



Effects of ferric and manganese precursors on catalytic activity of Fe-Mn/TiO₂ catalysts for selective reduction of NO with ammonia at low temperature

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Abstract

Fe-Mn/TiO₂ catalysts were prepared through the wet impregnation process to selective catalytic reduction of NO by NH₃ at low temperature, and series of experiments were conducted to investigate the effects of key precursors on their SCR performance. Ferric nitrate, ferrous sulfate, and ferrous chloride were chosen as Fe precursors while manganese nitrate, manganese acetate, and manganese chloride as Mn precursors. These precursors had been commonly used to prepare Fe-Mn/TiO₂ catalysts by numerous researchers. The results showed that there were distinct differences in NO conversion efficiencies at low temperature of catalysts prepared with different precursors. Catalysts prepared with ferric nitrate and manganese nitrate precursors exhibited the best catalytic performance at low temperature, while three kinds of catalysts prepared with manganese chloride precursors exhibited significantly low catalytic activity. All catalysts were characterized by XRD, SEM, H₂-TPR, NH₃-TPD, and XPS. The results indicated that when the catalysts were prepared with manganese nitrate or manganese acetate as precursors, Mn⁴⁺ contents and O_β/(O_β + O_α) ratios decreased in an order of ferric nitrate > ferrous sulfate > ferrous chloride, which was consistent with the change of catalytic activities of the corresponding catalysts at low temperature. It can be found that the excellent catalytic performance of Fe(A)-Mn(a)/TiO₂ was ascribed to high redox property and enrichment of Mn⁴⁺ species and surface chemical labile oxygen groups.

Keywords Nitrogen oxides · Precursors · Selective catalytic reduction · Fe-Mn/TiO₂ catalysts

Highlights

- The effects of Fe and Mn precursors on NH₃-SCR performance were investigated.
- The catalyst prepared using ferric nitrate and manganese nitrate precursors exhibited the best catalytic activity at low temperature, while the catalysts prepared with chloride precursors exhibited much lower catalytic activities.
- The choice of Fe and Mn precursors was crucial for preparing Fe-Mn/TiO₂ catalysts, which would probably affect the redox property, Mn⁴⁺ content, the surface chemisorbed labile oxygen content, and the dispersion of active species over support.

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Introduction

It is well known that nitrogen oxides (NO_x) emitted from stationary and mobile sources are serious gaseous pollutants, which have resulted in the severe impact on the atmospheric environment and human health. At present, there are a lot of NO_x removal technologies for practical applications. Among them, selective catalytic reduction (SCR) with NH_3 (or urea) is the most attractive one due to high reduction efficiency and low running cost. It has been widely used to remove NO_x from industrial boilers, diesel cars, and ocean-going vessels (Cimino et al. 2016), in which catalysts in SCR systems play a critical role in creating an efficient reaction and controlling the construction cost (Fan et al. 2017). Up to date, two kinds of SCR catalysts, $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ and $\text{V}_2\text{O}_5\text{-MoO}_3/\text{TiO}_2$, have been used extensively in commercial projects. However, there are still some shortcomings, such as narrow catalytic temperature window (300–450 °C) (Zhu et al. 2017) and toxic effect of V_2O_5 (Xu et al. 2018a, b), limiting their application in more and more cases. Especially when the flue gas temperature is much below 300 °C, it is very difficult to achieve a high NO_x removal efficiency for the commercial catalyst products. Thus, it is of great importance to develop an environmentally friendly SCR catalyst with excellent catalytic activity at low and middle temperatures.

During the past decades, researchers around the world had put a great deal of effort to develop high-performance low-temperature SCR catalysts. Several kinds of transition metals, such as Mn, Co, Fe, Cu, and Ce, had been introduced to prepare SCR catalysts (Qiu et al. 2016; Gao et al. 2019; Wang et al. 2019a, b; Liu et al. 2019). Since manganese oxides (Mn_3O_4 , Mn_2O_3 , MnO_2 , MnO) have multiple valences, labile oxygen, and diversiform oxidation states, MnO_x -based catalysts have attracted numerous researchers' interests (Li et al. 2017; Yang et al. 2019; Wu et al. 2007). In NH_3 -SCR reactions, MnO_x would undergo oxidation–reduction cycles, which reflected the ease of changing oxidation states of Mn ions (Kapteijn et al. 1994). Meanwhile, it was reported that TiO_2 was a favorable candidate as SCR support due to its good catalytic activity and sulfur resistance (Kantcheva 2001). Therefore, Mn/TiO_2 catalysts had been investigated extensively, and the results demonstrated that it was one of the most promising SCR catalysts for low-temperature application (Pena et al. 2004; Li et al. 2017; Yang et al. 2019; Wu et al. 2007). But there are still some challenges for MnO_x -based catalysts to deal with, such as poor N_2 selectivity and easy deactivation by H_2O . A feasible way to promote the NH_3 -SCR performance of Mn/TiO_2 catalysts was to introduce other modified metals. Several kinds of bimetallic Mn-based catalysts, such as $\text{Fe-Mn}/\text{TiO}_2$ (Qi and Yang 2003; Putluru et al. 2015; Zhang et al. 2018; Lin et al. 2018), $\text{Sm-Mn}/\text{TiO}_2$ (Sun et al. 2018), $\text{Cu-Mn}/\text{TiO}_2$ (Li et al. 2019), $\text{Ce-Mn}/\text{TiO}_2$ (Pan et al. 2018), $\text{Nd-Mn}/\text{TiO}_2$ (Huang et al. 2019), $\text{Sb-Mn}/\text{TiO}_2$ (Yang et al. 2016), and $\text{W-Mn}/\text{TiO}_2$ (Geng et al.

2018), had already been studied, and the results implied that there were obvious synergetic effects between MnO_x and other metal oxides in enhancing the SCR performance. Typically, the addition of Fe into MnO_x -based catalysts supported on TiO_2 could improve the catalytic activity significantly at low temperature. The reason might lie in that co-existing ferric oxides could be in favor to obtain a high dispersion of MnO_x on supports, thus enhancing the oxidation of NO into NO_2 (Qi and Yang 2003; Wu et al. 2007; Putluru et al. 2015; Deng et al. 2016). To some extent, $\text{Fe-Mn}/\text{TiO}_2$ catalysts were considered as one promising candidate for low-temperature SCR application.

It was reported that the types of metal precursors would induce different metal oxidation states during the preparation of SCR catalysts, which would exert a great impact to catalyst activities (Xu et al. 2018b; Kapteijn et al. 1994; Li et al. 2007; Huang et al. 2018). Previous studies showed that Mn/TiO_2 catalysts prepared from manganese nitrate exhibited better performance within 100–200 °C than that prepared from manganese acetate precursors (Pena et al. 2004). It was ascribed to a higher surface area of the catalysts prepared from manganese nitrate precursors and the formation of MnO_2 as active species. But an opposite result was reported that Mn/TiO_2 catalysts prepared from manganese acetate precursors could present higher low-temperature activity compared to that made from manganese nitrate (Li et al. 2007). An explanation was given that surface Mn concentration and surface Mn_2O_3 species were a little higher in the catalysts prepared from manganese acetate precursors. Similar conclusion could also be found in other researchers' work. A comparative study on the effects of three different precursors, manganese (II) nitrate, manganese (II) acetate, and manganese (III) acetate, on Mn/TiO_2 catalytic performance had been done (Hwang et al. 2016). Experimental results showed that Mn/TiO_2 catalysts prepared from manganese (III) acetate precursors had the highest denitrification efficiency, which was ascribed to the most enriched Mn concentration and MnO_2 species, together with strong acid sites on catalyst surface.

