

# 矿物极化效应影响下 $\text{MnO}_x/\text{TiO}_2$ 催化剂 SCR 活性

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**摘 要:**  $\text{MnO}_x/\text{TiO}_2$  催化剂的低温脱硝活性和稳定性是目前具有挑战性的研究方向。采用矿物极化效应对  $\text{MnO}_x/\text{TiO}_2$  催化剂进行了改性研究。适当细度的电气石对催化材料的脱硝性能有明显的改善, 在较宽的温度范围内脱硝效率保持在 90% 以上, 并延长了较高脱硝效率的持续时间。原位漫反射红外光谱分析结果表明, 改性前后的催化剂遵循 Langmuir-Hinshelwood 机理, 电气石极化可以加快反应气体的吸附速率, 生成易于参与后续反应的中间产物, 从而提高脱硝性能。

**关键词:** 催化剂; 矿物极化效应; 原位漫反射红外光谱; Langmuir-Hinshelwood 机理

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## Selective Catalytic Reduction Activity of $\text{MnO}_x/\text{TiO}_2$ Catalyst Under Impact of Mineral Polarization

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**Abstract:** The low denitration activity and stability of  $\text{MnO}_x/\text{TiO}_2$  catalyst are still challenging. In this work, a  $\text{MnO}_x/\text{TiO}_2$  catalyst was modified via a polarization effect with tourmaline. Tourmaline with a proper fineness can improve the denitration performance of the catalytic material, obtaining the greater denitration rate above 90% in a wide temperature range and the prolonged high-efficiency denitration time. Based on the results of *in-situ* Fourier transform infrared spectroscopy, the reaction mechanism of the catalysts before and after modification with tourmaline follows the Langmuir-Hinshelwood mechanism, and tourmaline polarization can accelerate the adsorption rate of reaction gas and generate intermediate products liable for subsequent reaction, thus improving the denitration performance.

**Keywords:** catalyst; mineral polarization; diffuse reflectance infrared Fourier transform spectroscopy; Langmuir-Hinshelwood mechanism

## 1 Introduction

Nitrogen oxides ( $\text{NO}_x$ ) are mainly originated from the stationary storage and transportation sectors such as industrial furnaces and automobiles, causing the natural disasters and seriously affecting humanbeing life and production<sup>[1]</sup>. To improve air quality, stricter nitrogen oxide control standards have been promulgated. For instance, a version of “Emission standard of air pollutants in cement industry” regulates that  $\text{NO}_x$  emissions in the sintering process must be below  $100 \text{ mg/Nm}^3$ .

Selective catalytic reduction (SCR) process has become a most effective denitration method due to its high denitration efficiency and lower operation cost, and

the choice of catalyst is particularly crucial<sup>[2]</sup>. Nevertheless, although the existing commercial  $\text{V}_2\text{O}_5\text{--WO}_3(\text{MoO}_3)/\text{TiO}_2$  catalysts possess a high denitration activity, their applicable temperature range is limited to some extent, and the application of this temperature range in cement kilns could immensely increase the possibility of catalyst poison and deactivation. Some manganese-based catalytic materials have attracted recent attention due to their strict requirements of denitration environment in cement kilns. Liu *et al.*<sup>[3]</sup> reported Fe-doped  $\text{Mn}_3\text{O}_4$  spinel nanoparticles with highly exposed  $\text{Fe}_{\text{oct}}\text{--O--Mn}_{\text{tet}}$  sites for efficient SCR of NO with  $\text{NH}_3$ . They found that the optimal  $\text{Fe}_{0.35}\text{Mn}_{2.65}\text{O}_4$  NPs could achieve 90% NO

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conversion in a broad temperature range and revealed an efficient  $\text{Fe}_{\text{oct}}\text{-O-Mn}_{\text{tet}}$  site. Yang *et al.* [4] synthesized  $\text{FeMnTiO}_x$  catalysts for  $\text{NH}_3\text{-SCR}$  process and revealed that the introduction of Fe could heighten the  $\text{N}_2$  selectivity and  $\text{H}_2\text{O}$  and  $\text{SO}_2$  resistance besides NO conversion. However, there are still some problems to maintain its long-term denitration stability, expand the denitration temperature range and improve the denitration rate at a lower temperature.

To solve the above problems of manganese catalysts, a nonmetallic mineral tourmaline was used to modify the catalytic materials. The essence of catalysis was the transfer of electrons, and the fundamental reason for the low denitration activity and stability was that the long-term stable denitration process cannot be maintained, and the intermediate products were difficult to decompose [5]. The pyroelectric effect of tourmaline can transform the distribution of bound electrons at both ends, *i.e.*, releasing or attracting the surface adsorption charges, thus changing the catalytic process [6]. The existing research work on the polarization effect of minerals are limited to photocatalysis and other fields, greatly restricting its application [7].

This paper was to investigate the influence of polarization modification effect on the thermal denitrification catalysis in the presence of tourmaline. In addition, the influence of polarization modification effect on the gas adsorption and reaction path in the process of catalyst denitrification was also analyzed.

