, solution B was slowly added to solution A, and the mixture was stirred for 12 h. The gel formed at a room temperature for 2 h. The gel was then dried at 105°C for 24 h and calcined at 500°C for 2 h in a 20% O_2 flow. The final sample was ground to a mesh size ranging from

20 to 40. The ratio of tetra-*n*-butyl titanate, ethanol, deionized water and acetic acid was 1:8:6:3. The molar ratio of manganese element and cerium was 2:3 (the same ratio used with the IP method outlined above).

2.2. Catalyst activity measurement

SCR activity of the catalyst was measured using a fixed bed, stainless steel tube reactor with an inner diameter of 11 mm and an outer diameter of 14 mm. Gas purchased to be used in the experiment contained specific concentrations of components to simulate flue gas. The feed gas mixture consisted of 500 ppm NH₃, 500 ppm NO, 3% O₂ (volume fraction), 0–200 ppm SO₂ (depending on the experiment) and a balance of N₂. The simulated gas flow rate was 1000 ml min⁻¹. A volume of 6 ml of catalyst was loaded into the reactor for each experiment. The temperature ranged 100°C and 300°C at a heating rate of 3°C/min with a gas hourly space velocity (GHSV) of 10 000 h⁻¹. The concentrations of NO were monitored at the inlet and outlet in real time using a gas analyser (Testo 340) to calculate the conversion rate using the following equation.

$$\text{NO conversion (\%)} = \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \times 100\%, \quad (2.1)$$

where [NO]_{in} and [NO]_{out} referred to the NO concentration at the reactor inlet and outlet, respectively. The concentration was measured when the reaction reached a steady-state condition (approx. 20–40 min) at each temperature, which reduced the measurement errors caused by instability.

2.3. Catalyst characterization

The powder X-ray diffraction (XRD) characterization of the samples was performed using a Bruker D8-Advance X-ray powder diffractometer with a Cu K α radiation source ($\lambda = 1.5406 \text{ \AA}$), a pulverized sample with scattering angles (2θ) of 5–85° and a 0.0197 step size operated at 50 kV and 50 mA. The diffraction lines were identified by matching them with reference patterns in the Joint Committee on Powder Diffraction Standards (JCPDS) database.

A ThermoFisher Escalab 250Xi X-ray powder photoelectron spectrometer was used to qualitatively analyse the X-ray photoelectron spectroscopy (XPS) characterization of the sample surface composition using an Al K α radiation source with a scattering of 0–5000 eV. The binding energy was calibrated using the C 1s peak contaminate carbon (BE = 284.6 eV) as an internal standard.

N₂ adsorption and desorption of each sample were measured at –196°C using the ASAP 2020 automatic rapid surface area and mesoporous/microporous analyser with a N₂ adsorption gas. The samples were degassed at 200°C for 12 h before the measurement took place. The specific surface area was calculated according to the Brunauer–Emmett–Teller (BET) method. The total pore volume was determined based on the amount of the adsorbed N₂ volume at a relative pressure of approximately $p/p_0 = 0.99$.

The surface morphology of the catalysts was characterized with scanning electron microscopy (SEM) using a Hitachi SU8010 with an acceleration voltage of 15 kV. Qualitative and quantitative analysis of catalyst elements were carried out using energy dispersive X-ray spectroscopy (EDS) on a HORIBA EX-350 with an acceleration voltage of 15 kV.

3. Results

3.1. Effect of synthetic method on the NH₃–SCR activity

SCR activities of the Ce(20)-Mn/TiO₂ catalysts synthesized by the SG and IP methods are shown in figure 1. These results reveal that the IP method had a better low-temperature denitration activity than the SG method. At a temperature range of 140–260°C, the NO conversion rate was higher than 90% in the presence of the IP catalyst. At a temperature range of 160–300°C, the NO conversion rate was higher than 90% in the presence of the SG catalyst. The NO conversion rate was approximately 99.7% at a temperature of 180°C using either method. The catalyst made using the IP method showed better low-temperature denitration activity, was easy to prepare, and had a low-cost preparation process. Therefore, the following Ce-Mn/TiO₂ catalysts used in this study were prepared using the IP method.