Undoubtedly, as bimetallic MnO_x -based catalysts, the physicochemical properties of $\text{Fe-Mn}/\text{TiO}_2$ catalysts were directly related to both ferric and manganese precursors. It was reported that compared with other nitrates of transition metals such as Cu, Ni, and Cr, ferric nitrate as Fe precursor could be in favor of improving NH_3 -SCR activity of $\text{Fe-Mn}/\text{TiO}_2$ catalyst, but the related mechanism had not been explored in detail (Wu et al. 2008). Hitherto, the major efforts had focused on $\text{Fe-Mn}/\text{TiO}_2$ in terms of preparation methods, other metal modification, calcination temperature, and catalytic behavior. To the best of our knowledge, few studies have been done to investigate the influence of ferric and manganese precursors on physicochemical properties of $\text{Fe-Mn}/\text{TiO}_2$ catalysts and their corresponding SCR performance. Therefore, it is very meaningful to conduct systematic experiments to study the effects of key precursors on the catalytic activity of $\text{Fe-Mn}/$

TiO₂ catalysts at low temperature. In the present work, Fe-Mn/TiO₂ catalysts were prepared with ferric precursors (ferric nitrate, ferrous sulfate, ferrous chloride) and manganese precursors (manganese nitrate, manganese acetate, manganese chloride) via the wet impregnation process. The reason for the choice of these six precursors lied in that they were commonly used to prepare Fe-Mn/TiO₂ catalysts in previous studies, and their catalytic performance was evaluated in a temperature range of 60–300 °C (Xu et al. 2018a, b; Chen et al. 2018; Li et al. 2007; Hwang et al. 2016; Zhang et al. 2012). N₂ adsorption/desorption, X-ray diffraction (XRD), scanning electron microscopy (SEM), H₂ temperature-programmed reduction (H₂-TPR), NH₃ temperature-programmed desorption (NH₃-TPD), and X-ray photoelectron spectroscopy (XPS) were employed to characterize the physicochemical properties of the prepared catalysts. And the influences of ferric and manganese precursors on SCR performance were also analyzed in detail.

Experimental

Catalyst preparation

Fe-Mn/TiO₂ catalysts were prepared by wet impregnation of TiO₂ (P25) with various ferric precursors (Fe(NO₃)₃·9H₂O or FeSO₄·7H₂O or FeCl₂·4H₂O) and manganese precursors (Mn(NO₃)₂·4H₂O or Mn(CH₃COO)₂·4H₂O or MnCl₂·4H₂O) successively, followed by stirring thoroughly at 80 °C for 2 h. Then ammonia was added dropwise until solution pH reached 10. The mixture solution was dried at 120 °C overnight and calcined at 500 °C for 3 h in air. Finally, catalyst powders were pressed, crushed, and sieved to 40–60 mesh before evaluation.

In this study, the molar ratio of Fe/Mn/Ti was fixed at 2:6:15. The prepared catalysts were denoted as Fe(*x*)-Mn(*y*)/TiO₂, where *x* represents *A* (ferric nitrate), *B* (ferrous sulfate), and *C* (ferrous chloride) and *y* represents *a* (manganese nitrate), *b* (manganese acetate), and *c* (manganese chloride). For example, Fe(*A*)-Mn(*a*)/TiO₂ corresponds to the catalyst prepared with Fe(NO₃)₃·9H₂O and Mn(NO₃)₂·4H₂O as precursor solutions.

Catalyst activity test

The SCR performance of all prepared catalysts was evaluated using a fixed-bed quartz reactor (inner diameter 9 mm) at a reaction temperature range of 60–300 °C under atmospheric pressure. The reactor was equipped with a temperature-programming controller. A catalyst of 1.5 g was used for catalytic assessment with a gas hourly space velocity (GHSV) of 25,000 h⁻¹. The total flow rate of simulated flue gas was 1.1 L/min, and the gas components were 0.08% NO,

0.08% NH₃, 5% O₂, 10% H₂O (when used), 0.01% SO₂ (when used), and N₂ as balance gas. An online flue gas analyzer (MRU, Germany) was used to monitor NO concentration in flue gas. The concentrations of N₂O, SO₂, NH₃, and H₂O in the outlet gas were measured by a Fourier-transform infrared spectrometer (Thermo fisher, USA). NO conversion efficiency and N₂ selectivity were calculated as Eqs. (1) and (2), respectively.

$$X_{\text{NO}}\% = \frac{[\text{NO}]_{\text{inlet}} - [\text{NO}]_{\text{outlet}}}{[\text{NO}]_{\text{inlet}}} \times 100\% \quad (1)$$

$$\begin{aligned} N_2 \text{ selectivity}\% \\ = 1 - \frac{[\text{NO}_2]_{\text{outlet}} + 2[\text{N}_2\text{O}]_{\text{outlet}}}{[\text{NO}]_{\text{inlet}} - [\text{NO}]_{\text{outlet}} + [\text{NH}_3]_{\text{inlet}} - [\text{NH}_3]_{\text{outlet}}} \times 100\% \end{aligned} \quad (2)$$

Catalyst characterization

The textural properties of the prepared catalysts, including the specific surface area, total pore volume, and average pore diameter, were measured at -196 °C using a N₂ adsorption analyzer (Quantachrome, USA) following a static-volumetric method. The specific surface areas were calculated via the Brunauer–Emmett–Teller (BET) model from the adsorption data. XRD patterns were obtained using an X-ray diffractometer (PANalytical B.V., Netherland) using Cu Kα as radiation source at 40 kV and 30 mA. The angle 2θ was scanned over a range of 10–80° at a step size of 0.02°. The surface morphology and structure of the catalysts were observed using SEM (Zeiss, Germany). H₂-TPR profiles were measured using a chemisorption analyzer (Micromeritics, USA). NH₃-TPD experiments were conducted using a chemisorption analyzer (Micromeritics, USA), and the TPD profiles were obtained under a He atmosphere (50 mL/min) from 100 to 500 °C (ramp rate of 10 °C/min). XPS profiles were collected using a surface analysis photoelectron spectrometer (ESCALAB, USA), with Al Kα as radiation source at 300 W.

Results and discussion

Effects on SCR performance

Figure 1 illustrated NO conversion efficiencies of the prepared Fe-Mn/TiO₂ catalysts across a temperature window of 60–300 °C. It could be observed that all of the catalysts exhibited good catalytic performance at reaction temperature above 240 °C. But when reaction temperature was below 240 °C, there were distinct differences in NO conversion efficiencies