## 2 Experimental

### 2.1 Catalyst preparation

A  $\text{MnO}_x/\text{TiO}_2$  catalytic material was prepared by a coprecipitation method and modified *via* mineral polarization effect with tourmaline. In the preparation/modification, a certain amount of titanyl sulfate was weighed and mixed with a certain proportion of manganese acetate solution under magnetic stirring for 30 min. A tourmaline powder with the fineness of 1 000 mesh (*i.e.*, 13  $\mu\text{m}$ ) was added into the mixture. The addition amount of tourmaline was 10% of the mass of catalyst active components. The modified catalytic material can be represented as  $\text{MnO}_x/\text{TiO}_2\text{-13 } \mu\text{m}$ . Afterwards, 25% (mass fraction) ammonia solution was dropped to control the pH value of the solution at 11, and subsequently instill 30% hydrogen peroxide in dropwise. The resulting mixture was dewatered by filtration and washed for several times with ethanol, and then calcined in air at 300  $^\circ\text{C}$  for 3 h. The calcined samples were ground and sieved for the coming characterizations.

### 2.2 Activity measurement

The SCR activity was evaluated in a fixed-bed quartz reactor containing 3 mL catalyst (40–60 mesh), as described in a previous work [8]. In this study, the gas flow rate was 1 350 mL/min and the gas hourly space velocity (GHSV) was 27 000  $\text{h}^{-1}$ , respectively. The concentrations

of NO,  $\text{NO}_2$ ,  $\text{NH}_3$ , and  $\text{N}_2\text{O}$  were continually monitored by a Fourier transform infrared spectrometer and Mass spectrometer, and the denitration data were determined at different temperatures for 5 min after the reaction gas ( $\text{NH}_3$ , NO) was injected. The rate of  $\text{NO}_x$  conversion was calculated by

$$\eta = \frac{\psi(\text{NO}_x)_{\text{in}} - \psi(\text{NO}_x)_{\text{out}}}{\psi(\text{NO}_x)_{\text{in}}} \quad (1)$$

where,  $[\text{NO}_x] = [\text{NO}] + [\text{NO}_2]$ ;  $\eta$  is  $\text{NO}_x$  conversion rate;  $\psi[\text{NO}_x]_{\text{in}}$  is concentration of inlet  $\text{NO}_x$ ;  $\psi[\text{NO}_x]_{\text{out}}$  is concentration of outlet NO.

The denitration stability test was performed on the denitration activity evaluation device under a nitrogen atmosphere at 200  $^\circ\text{C}$  for 10 h, and the change of  $\text{NO}_x$  conversion rate was recorded every hour. And the  $\text{N}_2$  selectivity can be expressed by

$$\text{N}_2 \text{ selectivity}(\%) = \left(1 - \frac{2(\text{N}_2\text{O})_{\text{out}}}{(\text{NO}_x)_{\text{in}} - (\text{NO}_x)_{\text{out}}}\right) \quad (2)$$

where  $[\text{N}_2\text{O}]_{\text{out}}$  is the concentration of emitted  $\text{N}_2\text{O}$ ;  $[\text{NO}_x]_{\text{in}}$  is the  $\text{NO}_x$  concentration before the sample;  $[\text{NO}_x]_{\text{out}}$  is the concentration of  $\text{NO}_x$  after the sample.

### 2.3 Polarization effect test

Pyroelectric coefficient test of these samples was performed. The model of the instrument was obtained by TF Analyzer 3 000 at 30–300  $^\circ\text{C}$  at a heating rate of 5  $^\circ\text{C}/\text{min}$ . During the test, 0.2 g of sample was weighed and evenly ground in an agate mortar, and then the ground sample was transferred to a cylindrical mold with a diameter of 10 mm, and pressed into a cylindrical sheet with a diameter of 10 mm and a thickness of 1 mm by a press. Afterwards, a conductive silver glue was coated on the upper and lower surfaces of the cylindrical sheet, respectively, and the coated sheet was dried in an oven at 60  $^\circ\text{C}$  for 1 h to make the sample fully contact with the conductive silver glue.

### 2.4 Transient diffused reflectance infrared Fourier transform spectra (DRIFTS)

The *in-situ* DRIFT spectra were recorded by a model VERTEX 70 diffused reflectance infrared Fourier transform spectroscope with KBr windows. For experimental purpose, the wafers consisting of 50 mg catalyst powder were put into a cell with gas flow and poured with high purity nitrogen at 400  $^\circ\text{C}$  for 3 h to remove any adsorbed impurities and then cooled to the desired temperature. The background spectrum was recorded simultaneously and then subtracted from the sample spectrum.

For the adsorption of  $\text{NH}_3$  (or  $\text{NO} + \text{O}_2$  or  $\text{NH}_3 + \text{NO} + \text{O}_2$ ), the catalyst was exposed to a 20 mL/min  $\text{NH}_3$  (or  $\text{NO} + \text{O}_2$  or  $\text{NH}_3 + \text{NO} + \text{O}_2$ ) to obtain the time-dependent changes of the DRIFT spectra, subsequently purged with argon. In the transient studies, the catalyst was first pre-exposed to a 20 mL/min  $\text{NH}_3(\text{NO} + \text{O}_2)$  for 40 min, and then exposed to the mixture of  $\text{NO} + \text{O}_2(\text{NH}_3)$  at 300  $^\circ\text{C}$  to obtain the time-dependent changes of the DRIFT spectra. All the

spectra were recorded by accumulating 100 scans at a spectra resolution of  $4\text{ cm}^{-1}$ .