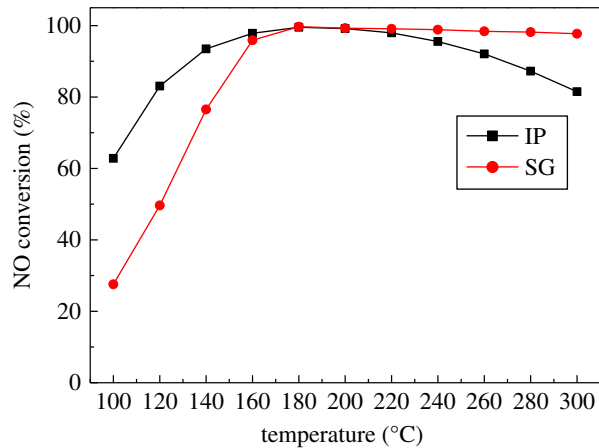


Figure 1. The influence of synthesis methods on NH₃-SCR activity. IP, impregnation method; SG, sol-gel method (500 ppm NO, 500 ppm NH₃, 3% O₂, N₂ balance gas, GHSV = 10 000 h⁻¹).

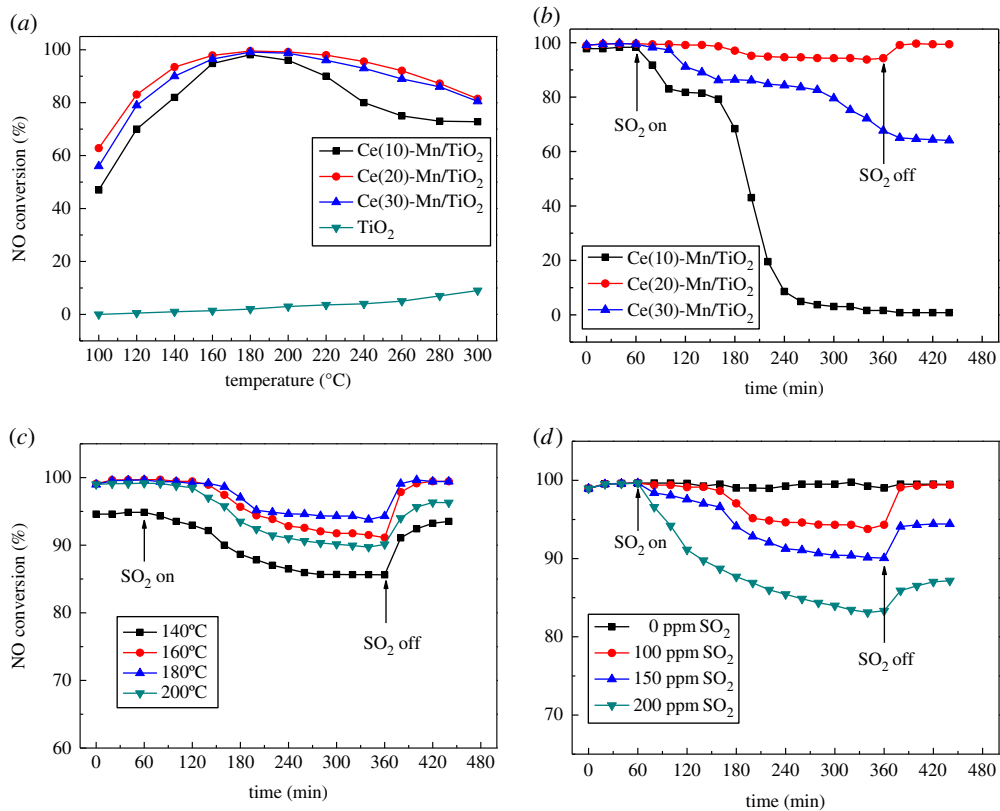


Figure 2. (a) Catalytic activity of Ce-Mn/TiO₂ catalyst for NH₃-SCR. Catalysts were loaded with 10%, 20% and 30% Ce and denoted as Ce(10), Ce(20) and Ce(30), respectively. Pure TiO₂ was also used for comparison. (b) The effect of various Ce concentrations using a Ce-Mn/TiO₂ catalyst on SO₂ resistance. (c) The effects of reaction temperature on NO conversion of the Ce(20)-Mn/TiO₂ catalyst in the presence of SO₂. The above three types of reactions were performed at: 500 ppm NO, 500 ppm NH₃, SO₂ 100 ppm, 3% O₂, N₂ balance gas, GHSV = 10 000 h⁻¹. (d) The effects of SO₂ concentration on NO conversion of Ce(20)-Mn/TiO₂ catalysts ($T = 180^{\circ}\text{C}$, 500 ppm NO, 500 ppm NH₃, 3% O₂, N₂ balance gas, GHSV = 10 000 h⁻¹).