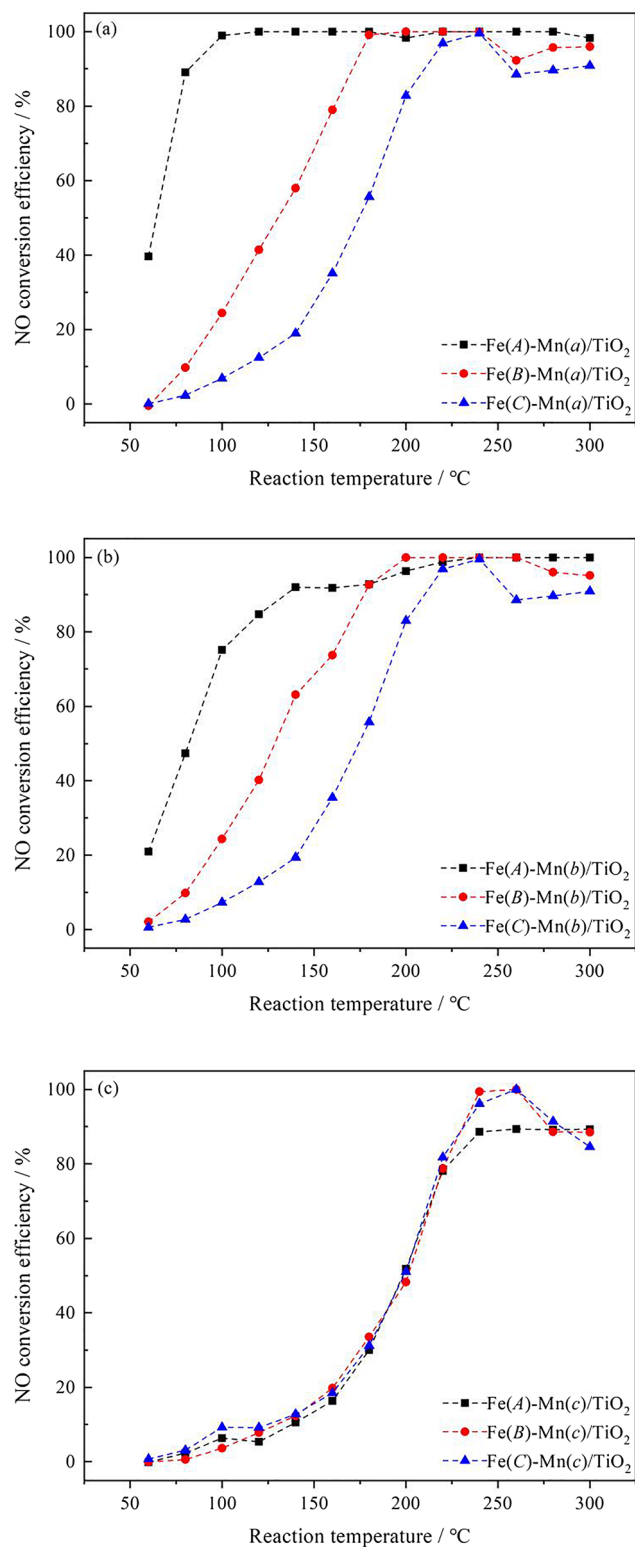


Fig. 1 Effects of Fe and Mn precursors on NH₃-SCR activity of the prepared Fe(x)-Mn(y)/TiO₂ catalysts. Reaction conditions: 1.5 g catalyst, 0.08% NO, 0.08% NH₃, 5% O₂, N₂ balance gas, GHSV = 25,000 h⁻¹

of the catalysts prepared with different precursors. It indicated that both Fe and Mn precursors influenced SCR performance

apparently. According to the results, NO removal performance of the prepared catalysts at low temperature was approximately in an order of Fe(A)-Mn(a)/TiO₂ > Fe(A)-Mn(b)/TiO₂ > Fe(B)-Mn(a)/TiO₂ ≈ Fe(B)-Mn(b)/TiO₂ > Fe(C)-Mn(b)/TiO₂ ≈ Fe(C)-Mn(a)/TiO₂ > Fe(A)-Mn(c)/TiO₂ ≈ Fe(B)-Mn(c)/TiO₂ ≈ Fe(C)-Mn(c)/TiO₂. Clearly, the catalysts prepared with ferric nitrate and manganese nitrate precursors exhibited superior catalytic performance over other catalysts at low temperature. But some previous studies showed that the catalytic performance of the catalyst prepared with ferric nitrate and manganese acetate could be superior over that of the catalyst prepared with ferric nitrate and manganese nitrate. To some extent, it demonstrated that not only the precursors but also the preparation process would influence the catalytic performance, obviously. Mu et al. had prepared Fe-Mn/TiO₂ catalysts with ferric nitrate and manganese acetate as precursors by an impregnation method (Mu et al. 2018). By simple comparison, it could be seen that the catalytic performance of Fe(A)-Mn(b)/TiO₂ prepared in this work was similar to that without the assistance of ethylene glycol (EG) in Mu’s work. In other words, Mu et al. improved the catalytic performance of Fe(A)-Mn(b)/TiO₂ by adding EG in the precursor solution while that could be achieved similarly by replacing manganese acetate with manganese nitrate in our work. The results showed that the light-off temperature (where NO conversion achieved 50%) for the Fe(A)-Mn(a)/TiO₂ catalyst was ~70 °C, and it achieved 100% NO conversion efficiency at 100 °C with a wide temperature window from 75 to 300 °C.

As shown in Fig. 1, three kinds of catalysts prepared with manganese chloride precursors exhibited significantly lower catalytic activity at low temperature. It could be ascribed to a lower degree of manganese chloride decomposition.

For the catalysts prepared using manganese nitrate and manganese acetate precursors, it could be seen that the catalytic activities at low temperature for catalysts prepared using different ferric precursors were in an order of ferric nitrate > ferrous sulfate > ferrous chloride. Besides, the results indicated that when ferrous sulfate or ferrous chloride was used as precursor, there were few differences in catalytic performance between the catalysts prepared using manganese nitrate and manganese acetate precursors. But a distinct difference existed in Fe(x)-Mn(a)/TiO₂ catalysts at low temperature. It implied that ferric precursors imposed a great effect on the catalytic performance of Fe-Mn/TiO₂ catalysts at low temperature, which was possibly related with the degree of ferric precursor decomposition and the dispersion of MnO_x species. Here, the performance of Fe-Mn/TiO₂ catalysts prepared with various precursors was quite different from that in previous comparison work on the effects of precursors on Mn/TiO₂ catalyst (Li et al. 2007). It was obvious that the presence of transition metal Fe had changed the influences of single Mn precursor on catalytic activity at low temperature.

Since the Fe(A)-Mn(a)/TiO₂ catalyst displayed the excellent NO conversion, thus, it was selected to study the N₂ selectivity during the NH₃-SCR reaction, and the results are presented in Fig. 2. As shown in Fig. 2, N₂ selectivity of Fe(A)-Mn(a)/TiO₂ catalyst was 88% at 100 °C, while NO conversion efficiency reached 100% at the same time. But there was a decreasing trend of N₂ selectivity with the increase of the reaction temperature. This phenomenon was ascribed to the generation of more unwanted N₂O through some side reactions (Han et al. 2019). It is known that Mn is the main active phase for SCR reactions; so, the formation routines of N₂O with Fe(A)-Mn(a)/TiO₂ as catalyst in our experiments is similar to those with Mn/TiO₂ as catalysts. Wang et al. had investigated the sources of N and O in formed N₂O over MnO_x/TiO₂ catalysts in the NH₃-SCR process (Wang et al. 2019b). Their experimental results showed that both NH₃ oxidation reaction (2NH₃ + 2O₂ → N₂O + 3H₂O) and nonselective catalytic reduction (NSCR) of NO with NH₃ (4NO + 4NH₃ + 3O₂ → 4N₂O + 6H₂O) accounted for N₂O formation. Other researchers pointed out that the reaction rate of these side reactions would increase with the increase of reaction temperature, so it was normal that the production of N₂O would increase with the temperature increasing (Părvulescu et al. 1998). Therefore, it was still a common issue that, for Mn-based catalysts, N₂ selectivity would decrease with the increase of reaction temperature.