### 3 Results and discussion

#### 3.1 SCR activity

Fig. 1 shows the  $\text{NO}_x$  conversion rate of  $\text{MnO}_x/\text{TiO}_2$  catalysts before and after mineral polarization modification with tourmaline. Clearly, the catalysts modified by mineral polarization effect with tourmaline has superior low-temperature denitration activity, stability and  $\text{N}_2$  selectivity. In Fig. 1, the  $\text{NO}_x$  conversion rate of the modified catalytic material is improved, and the optimum temperature range is at  $200\text{--}250\text{ }^\circ\text{C}$ . For  $\text{MnO}_x/\text{TiO}_2$  catalyst, the  $\text{NO}_x$  conversion rate is 88% when the temperature increases to  $200\text{ }^\circ\text{C}$ , but the  $\text{NO}_x$  conversion rate begins to decline as the temperature further increases. The  $\text{NO}_x$  conversion rate of  $\text{MnO}_x/\text{TiO}_2$  catalyst modified with tourmaline (i.e.,  $\text{MnO}_x/\text{TiO}_2\text{-}13\text{ }\mu\text{m}$ ) is greater than that of  $\text{MnO}_x/\text{TiO}_2$  catalyst in the entire temperature range, which is up to 97% at  $200\text{ }^\circ\text{C}$ . This could be ascribed to the surface electric field generated by the spontaneous polarization effect of tourmaline, which can accelerate the electron transfer and improve the adsorption rate of reaction gas molecule, thus improving the denitration performance effectively.

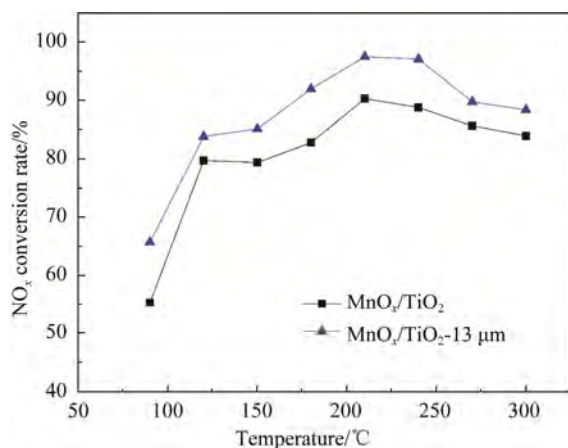


Fig. 1  $\text{NO}$  conversion rates of  $\text{MnO}_x/\text{TiO}_2$  catalyst before and after polarization modification with tourmaline at different temperatures

Fig. 2 shows the denitration stability of  $\text{MnO}_x/\text{TiO}_2$  catalysts before and after polarization modification with tourmaline at  $200\text{ }^\circ\text{C}$  for 10 hours. In Fig. 2, the removal rate of nitrogen oxide for  $\text{MnO}_x/\text{TiO}_2$  catalyst decreases rapidly from 93% to  $>80\%$  after 10 h denitration process. However, the  $\text{NO}_x$  removal rate of  $\text{MnO}_x/\text{TiO}_2$  catalyst modified with tourmaline immediately increases to 96%, and is still above 92% after 10 h denitration process. Fig. 3 shows the  $\text{N}_2$  selectivity of  $\text{MnO}_x/\text{TiO}_2$  catalysts before and after polarization modification with tourmaline at different temperatures. In Fig. 3, the addition of tourmaline into  $\text{MnO}_x/\text{TiO}_2$  catalyst has a negative impact on the selectivity of the catalyst. This may be related to

the change of the higher valence manganese content in the catalyst.

Table 1 also shows the denitration rates of  $\text{MnO}_x/\text{TiO}_2$  catalyst modified with tourmaline synthesized and some existing low-temperature denitration catalytic materials developed in recent years.

Table 1 Denitration rates of low-temperature denitration catalytic materials

| Catalyst                                          | Temperature/ $^\circ\text{C}$ | Denitration rate/% |
|---------------------------------------------------|-------------------------------|--------------------|
| $\text{MnO}_x/\text{TiO}_2\text{-tourmaline}$     | 200–240                       | 97                 |
| $\text{Fe-Mn-Ce}/\gamma\text{-Al}_2\text{O}_3$    | 250–350                       | 95                 |
| $\text{Mn-Ce-Fe}/\text{AC}$                       | 125                           | 90                 |
| $\text{Ag-Mn-Ce}/\gamma\text{-Al}_2\text{O}_3$    | 250–300                       | 95                 |
| $\text{MnO}_x\text{-CeO}_2\text{-Al}_2\text{O}_3$ | 150–300                       | 90                 |