3.2. Resistance to SO₂ poisoning on Ce-Mn/TiO₂ catalysts

The addition of active components has a crucial effect on the catalyst performance in NH₃-SCR. As shown in figure 2a, the NO_x conversion rate on pure TiO₂ was less than 10% in the temperature range of 100–300°C, indicating that the carrier was inactive for denitration. After adding Ce and Mn, the catalytic

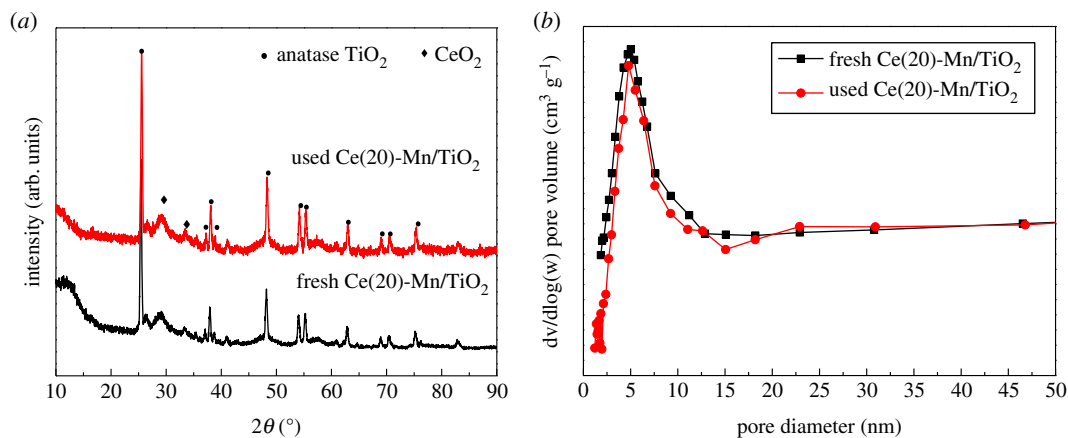


Figure 3. (a) XRD patterns and (b) pore size distribution of fresh and used Ce(20)-Mn/TiO₂ catalysts.

activity of Ce-Mn/TiO₂ was enhanced substantially. Catalysts were loaded with 10%, 20% and 30% Ce and denoted as Ce(10), Ce(20) and Ce(30), respectively. The temperature windows for obtaining a denitration rate higher than 90% included 160–220°C for the Ce(10)-Mn/TiO₂ catalyst, 140–260°C for the Ce(20)-Mn/TiO₂ catalyst and 160–240°C for the Ce(30)-Mn/TiO₂ catalyst. Therefore, the Ce(20)-Mn/TiO₂ catalyst had the highest NO conversion rate of 99.7% with a wide denitration low-temperature window.

In the absence of SO₂, all three Ce-Mn/TiO₂ catalysts had a NO conversion of approximately 100% (during the initial 1 h shown in figure 2b). After adding 100 ppm of SO₂, the NH₃-SCR activity of Ce(10)-Mn/TiO₂ and Ce(30)-Mn/TiO₂ decreased rapidly to 0% and 68% in 5 h, respectively. After SO₂ was removed from the stream, the Ce(10)-Mn/TiO₂ catalyst lost all of its activity, while the Ce(30)-Mn/TiO₂ catalyst only maintained an activity of approximately 65%. However, the Ce(20)-Mn/TiO₂ catalyst had only a small decrease of 6% in the NO conversion after 100 ppm of SO₂ was added in 5 h. After SO₂ was removed from the stream, the NH₃-SCR activity involving the Ce(20)-Mn/TiO₂ catalyst recovered completely and reached 100% NO conversion.

The effect of reaction temperature on the sulfur resistance of the Ce(20)-Mn/TiO₂ catalyst was investigated, and the results are shown in figure 2c. The addition of SO₂ at various reaction temperatures all had an inhibitory effect on the catalytic activity. The conversion rate of NO constantly decreased with the addition of 100 ppm SO₂. The decrease in catalytic activity at 140°C was the most pronounced, while the catalyst activity at 180°C had the best sulfur resistance.