N₂ adsorption/desorption

N₂ adsorption–desorption isotherms of Fe(x)-Mn(y)/TiO₂ catalysts are shown in Fig. 3. According to the IUPAC classification, the adsorption isotherms of the catalysts were type IV, suggesting that the prepared catalysts belonged to mesoporous

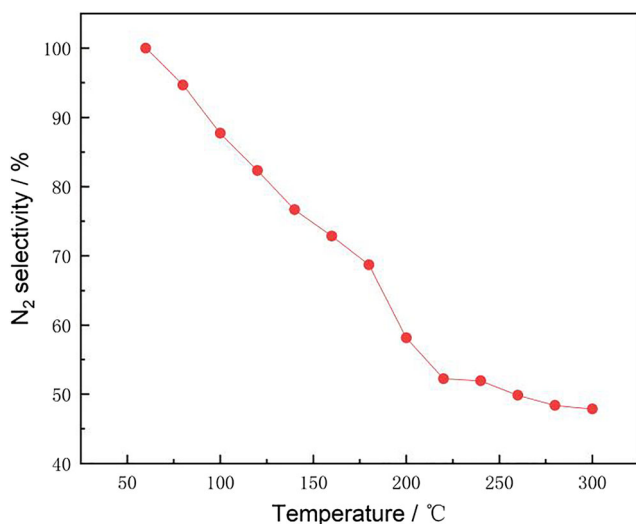


Fig. 2 N₂ selectivity of the Fe(A)-Mn(a)/TiO₂ catalyst. Reaction conditions: 1.5 g catalyst, 0.08% NO, 0.08% NH₃, 5% O₂, N₂ balance gas, GHSV = 25,000 h⁻¹

materials. The specific surface areas, pore volumes, and pore sizes are summarized in Table S1. The results showed that the physical properties of the catalysts were quite different from

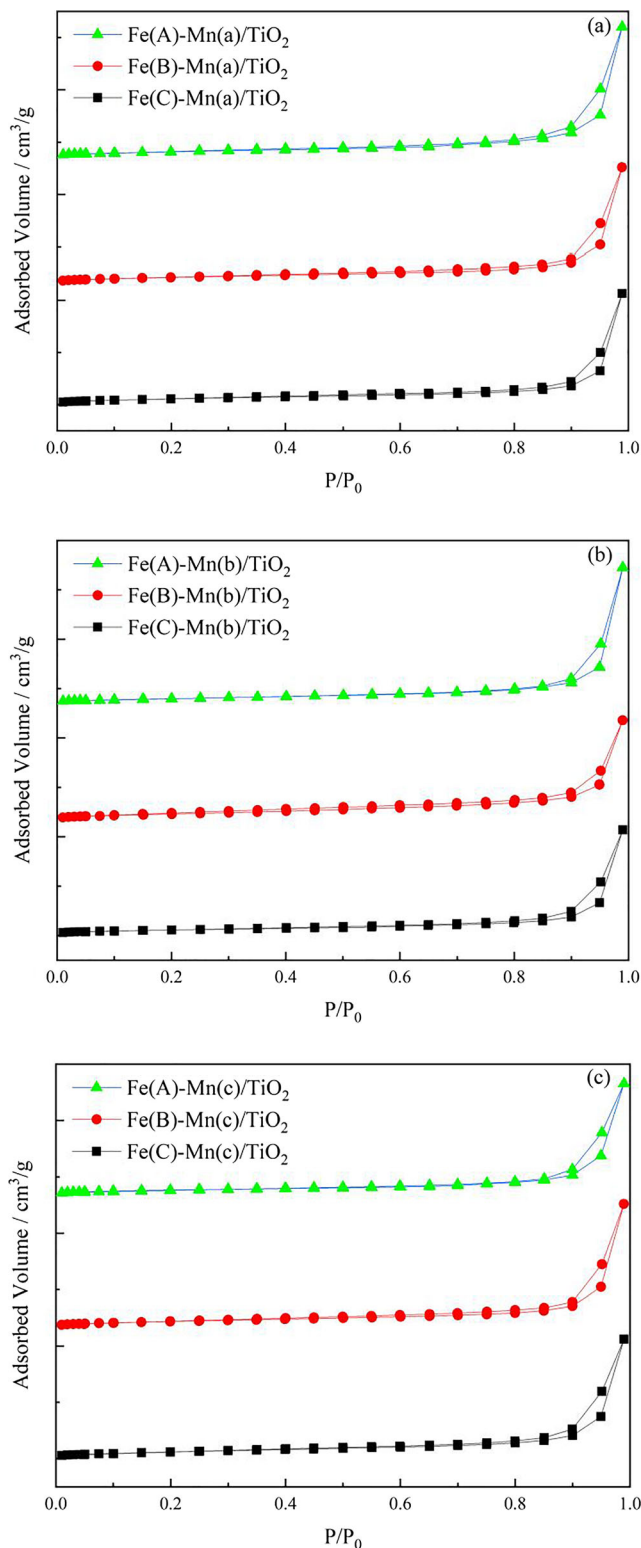


Fig. 3 N₂ adsorption/desorption isotherm of the prepared Fe(x)-Mn(y)/TiO₂ catalysts

each other. The specific surface areas of the five kinds of catalysts prepared with chloride precursors were less than 45 m²/g, which exhibited the greatest loss of specific surface areas compared with the other four kinds of catalysts. The reason for the latter catalysts possessing higher specific surface areas might be attributed to MnO_x species being highly dispersed over the catalysts. It was in favor of improving the catalytic activity. The result suggested that the changes in textural properties correlated to the catalytic performance to some degree, though they were not the main factors influencing the catalytic activity at low temperature.

XRD

Figure 4 presents the XRD patterns of the prepared Fe(x)-Mn(y)/TiO₂ catalysts. In the XRD patterns, the peaks at 2θ of 25.3°, 36.9°, 37.9°, 38.7°, 48.0°, 54.0°, 55.0°, and 62.7° could be attributed to anatase TiO₂ (PDF#21–1272). Though the diffraction peaks of TiO₂ were apparent in all catalysts, the diffraction peaks of Fe and Mn oxides could only be detected in the patterns of five kinds of catalysts prepared with chloride precursors. It indicated that Fe and Mn oxides existed in the form of crystal states, and their sizes were relatively large, which would impose some adverse effects on catalytic performance. Therefore, the catalytic activities of catalysts prepared with chloride precursors were obviously inferior to those with other kinds of precursors. This agreed well with the aforementioned results of SCR activity and N₂ adsorption/desorption tests.

In other words, it could be known from Fig. 4 that for the catalysts prepared using non-chloride precursors, Fe and Mn oxides were well dispersed in amorphous or crystallite states with very small particle sizes on anatase TiO₂ support. That was because nitrates, sulfate, and acetate could decompose into metal oxides easily during the calcination process, and the presence of transition metal Fe was beneficial to promote the transformation of MnO_x from crystalline state to amorphous state (Mu et al. 2018). In addition, the addition of Fe could improve the dispersion of Mn oxides on the supports, which might also have a correlation with the increasing surface area. A well dispersion of active species would be beneficial to obtain a well distribution of active sites, thus enhancing the catalytic activity (Yang et al. 2019; Wu et al. 2019). Therefore, the high dispersion property of the active species was a preferable aspect for the selection of precursors for preparing Fe-Mn/TiO₂ catalysts.