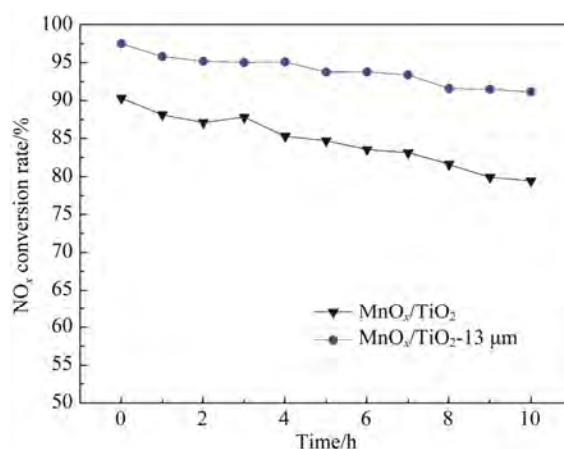


Fig. 2 Denitration stability of  $\text{MnO}_x/\text{TiO}_2$  catalysts before and after polarization modification with tourmaline at  $200\text{ }^\circ\text{C}$  for 10 h

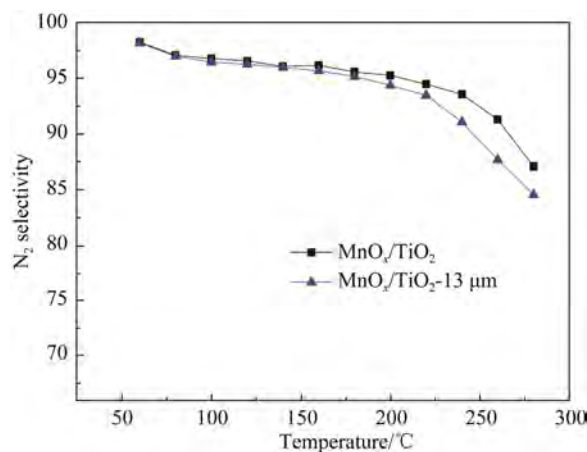


Fig. 3  $\text{N}_2$  selectivity of  $\text{MnO}_x/\text{TiO}_2$  catalysts before and after polarization modification with tourmaline at different temperatures

#### 3.2 Characterizations of catalysts

Fig. 4 shows the XRD patterns of  $\text{Mn}_3\text{O}_4$ ,  $\text{TiO}_2$ , tourmaline and  $\text{MnO}_x/\text{TiO}_2$  catalyst before and after polarization modification with tourmaline. Clearly, there are some sharp diffraction peaks at  $2\theta$  of  $21.0^\circ$ ,  $22.2^\circ$ ,

25.6°, 34.7°, 44.3° and 63.9°, which correspond to a typical fofite (JCPDS 46-1460) without other impurities, for  $\text{MnO}_x/\text{TiO}_2$  catalyst before polarization modification,

and the main ingredient is anatase (*i.e.*, titanium dioxide). For the catalyst modified with tourmaline, a characteristic peak of  $\text{Mn}_3\text{O}_4$  appears, and tourmaline is also detected.

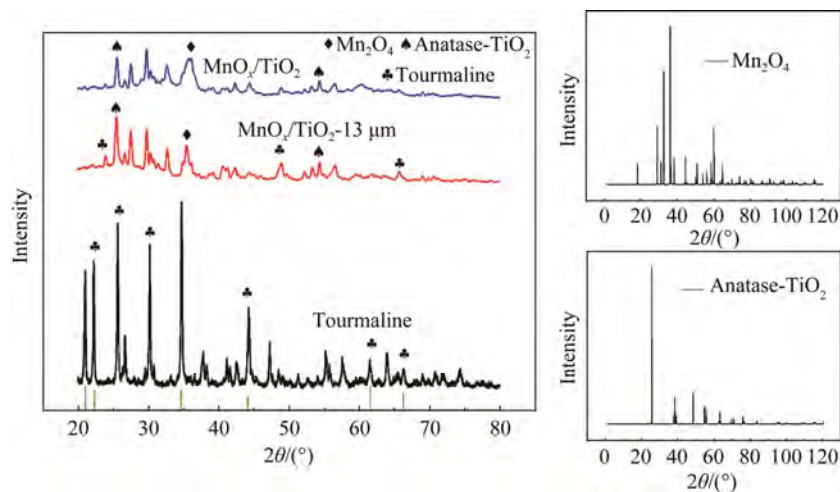


Fig. 4 XRD patterns of  $\text{Mn}_3\text{O}_4$ ,  $\text{TiO}_2$ , tourmaline and  $\text{MnO}_x/\text{TiO}_2$  catalysts before and after polarization modification with tourmaline

Table 2 shows the BET specific surface area, pore volume and pore-size of fofite and  $\text{MnO}_x/\text{TiO}_2$  catalysts before and after polarization modification with tourmaline. In Table 2, the BET specific surface area, pore volume and pore size of tourmaline are 2.9  $\text{m}^2/\text{g}$ , 0.008  $\text{cm}^3/\text{g}$  and 11.5 nm, respectively.  $\text{MnO}_x/\text{TiO}_2$  catalyst has a specific surface area of 163.0  $\text{m}^2/\text{g}$ , while the catalyst modified with tourmaline has a specific surface area of 260.2  $\text{m}^2/\text{g}$ . This is since the addition of tourmaline into the catalyst can provide effective nucleation sites, promote the activation of water molecule and accelerate the ion transfer in liquid phase<sup>[10]</sup>. Fig. 5 shows the pore size distributions of  $\text{MnO}_x/\text{TiO}_2$  catalytic materials modified with tourmaline at different contents. Clearly, the hysteresis loop shows that the catalytic materials before and after polarization modification with tourmaline belong to a mesoporous structure, and the pore sizes are between 2 and 50 nm (see Table 2).