The effect of the SO₂ concentration on the activity of the best Ce(20)-Mn/TiO₂ catalyst was investigated, and the results are shown in figure 2d. When the catalyst was at 180°C for 1 h, the addition of SO₂ in different concentrations decreased the catalytic activity, and there were different levels of recovery after SO₂ was removed from the stream. SO₂ had a toxic effect on the Ce(20)-Mn/TiO₂ catalyst, and as the concentration of SO₂ increased, the catalyst activity decreased. The addition of 100, 150 and 200 ppm SO₂ decreased the NO conversion rate from 99.7% to 94%, 90% and 83%, respectively. After removing 100 ppm of SO₂, the catalyst activity fully recovered; however, only partial recovery was seen after the catalyst was submitted to the higher SO₂ concentrations.

3.3. Catalyst characterization

The Ce(20)-Mn/TiO₂ catalyst had the best NH₃-SCR performance, so only fresh and used Ce(20)-Mn/TiO₂ catalyst were analysed for determining specific catalyst characteristics. The used catalyst was extracted after the reaction was carried out in a 100 ppm SO₂ atmosphere for 5 h at 180°C. The XRD patterns in figure 3a showed that no new peaks were observed in the used catalyst, indicating that the catalyst did not form any (or negligible) crystalline states of sulfate or the amount of the formed phase was too small in the SO₂ atmosphere. Based on the activity discussion mentioned above, the NO conversion rate of the Ce(20)-Mn/TiO₂ catalyst was approximately 94% after the addition of 100 ppm SO₂. Therefore, the Ce(20)-Mn/TiO₂ catalyst had an ideal sulfur resistance.

The specific surface area, pore volume and average pore size of the different Ce(wt%)-Mn/TiO₂ catalysts are summarized in table 1. Owing to the large specific surface area of CeO₂, the loading amount

Table 1. Physical properties of Ce(wt%)-Mn/TiO₂

catalyst	specific surface area (m ² g ⁻¹)	pore volume (cm ³ g ⁻¹)	average pore size (nm)
Ce(10)-Mn/TiO ₂	23.822	0.0575	11.16
Ce(20)-Mn/TiO ₂	35.024	0.0631	8.09
Ce(30)-Mn/TiO ₂	34.839	0.0504	5.06

Table 2. Physical properties of fresh and used Ce(20)-Mn/TiO₂ catalyst.

catalyst	specific surface area (m ² g ⁻¹)	pore volume (cm ³ g ⁻¹)	average pore size (nm)
fresh Ce(20)-Mn/TiO ₂	35.024	0.0631	8.09
used Ce(20)-Mn/TiO ₂	28.092	0.0624	6.15

of Ce had a significant impact on the specific surface area of the catalyst. With the increase in the loading amount, the specific surface area showed a tendency to increase first and then decrease. The increase in the loading amount of Ce led to a discernable change of the specific surface area from 23.822 to 35.024 m² g⁻¹ and finally to 34.839 m² g⁻¹, indicating that the doping of Ce played an important role in the variation of the specific surface area of the catalyst. The surface area of Ce(10)-Mn/TiO₂ is relatively small, which corresponds to the lowest catalytic activity of Ce(10)-Mn/TiO₂ in figure 2a.

The specific surface area, pore volume and average pore size of the fresh and used catalyst are summarized in Table 2. The physical properties of the catalyst were impaired by SO₂. The addition of 100 ppm SO₂ decreased the respective specific surface area, pore volume and average pore size of the Ce(20)-Mn/TiO₂ catalyst from 35.024 m² g⁻¹, 0.0631 cm³ g⁻¹ and 8.09 nm to 28.092 m² g⁻¹, 0.0624 cm³ g⁻¹ and 6.15 nm, respectively. The pore size distribution of fresh and used Ce(20)-Mn/TiO₂ catalysts are shown in figure 3b. The pore structure of the fresh Ce(20)-Mn/TiO₂ catalyst was in the range of 2–10 nm. After the reaction, the number of pores in the range of 8–10 nm decreased slightly, while the number of pores in the 2–8 nm range did not change, ensuring there was sufficient catalytic activity. The decreased NO conversion was due to the change in the catalyst structure in terms of the pore size distribution and surface area.