H₂-TPR

The reducibility of the metal oxides could be investigated via H₂-TPR. It was known that ease of reduction of metals was in favor of low-temperature SCR activity. The redox properties of the prepared catalysts were illustrated in Fig. 5, and the

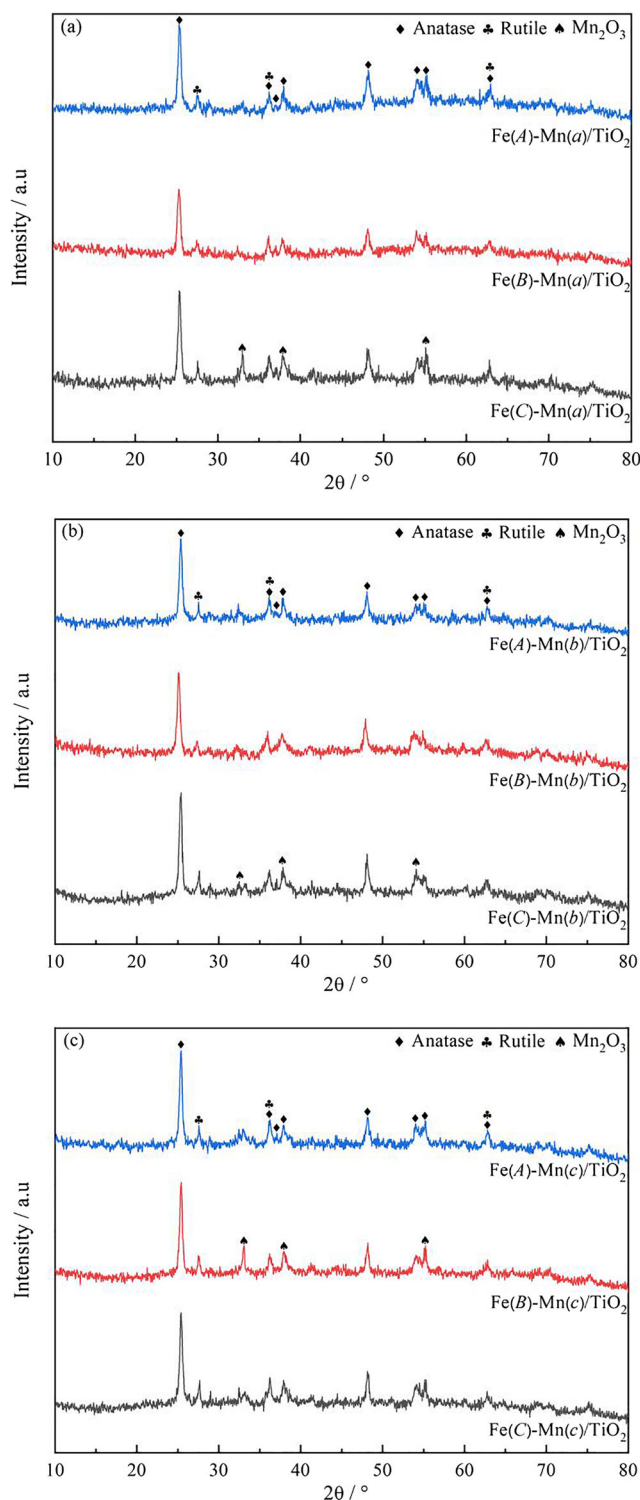


Fig. 4 XRD patterns of the prepared Fe(x)-Mn(y)/TiO₂ catalysts

reduction peak temperatures and H₂ consumption values are listed in Table S2. It could be seen that there were three reduction peaks in the profile of Fe(A)-Mn(a)/TiO₂ catalyst. The low-temperature reduction peak center was at about 296 °C, which could be assigned to the reduction of MnO₂ to Mn₂O₃ (Putluru et al. 2015; Wu et al. 2015). The peak centered at

about 418 °C in the profile belonged to the reduction of Mn_2O_3 to MnO or Fe_2O_3 to Fe , while the peak centered at about 554 °C belonged to the reduction of Mn_3O_4 to MnO (Putluru et al. 2015). The redox ability of samples could be determined by the low-temperature peak centers. $\text{Fe}(A)\text{-Mn}(a)/\text{TiO}_2$ catalyst was being reduced at relatively lower temperature compared with other catalysts. Apparently, with manganese nitrate or manganese acetate as precursor, the low-temperature peak centers for catalysts with different ferric precursors were in an order of ferric nitrate > ferrous sulfate > ferrous chloride. The variation trend was consistent with that of H_2 consumption values of these samples as shown in Table S2. With the same manganese precursor, H_2 consumption values for catalysts with different ferric precursors were also in the order of ferric nitrate > ferrous sulfate > ferrous chloride. This trend was also corresponding with the varieties of Mn/Ti ratios and contents of surface-adsorbed oxygen on the surface of catalysts. It suggested that more manganese species incorporated into TiO_2 crystalline phase and higher abundance of active oxygen species were contributed to the enhancement of low-temperature redox ability for $\text{Fe}(a)\text{-Mn}(y)/\text{TiO}_2$ catalyst (Xu et al. 2018b). The shift of low-temperature peak centers for catalysts prepared with ferrous sulfate and ferrous chloride was also possibly due to a formation of larger particle crystals and a decrease of surface-adsorbed oxygen (Wu et al. 2015). Since lower reduction temperature and greater H_2 consumption signified the stronger redox behavior and oxygen storage capacity of the catalysts, which was of great importance for SCR reactions (Zhang et al. 2018), the choice of Fe and Mn precursors would lead to the shift of low-temperature peak centers and influence the H_2 consumption for $\text{Fe-Mn}/\text{TiO}_2$ catalysts, further influencing their catalytic performance at low temperature (Wang et al. 2013). As to the catalysts prepared with manganese chloride and/or ferrous chloride as precursors, the low-temperature peak centers were obviously much higher than those of other

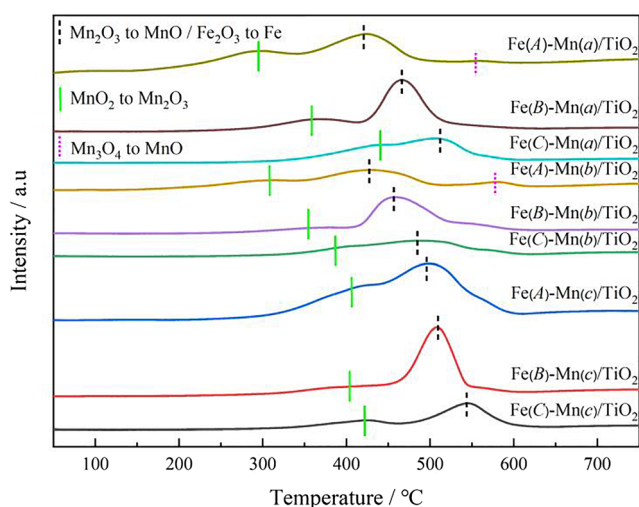


Fig. 5 H_2 -TPR profiles of the prepared $\text{Fe}(x)\text{-Mn}(y)/\text{TiO}_2$ catalysts

catalysts. It implied that to a great extent, the low-temperature reducibility and catalytic activity of catalysts prepared with chloride precursors were related to a low decomposition degree of chloride species and a low dispersion degree of MnO_x over supports.