**Table 2** Specific surface areas of tourmaline and  $\text{MnO}_x/\text{TiO}_2$  catalysts before and after polarization modification with tourmaline

| Sample                                        | $S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$ | Pore volume/<br>( $\times 10^{-2} \text{ cm}^3 \cdot \text{g}^{-1}$ ) | Average pore<br>diameter/nm |
|-----------------------------------------------|---------------------------------------------------|-----------------------------------------------------------------------|-----------------------------|
| Tourmaline                                    | 2.9                                               | 0.008                                                                 | 11.5                        |
| $\text{Mn}_3\text{O}_4$                       | 13.7                                              | 4.9                                                                   | 10.3                        |
| $\text{TiO}_2$                                | 27.6                                              | 9.0                                                                   | 13.8                        |
| $\text{MnO}_x/\text{TiO}_2$                   | 163.0                                             | 25.2                                                                  | 6.2                         |
| $\text{MnO}_x/\text{TiO}_2$ -13 $\mu\text{m}$ | 260.2                                             | 30.2                                                                  | 3.0                         |

$S_{\text{BET}}$ : Specific surface area of materials.

Pyroelectricity is strictly defined as the temperature-dependent spontaneous polarization in certain anisotropic solids<sup>[11-12]</sup>. The pyroelectric effect is represented by

$$P_s = \frac{d\vec{D}}{dT} = \frac{d\vec{P}}{dT} \quad (3)$$

where  $P_s$  is the pyroelectric coefficient;  $\vec{D}$  is the dielectric displacement;  $\vec{P}$  is the spontaneous polarization;  $T$  is Kelvin temperature. In this work, the pyroelectric coefficient is calculated by a temperature ramping method<sup>[13]</sup> through measuring the voltage response  $V$  or the electric current  $I$ . The relevant calculation formula is presented as

$$P_s = \frac{V \cdot C_F}{A \cdot (T_2 - T_1)} = \frac{I}{A \cdot \frac{dT}{dt}} \quad (4)$$

where  $C_F$  is a feedback capacitor;  $A$  is the parallel plate capacitor of area. Clearly, the pyroelectric coefficient is linearly related to the electric current at a definite temperature change rate. Hence, the pyroelectric coefficient can be easily obtained via measuring the electric current.

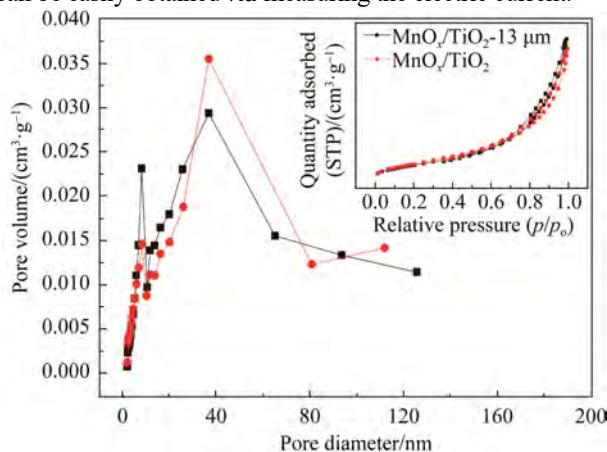


Fig. 5 Pore size distributions of  $\text{MnO}_x/\text{TiO}_2$  catalysts before and after polarization modification with tourmaline

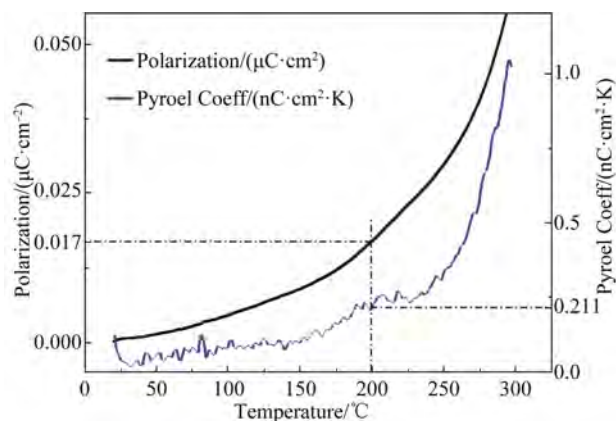


Fig. 6 Polarization intensity and pyroelectric coefficient of tourmaline at different temperatures

Fig. 6 shows the polarization intensity and pyroelectric coefficient of tourmaline at different temperatures. In Fig. 6, the polarization intensity and pyroelectric coefficient of tourmaline increase with the increase of temperature. The polarization intensity and pyroelectric coefficient change slowly at 25–150 °C, while increase rapidly at > 150 °C. According to the measured value of polarization intensity  $P_s$  of 0.017  $\mu\text{C}/\text{cm}^2$  at 200 °C, the electric field intensity can be calculated by a surface electric field  $E_0 = P_s / 2\epsilon_0$ , and the calculated electric field intensity is equal to  $9.6 \times 10^6 \text{ V/m}^{[14]}$ .