The fresh and used Ce(20)-Mn/TiO₂ catalysts were also characterized by SEM-EDS, and the results are shown in figure 4. An agglomeration phenomenon, though not obvious, occurred on the surface of the catalyst after undergoing reactions in the SO₂ atmosphere (figure 4a–b). EDS mapping results (figure 4c–d and table 3) verified the existence of S and N on the surface, implying that the ammonium sulfate material formed on the surface of the used catalyst. This covered the active sites and decreased the catalytic activity. However, the XRD patterns imply that the ammonium sulfate material was not obviously detected because there is no formation or only a relatively small amount was present and therefore accounted for only a negligible decrease of the catalytic activity in the SO₂ atmosphere.

XPS spectra of the Ce 3d, Mn 2p and O 1s of the fresh and used Ce(20)-Mn/TiO₂ catalysts are shown in figure 5a–c. Figure 5a shows the Ce 3d in the fresh and used catalysts had eight peaks, where the V', U' were the characteristic peaks of Ce³⁺ (Ce₂O₃), and V, V'', V''', U, U'', U''' were the characteristic peaks of Ce⁴⁺. The leading form of the Ce oxide in both catalysts was CeO₂ (Ce⁴⁺) which was beneficial for oxygen storage capacity. The conversion between Ce³⁺ and Ce⁴⁺ accomplished a storage-release cycle of oxygen for better promoting the process of denitration. Figure 5b illustrates that the peak of Mn 2p_{1/2} was located near 653.3 eV, while the peak of Mn 2p_{3/2} was composed of Mn²⁺, Mn³⁺ (642.0 eV) and Mn⁴⁺ (643.0 eV). The leading form of Mn in the Ce(20)-Mn/TiO₂ catalyst was Mn⁴⁺ (table 4). The catalytic effect of MnO_x was related to its valence state, where MnO₂ > Mn₂O₃ > MnO [22]. This has also been demonstrated by Thirupathi & Smirniotis [23]. Their group indicated that MnO₂ was the most active component among a series comprising MnO₂, Mn₅O₈, Mn₂O₃ and Mn₃O₄. Therefore, Mn⁴⁺ had a superior catalytic denitration activity, and this corresponded to the best catalytic denitration activity of Ce(20)-Mn/TiO₂. The peaks of the Mn 2p_{1/2} and Mn 2p_{3/2} of the used catalyst shifted in the direction of a higher electron bonding energy, and the offsets were approximately 0.06 eV and 0.1 eV, respectively. This indicated that a metal sulfate formed which resulted from the sulfation of Mn [24]. The decrease of Mn⁴⁺/Mn³⁺ from 84.4% to 75.4% is a possible reason for the decreased NH₃-SCR activity. The