NH_3 -TPD

NH_3 -TPD was frequently adopted for determining the amounts and strength of surface acid sites of solid-phase catalysts. It was considered that the presence of acid sites would favor NO conversion due to the preferential adsorption of NH_3 on these sites thus initiating SCR reaction. Thus, the SCR activity of catalysts might correlate with the amount of total acid sites (Lewis and Brønsted acid sites) and acid strength (T_{max} of ammonia desorption). Figure 6 shows the NH_3 -TPD desorption patterns of the prepared $\text{Fe-Mn}/\text{TiO}_2$ catalysts. Generally, the total amounts of adsorbed ammonia were determined from the areas under TPD curves. It could be seen from Fig. 6 that most of the catalysts had two broad desorption peaks in a wide temperature range, which was due to the variability of adsorbed NH_3 species with different thermal stabilities (Xiong et al. 2015). These two peaks could be assigned to physically adsorbed ammonia (desorption temperature below 300 °C) and chemically adsorbed ammonia (desorption temperature above 300 °C). At low reaction temperature, the amount of physically adsorbed ammonia would play a key role in evaluating the catalytic activities of $\text{Fe-Mn}/\text{TiO}_2$ catalysts. As shown in Fig. 6, $\text{Fe}(A)\text{-Mn}(a)/\text{TiO}_2$ and $\text{Fe}(B)\text{-Mn}(a)/\text{TiO}_2$ catalysts exhibited much better ammonia adsorption properties than the other catalysts in the temperature range of 100–300 °C, which was advantageous to the adsorption of ammonia. However, as to the $\text{Fe}(B)\text{-Mn}(a)/\text{TiO}_2$ catalyst, it was considered that the inhibiting action of ammonia occurred on the fast SCR activity at low temperature (Grossale

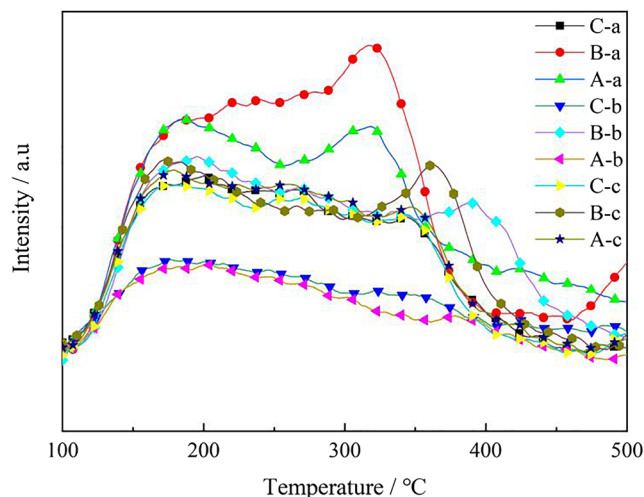


Fig. 6 NH_3 -TPD profile of the prepared $\text{Fe}(x)\text{-Mn}(y)/\text{TiO}_2$ catalysts. ($\text{Fe}(x)\text{-Mn}(y)/\text{TiO}_2$ is denoted as $x\text{-}y$)

et al. 2009). It was mainly ascribed to either a competitive adsorption of NH_3 onto the metal sites which are involved in NO activation, or an adverse electronic interaction of adsorbed NH_3 with metal oxidation centers (Nova et al. 2006). For $\text{Fe}(x)\text{-Mn}(b)/\text{TiO}_2$ catalysts, $\text{Fe}(B)\text{-Mn}(b)/\text{TiO}_2$ catalysts had adsorbed much more ammonia than $\text{Fe}(A)\text{-Mn}(b)/\text{TiO}_2$ and $\text{Fe}(C)\text{-Mn}(b)/\text{TiO}_2$ catalysts, and it also suggested that ferrous sulfate as precursor was beneficial to enhance the surface acidity. $\text{Fe}(x)\text{-Mn}(c)/\text{TiO}_2$ catalysts adsorbed more or less the same ammonia in the whole temperature range, indicating that the ammonia adsorption properties were possibly determined by manganese chloride precursors.

The total surface acidity for each sample could be calculated according to the integral peak area of the corresponding TPD profile, and the results are shown in Table S3. Among of the prepared samples, $\text{Fe}(B)\text{-Mn}(y)/\text{TiO}_2$ catalysts exhibited a higher total surface acidity than the catalysts prepared with the same manganese precursors. Except for the catalysts prepared with manganese acetate precursors, the total surface acidities for the other catalysts prepared with different ferric precursors decreased in an order of ferrous sulfate > ferric nitrate > ferrous chloride. It indicated that it was easy to obtain a relatively higher total surface acidity by adopting ferrous sulfate to prepare $\text{Fe-Mn}/\text{TiO}_2$ catalysts. Since NO removal performance of $\text{Fe}(A)\text{-Mn}(y)/\text{TiO}_2$ catalysts at low temperature was much higher than that of $\text{Fe}(b)\text{-Mn}(y)$ catalysts, it suggested that the total surface acidity was not the determinant factor for SCR performance of the prepared $\text{Fe-Mn}/\text{TiO}_2$ catalysts.

Overall, the results showed that the acidity property of the catalysts was closely related with the redox property, and it was necessary to achieve a proper balance between acidity property and redox property to obtain an optimal catalytic activity (Wang et al. 2018; Tang et al. 2016).

XPS

XPS analysis was performed to further explore the chemical species and surface atomic composition of the catalysts prepared using different Fe and Mn precursors. Figures 7, 8 and 9 displayed the spectra of Fe 2p, Mn 2p, and O 1s on the catalysts. According to the measurement results, surface atomic concentrations ratios of Fe, Mn, and O are calculated and listed in Table S2. The surface concentration ratios of Mn/Ti on $\text{Fe}(A)\text{-Mn}(a)/\text{TiO}_2$, $\text{Fe}(A)\text{-Mn}(b)/\text{TiO}_2$, and $\text{Fe}(B)\text{-Mn}(b)/\text{TiO}_2$ catalysts were more than 50%, suggesting a high dispersion of MnO_x in these catalysts, which was beneficial to improve the catalytic performance.

As shown in Fig. 7, there were two main peaks in XPS spectra of Fe 2p. These two peaks observed for all samples were assigned to $\text{Fe } 2p_{3/2}$ at 710.9 eV and $\text{Fe } 2p_{1/2}$ at 723.9 eV. It indicated that Fe species in these samples were in Fe^{3+} oxidation states. The results showed that the changes in the chemical states of Fe species were not a main reason for

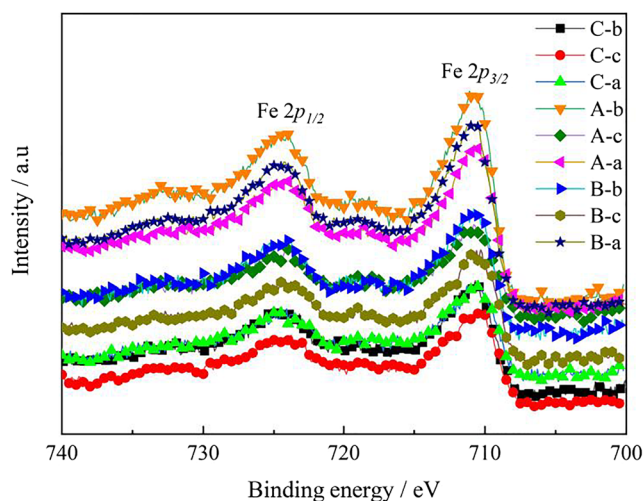


Fig. 7 XPS spectra of Fe 2p over the prepared $\text{Fe}(x)\text{-Mn}(y)/\text{TiO}_2$ catalysts. ($\text{Fe}(x)\text{-Mn}(y)/\text{TiO}_2$ is denoted as x-y)

the difference in the SCR activities of these catalysts, because the corresponding binding energies did not show a significant variation (Mu et al. 2018).