Fig. 7 shows the XPS spectra of Mn 2p for  $\text{MnO}_x/\text{TiO}_2$  catalysts before and after polarization modification with tourmaline. In Fig. 7, the binding energies of Mn  $2p_{3/2}$  and Mn  $2p_{1/2}$  peaks located at 641.9 and 653.4 eV occur, indicating that the manganese species in the pure  $\text{MnO}_x/\text{TiO}_2$  catalyst are the oxidation state of  $\text{Mn}^{4+}$  <sup>[15]</sup>. Meanwhile, the proportion of manganese ions in the catalyst after polarization modification with tourmaline changes, and the modification of tourmaline for the catalyst increases a ratio of  $\text{Mn}^{4+}$  to  $\text{Mn}^{3+}$  from 1.46 to 2.39. Fig. 8 shows the XPS spectra of O 1s for  $\text{MnO}_x/\text{TiO}_2$  catalysts before and after polarization modification with tourmaline. The modification with tourmaline can also affect the ratio of  $\text{O}_\alpha$  to  $\text{O}_\beta$  with respect to the lattice oxygen and chemically adsorbed oxygen, and the modification with tourmaline increases the ratio of  $\text{O}_\alpha$  to  $\text{O}_\beta$  from 0.93 to 3.85, due to the far-infrared radiation and spontaneous polarization characteristics of tourmaline, leading to the increase of particles thermal vibration and the acceleration of ion movement<sup>[16]</sup>. The modification with tourmaline in  $\text{MnO}_x/\text{TiO}_2$  catalyst gives rise to the more adsorption of oxygen ions on the surface of catalyst particles in the process of nucleation and growth, and results in the enhancement of oxygen adsorption during calcination.

As is known, the chemisorption and activation of  $\text{NH}_3$  on the surface acid sites of catalysts are generally regarded as a decisive step during the process of denitration<sup>[17]</sup>. Fig. 9 shows the  $\text{NH}_3$ -TPD diagram of  $\text{MnO}_x/\text{TiO}_2$  catalysts before and after polarization modification with tourmaline. For the pure  $\text{MnO}_x/\text{TiO}_2$

catalyst, the desorption peak of ammonia gas is concentrated at 200, 480 °C and 600 °C, which correspond to the desorption peaks at low, mid and high temperatures, respectively. The area of each peak can represent the number of acid sites of the catalyst in a certain extent. Also, the pure  $\text{MnO}_x/\text{TiO}_2$  catalyst contains weak acid sites (124), medium strong acid sites (32) and strong acid sites (57), in which the weak acid sites occupy the most content. For  $\text{MnO}_x/\text{TiO}_2$  catalyst modified with tourmaline (i.e.,  $\text{MnO}_x/\text{TiO}_2$ -13  $\mu\text{m}$ ), the peak area of all temperature segments significantly enhances to 153, 18 and 97, respectively, showing that the content of weak acid increases, and the megatemperature desorption peak moves to a higher temperature. This indicates that the acid strength increases and  $\text{NH}_3$  molecules adsorb more firmly.

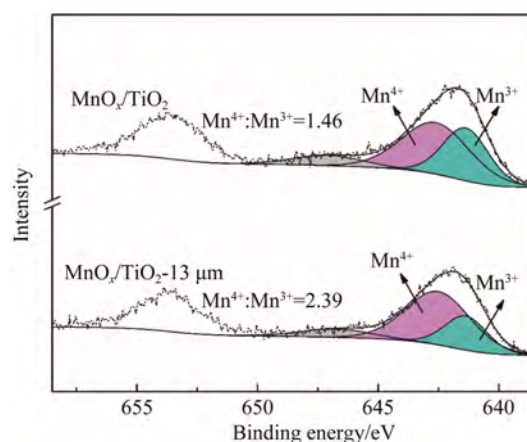


Fig. 7 XPS spectra of Mn2p for  $\text{MnO}_x/\text{TiO}_2$  catalysts before and after polarization modification with tourmaline

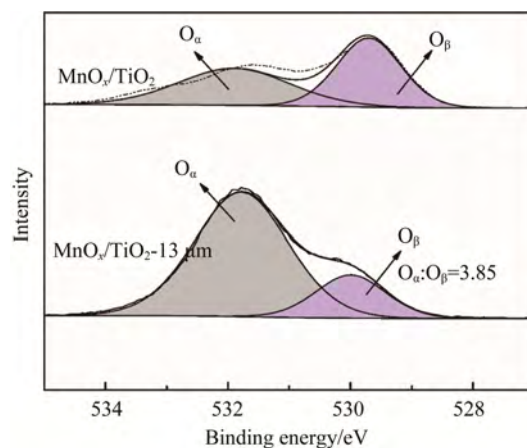


Fig. 8 XPS spectra of O1s for  $\text{MnO}_x/\text{TiO}_2$  catalysts before and after polarization modification with tourmaline