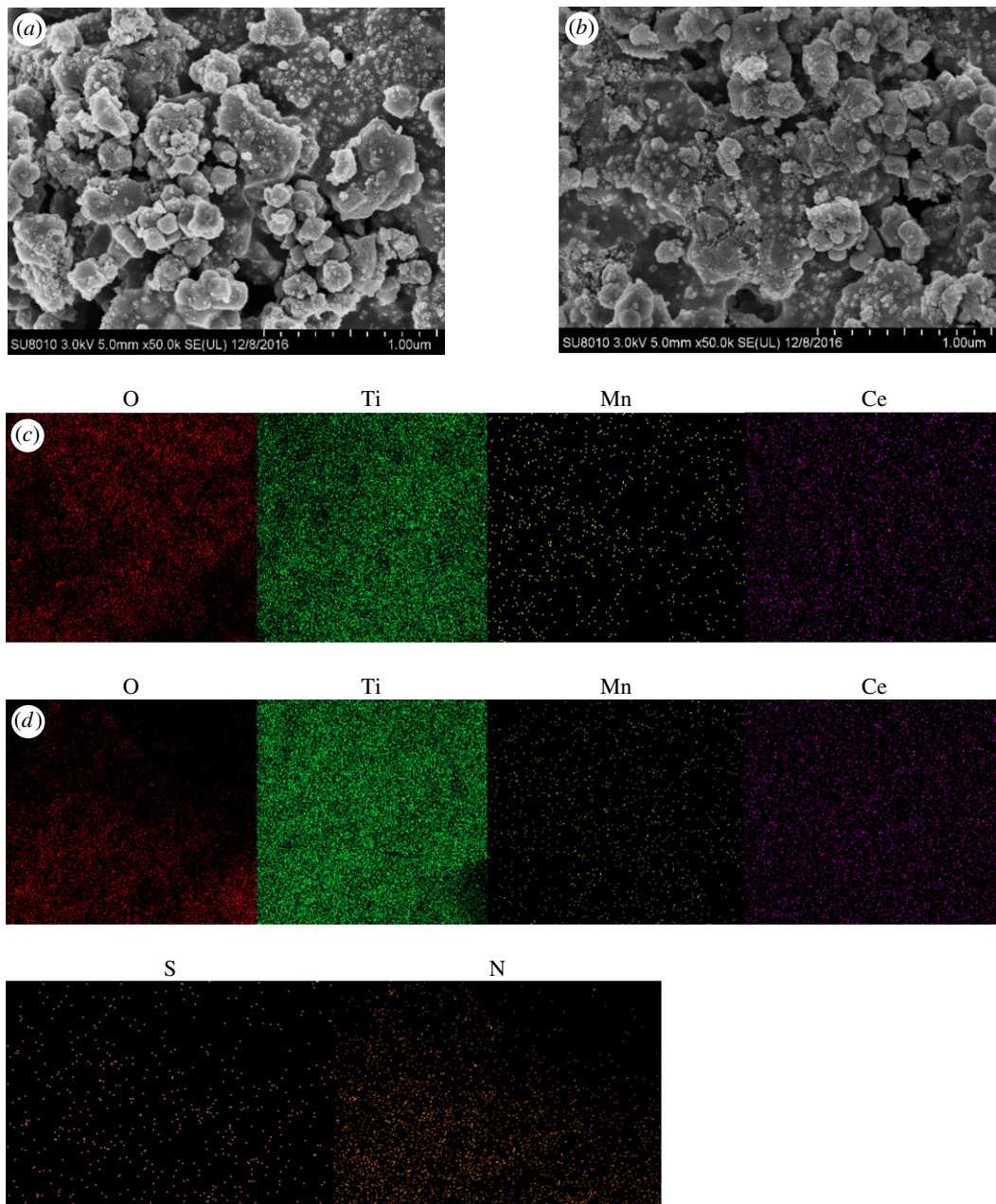


Figure 4. SEM micrographs of (a) fresh and (b) used Ce(20)-Mn/TiO₂ catalysts as well as energy dispersive spectrometer images of (c) fresh and (d) used Ce(20)-Mn/TiO₂ catalyst.

Table 3. Surface element concentration of fresh and used Ce(20)-Mn/TiO₂ catalyst.

catalyst	the concentration of surface elements (%)					
	Ce	Mn	O	Ti	S	N
fresh Ce(20)-Mn/TiO ₂	10.37	8.96	75.22	5.45	—	—
used Ce(20)-Mn/TiO ₂	10.1	8.01	71.41	5.23	3.28	1.97

spectrum of O 1s in figure 5c contains characteristic peaks of O_α and O_β, where O_β belongs to the characteristic peak of lattice oxygen at a binding energy of 529.5–529.8 eV. O_α belongs to the surface adsorption characteristic peaks of oxygen at a binding energy of 531.8–532.5 eV [10]. In table 4, the surface adsorption of the oxygen concentration was 48.8% in the fresh catalyst, and this increased to 40.5% in the