Two main peaks assigned to $\text{Mn } 2p_{3/2}$ and $\text{Mn } 2p_{1/2}$ could be observed from Fig. 8 for all samples in a binding energy range of 641 ~ 653 eV. The overlapping peaks of $\text{Mn } 2p_{3/2}$ could be deconvoluted into several peaks with Shirley-type background to identify the surface MnO_x phases, and the results are shown in Table S4. Then it could be obtained that $2p_{3/2}$ binding energy peaks of MnO_2 (Mn^{4+}) and Mn_2O_3 (Mn^{3+}) appeared at about 642.6 eV and 641.2 eV, respectively, while the binding energy peaks at 644.7 eV represented manganese nitrate (Mu et al. 2018; Hwang et al. 2016; Xu et al. 2018b). The SCR activities of MnO_x at low temperature had been investigated by Kapteijn et al. (1994), and they found that NO_x removal efficiency for manganese oxides decreased in an order of $\text{MnO}_2 > \text{Mn}_5\text{O}_8 > \text{Mn}_2\text{O}_3 > \text{Mn}_3\text{O}_4$. It demonstrated that MnO_2 (Mn^{4+}) would play a key role in catalytic removal of NO. As shown in Table S2, $\text{Fe}(A)\text{-Mn}(a)/\text{TiO}_2$ catalyst prepared in this work had the most enriched Mn^{4+} species (MnO_2) over TiO_2 supports. So it was normal to obtain an excellent catalytic performance at low temperature for $\text{Fe}(A)\text{-Mn}(a)/\text{TiO}_2$ catalysts. In addition, for the catalysts prepared using manganese nitrate or manganese acetate precursors, Mn^{4+} contents were in an order of ferric nitrate > ferrous sulfate > ferrous chloride, which was consistent with the change of catalytic activities at low temperature for these catalysts. It demonstrated that the content of Mn^{4+} species over TiO_2 supports was essential for the catalytic activity of $\text{Fe-Mn}/\text{TiO}_2$ catalysts.

XPS spectra of O 1s in the prepared catalysts were presented in Fig. 9. The sub-bands at a binding energy peak of 529.8 eV could be assigned to the lattice oxygen O^{2-} (denoted as O_α), and the sub-bands at a binding energy peak of 531.2 eV could be assigned to the surface chemisorbed labile