Fig. 10 shows the SEM image and EDS mappings of  $\text{MnO}_x/\text{TiO}_2$  catalyst. Clearly, the  $\text{MnO}_x/\text{TiO}_2$  catalyst particles are agglomerated as clumps, which hinder the adsorption of reaction gas, thus reducing the denitration activity. Fig. 11 shows the SEM images of  $\text{MnO}_x/\text{TiO}_2$  catalyst after polarization modification with tourmaline. The agglomeration of the catalyst is weakened when the

catalyst is modified by tourmaline, and the catalyst particles are distributed on the surface of the lamellar tourmaline, indicating that tourmaline can effectively promote the uniform distribution of particles.

### 3.3 In-situ DRIFTS

3.3.1 Adsorption of  $\text{NH}_3$  and reaction between  $\text{NH}_3$  and  $\text{NO}$  Fig. 12 shows the *in-situ* DRIFT spectra of  $\text{NH}_3$  for the  $\text{MnO}_x/\text{TiO}_2$  catalyst before polarization modification at  $200^\circ\text{C}$  for 30 min. In Fig. 12, for the pure catalyst, some obvious peaks appear after introducing  $\text{NH}_3$  to the IR cell, in which two peaks at wavenumbers of  $1\,309\text{ cm}^{-1}$  and  $1\,403\text{ cm}^{-1}$  represent the adsorption of  $\text{NH}_3$  on the Lewis acid sites and the Bronsted acid sites, respectively, a peak at  $3\,506\text{ cm}^{-1}$  is related to the symmetric N—H stretching vibrations of the coordinated  $\text{NH}_3$  on the Lewis acid sites, and peaks at  $3\,662\text{ cm}^{-1}$  and  $3\,750\text{ cm}^{-1}$  are assigned to active hydrogen on amino group<sup>[19]</sup>. Two slender absorption peaks at  $3\,330\text{ cm}^{-1}$  and  $1\,614\text{ cm}^{-1}$  appear after introducing  $\text{NH}_3$  gas for 10 min and 25 min, respectively, which belong to the adsorption of  $\text{NH}_3$  on the Lewis acid sites. All the peaks gradually

become intense with the continuous introduction of ammonia gas, indicating that the adsorption capacity of ammonia gas gradually increases.

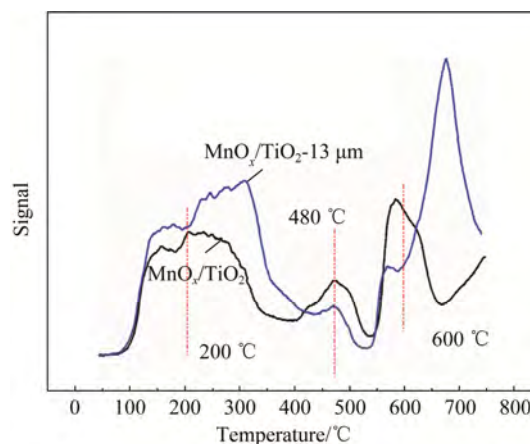


Fig. 9  $\text{NH}_3$ -TPD diagram of  $\text{MnO}_x/\text{TiO}_2$  catalysts before and after polarization modification with tourmaline