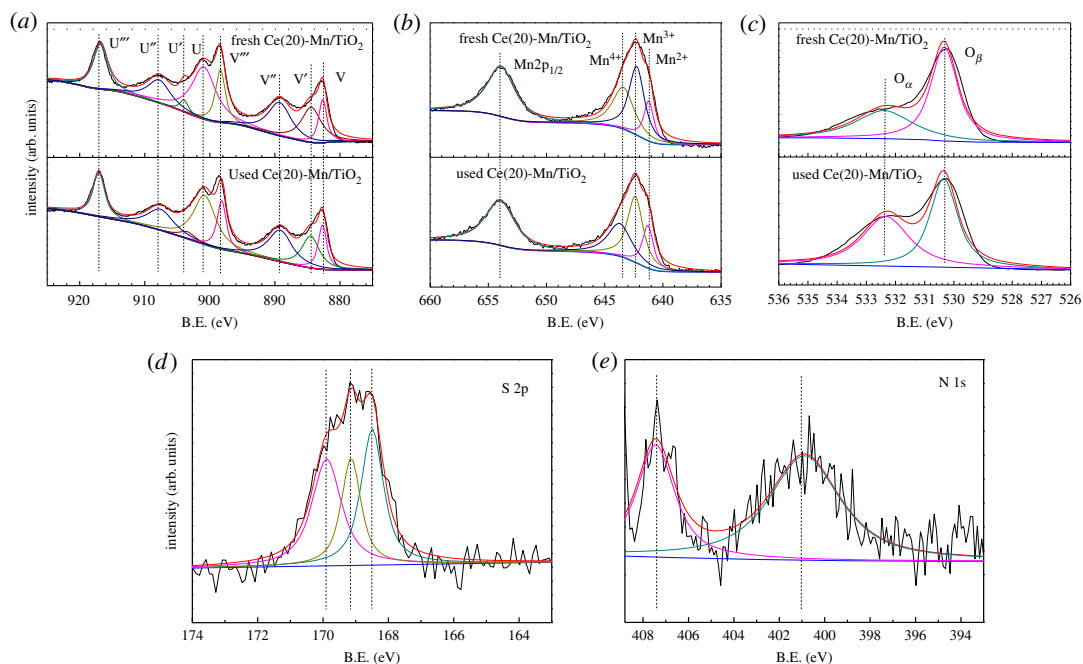


Figure 5. XPS spectra of fresh and used Ce(20)-Mn/TiO₂. (a) Ce 3d, (b) Mn 2p, (c) O 1s, (d) S 2p and (e) N 1s.

Table 4. Surface elemental valence distribution of fresh and used Ce(20)-Mn/TiO₂ catalyst.

catalyst	the valence ratio of the surface elements (%)		
	Ce ³⁺ /Ce ⁴⁺	Mn ⁴⁺ /Mn ³⁺	O _α /(O _α +O _β)
fresh Ce (20)-Mn/TiO ₂	17.5	84.4	48.8
used Ce (20)-Mn/TiO ₂	18.0	75.3	40.5

used catalyst. The high concentration of the surface adsorption of oxygen had a strong oxidation effect, which not only completed the oxidation and reduction cycle but also enhanced the oxidation process of NO to NO₂. This promoted a rapid response to the SCR reaction [25,26].

XPS spectra of the S 2p and N 1s of the used Ce(20)-Mn/TiO₂ catalysts are shown in figure 5d–e. Figure 5d shows that the leading form of S in the used catalyst was S⁴⁺ and S⁶⁺. The peak at 168.5 eV belonged to SO₃²⁻, while the peaks at 169.9 and 169.1 eV were assigned to SO₄²⁻ [24]. S⁶⁺ accounted for approximately 63% of S and included some sulfate material which formed on the catalyst surface after undergoing reactions in the SO₂ atmosphere. Figure 5e demonstrates the peaks of N located in the vicinity of 400.8 eV and 407.3 eV were characterized as NH₄⁺ and NO₃⁻, respectively [27]. NH₄⁺ accounted for approximately 64% of the total N. The conversion of NH₃ to NH₄⁺ and NO₃⁻ was indicated by the results.

4. Conclusion

NH₃-SCR activity was measured after using an IP method and a SG method to form a Ce-Mn/TiO₂ catalyst. The catalyst formed with the IP method had a better low-temperature denitration activity than the catalyst synthesized using the SG method. The Ce-Mn/TiO₂ catalyst loaded with 20% Ce had the best low-temperature activity with a NO conversion rate of 99.7% at 180°C. Despite the addition of 100 ppm SO₂ at 180°C for 5 h, the NO conversion rate of the Ce(20)-Mn/TiO₂ catalyst was still as high as 94% and recovered when SO₂ was removed from the stream. The SO₂ resistance of the Ce(20)-Mn/TiO₂ catalyst is attributed to the widely distributed elements of Mn and Ce. This led to the inability of the sulfate material to remain on the surface. Characterization of fresh and used Ce(20)-Mn/TiO₂ catalysts was performed using XRD, BET, XPS and SEM-EDS. These results indicated that there was a decrease in Ce⁴⁺ and Mn⁴⁺

in the used catalysts. These results also showed that the sulfate phase formation and the change of the pore structure accounted for a decrease in NH_3 -SCR activity.

Data, accessibility. Our data are deposited at Dryad: <https://doi.org/10.5061/dryad.pv12j> [28].

Authors' contributions. Q.X. designed the study; W.Y. and S.C. performed the laboratory experiment; Q.X. and Y.L. analysed data; Q.X., Y.L. and J.S. edited the manuscript for important intellectual content; all authors wrote the manuscript and gave final approval for publication.

Competing interests. We have no competing interests.

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