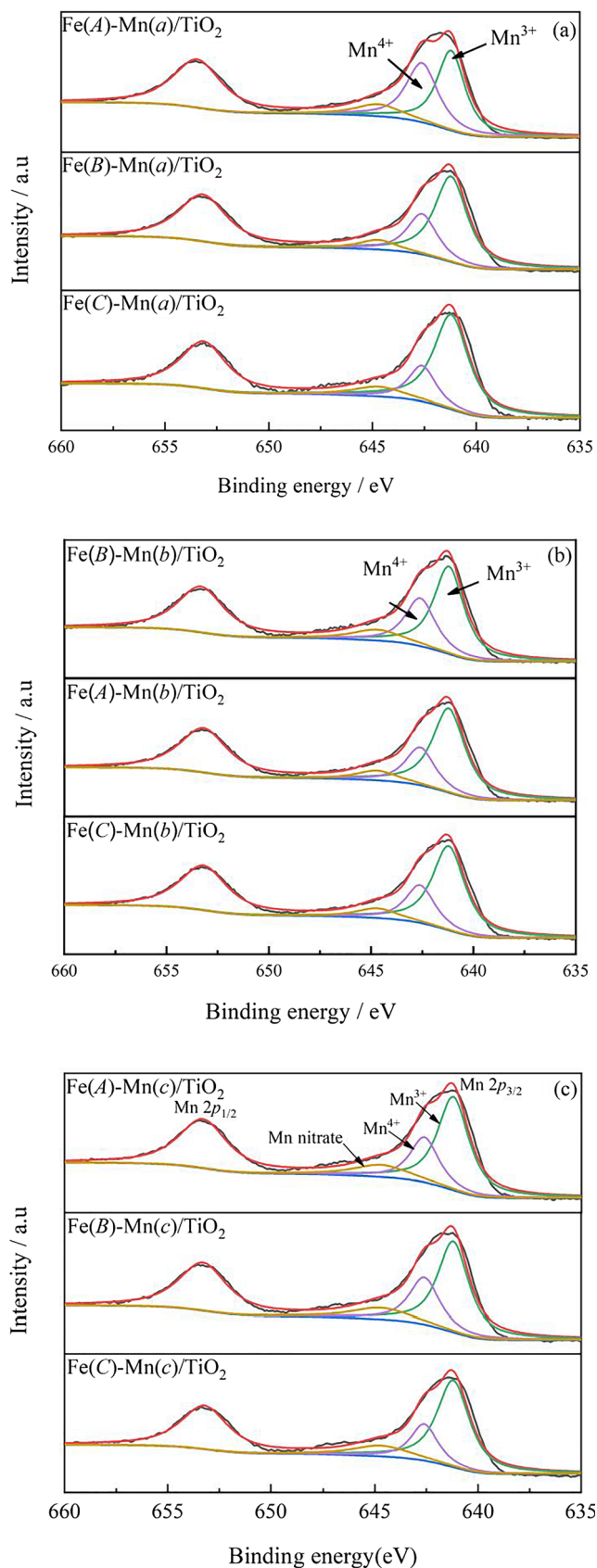


Fig. 8 XPS spectra of Mn 2p over the prepared Fe(x)-Mn(y)/TiO₂ catalysts

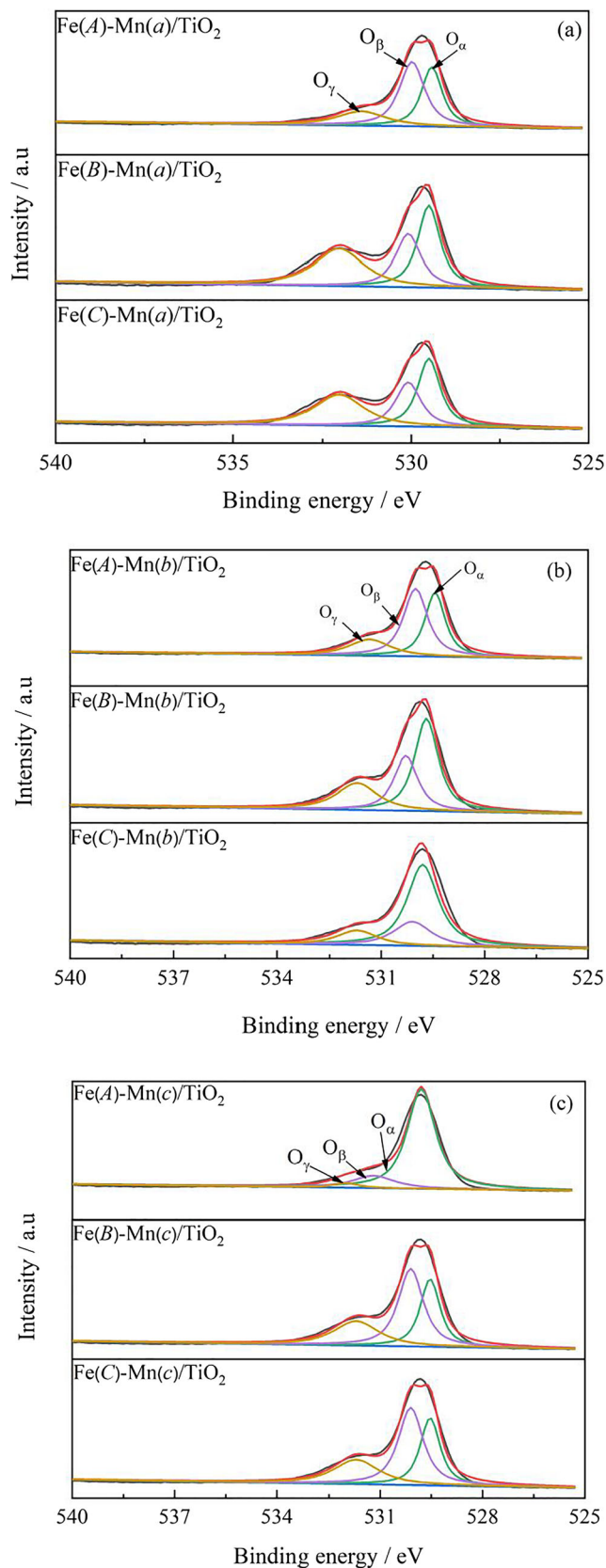


Fig. 9 XPS spectra of O 1s over the prepared Fe(x)-Mn(y)/TiO₂ catalysts

oxygen (denoted as O_{β}). Here, O_{γ} referred to the defect oxide and/or hydroxyl-like groups. The quantitative data of $O_{\beta}/(O_{\beta} + O_{\alpha})$ ratios of the catalysts were calculated by the relative peak areas, and they are also presented in Table S4. It could be seen that Fe(A)-Mn(a) catalyst had the highest ratio of $O_{\beta}/(O_{\beta} + O_{\alpha})$. Some previous studies had pointed out that surface chemisorbed labile oxygen (O_{β}) was of great importance to the SCR process at low temperature. It had been considered as the most active oxygen because it was of high mobility and played a critical role in oxidation reaction. Therefore, the high ratio of $O_{\beta}/(O_{\beta} + O_{\alpha})$ was conducive to oxidizing NO into NO_2 , then further enhancing the low-temperature catalytic performance via a fast SCR route. The effect of $O_{\beta}/(O_{\beta} + O_{\alpha})$ ratios on SCR performance was similar to that of Mn^{4+} contents over TiO_2 supports. For the catalysts prepared using manganese nitrate or manganese acetate precursors, the $O_{\beta}/(O_{\beta} + O_{\alpha})$ ratio decreased in an order of ferric nitrate > ferrous sulfate > ferrous chloride, which was also consistent with the change of catalytic activities at low temperature for the corresponding catalysts. It demonstrated that the $O_{\beta}/(O_{\beta} + O_{\alpha})$ ratio was another important factor influencing the catalytic activity of Fe-Mn/ TiO_2 catalysts greatly.

Effects of H_2O and SO_2

In general, flue gas exhausted from stationary and mobile sources contained a certain amount of SO_2 and H_2O , so it was important to evaluate the effects of SO_2 and H_2O on the activity of NH_3 -SCR.

The resistance of H_2O and SO_2 over the Fe(A)-Mn(a)/ TiO_2 catalyst at 200 °C is presented in Fig. 10. At first, 10% H_2O was introduced, there was a slight drop in NO conversion efficiency. However, after stopping injection of water vapor,

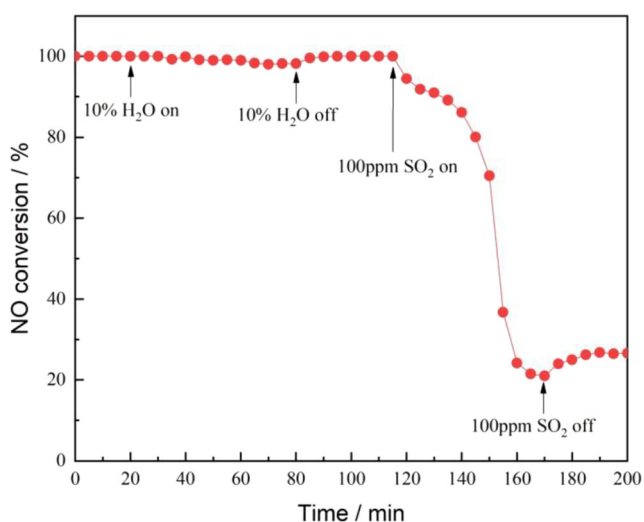


Fig. 10 Effects of H_2O and SO_2 over the Fe(A)-Mn(a)/ TiO_2 catalysts at 200 °C. Reaction conditions: 1.5 g catalyst, 0.08% NO, 0.08% NH_3 , 5% O_2 , 10% H_2O , 0.01% SO_2 , N_2 balance gas, GHSV = 25,000 h^{-1}

NO conversion efficiency recovered to 100% within 30 min. It indicated that Fe(A)-Mn(a)/ TiO_2 catalysts possessed a good resistance to H_2O at low temperature. However, when 0.01% of SO_2 was added to the reaction gas mixtures, a rapid decrease of NO conversion was observed, indicating that the inhibition effect of SO_2 was presented on the SCR reaction over the Fe(A)-Mn(a)/ TiO_2 catalysts. In addition, NO conversion efficiency did not recover after the shutoff of SO_2 injection. This demonstrated that the poisoning effects of sulfur on Fe(A)-Mn(a)/ TiO_2 catalyst were difficult to reverse. The causes of catalyst deactivation might have resulted from the sulfation of Mn and the formation of ammonium salts, which resulted in some adverse effects on SCR properties. Much more efforts will be devoted to improve the sulfur resistance of the catalyst in our future research (Li et al. 2019).

Conclusion

In this work, Fe-Mn/ TiO_2 catalysts were prepared via the wet impregnation method, and the effects of various Fe and Mn precursors on NH_3 -SCR performance were investigated. The results indicated that both Fe and Mn precursors influenced low-temperature SCR performance obviously. Overall, the catalytic activity below 200 °C was in the orders of manganese nitrate > manganese acetate > manganese chloride and ferric nitrate > ferrous sulfate > ferrous chloride. The results indicated that chloride precursors were not suitable for preparing Fe-Mn/ TiO_2 catalysts due to a low decomposition degree of chloride species during calcination process. On the other hand, it was difficult for catalysts prepared with chloride precursors to obtain a high BET area and high dispersion of Fe and Mn active species over supports. H_2 -TPR tests showed that, Fe(A)-Mn(a)/ TiO_2 catalyst could be reduced at relatively lower temperatures compared with other catalysts, which was ascribed to high contents of MnO_x and surface chemisorbed labile oxygen on TiO_2 support when manganese nitrate and ferric nitrate were adopted as precursors. XPS analysis implied that both Mn^{4+} species (MnO_2) over TiO_2 surface and $O_{\beta}/(O_{\beta} + O_{\alpha})$ ratios imposed great impact on the catalytic performance of Fe-Mn/ TiO_2 catalysts at low temperature. When the catalysts were prepared with manganese nitrate or manganese acetate precursors, Mn^{4+} contents and $O_{\beta}/(O_{\beta} + O_{\alpha})$ ratios decreased in an order of ferric nitrate > ferrous sulfate > ferrous chloride, which was consistent with the change of catalytic activities at low temperature for the corresponding catalysts. The results demonstrated that the choice of Fe and Mn precursors was vital for preparing Fe-Mn/ TiO_2 catalysts, because it would probably affect the Mn^{4+} content, the surface chemisorbed labile oxygen content, the redox property and the dispersion of active species over support, thus influencing the catalytic performance at low temperature obviously. The Fe(A)-Mn(a)/ TiO_2 catalysts showed a good resistance to

H₂O at low temperature. However, the N₂ selectivity and resistance to SO₂ needs to be further improved.

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Compliance with ethical standards

Conflict of interest The authors declare no competing financial interest.

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