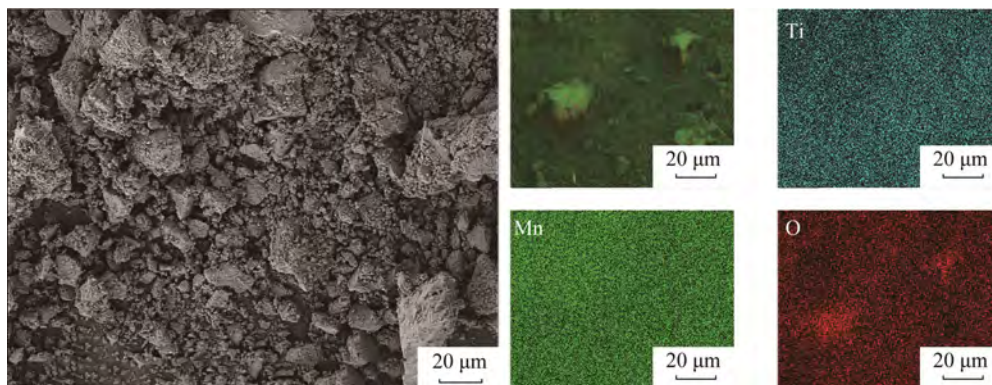


Fig. 10 SEM images and EDS mappings of  $\text{MnO}_x/\text{TiO}_2$  catalyst

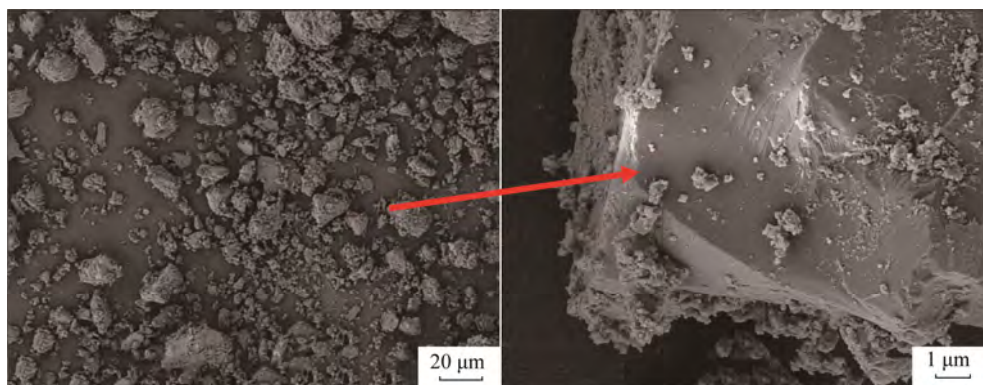


Fig. 11 SEM images of  $\text{MnO}_x/\text{TiO}_2$  catalyst after polarization modification with tourmaline

Fig. 13 shows the DRIFT spectra of  $\text{NO}$  for the pure  $\text{MnO}_x/\text{TiO}_2$  catalyst pre-adsorbed  $\text{NH}_3$  at  $200^\circ\text{C}$ . Clearly, several absorption peaks of ammonia become weak to some extent after 5 min, indicating that ammonia reacts with  $\text{NO}$  partially, while the peaks of  $\text{NH}_3$  adsorbed on the Lewis acid sites at  $3\,330\text{ cm}^{-1}$  and  $1\,309\text{ cm}^{-1}$  disappear completely after 25 min. Some nitrate peaks

also appear after introducing  $\text{NO}$  and  $\text{O}_2$  for 10 min, indicating that  $\text{NO}$  can adsorb on the surface of catalytic materials and form nitrates with different coordination modes. Among them, the absorption peaks of monodentate nitrate and bridge nitrate appear at  $1\,556\text{ cm}^{-1}$  and  $1\,625\text{ cm}^{-1}$ , and the peak at  $1\,911\text{ cm}^{-1}$  represents weakly adsorbed  $\text{NO}$ <sup>[20]</sup>.

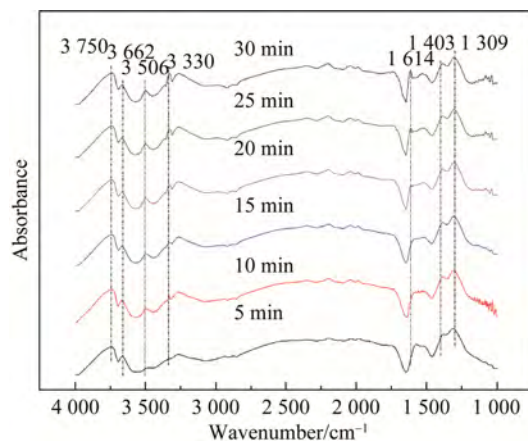


Fig. 12 DRIFT spectra of  $\text{NH}_3$  for pure  $\text{MnO}_x/\text{TiO}_2$  catalyst at  $200\text{ }^\circ\text{C}$

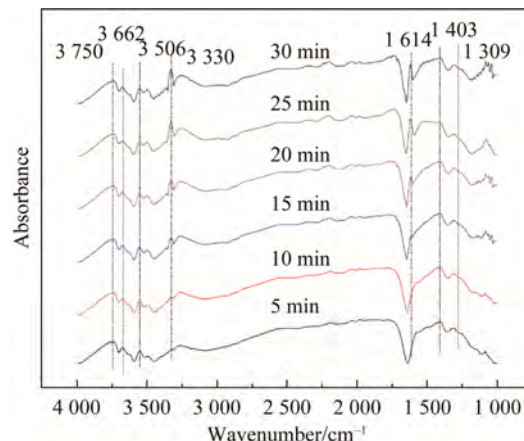


Fig. 14 DRIFT spectra of  $\text{NH}_3$  for  $\text{MnO}_x/\text{TiO}_2$  catalyst modified with tourmaline at  $200\text{ }^\circ\text{C}$

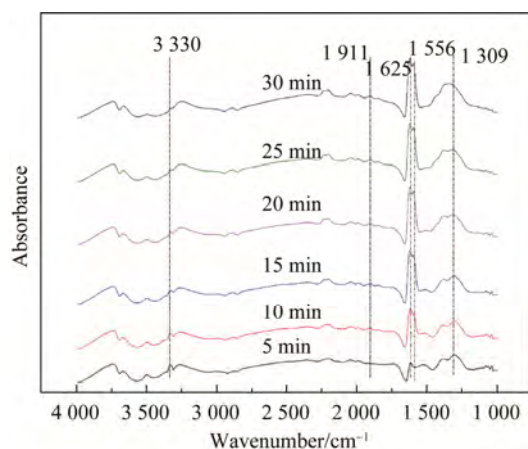


Fig. 13 DRIFT spectra of  $\text{NO}$  for the pure  $\text{MnO}_x/\text{TiO}_2$  catalyst pre-adsorbed  $\text{NH}_3$  at  $200\text{ }^\circ\text{C}$

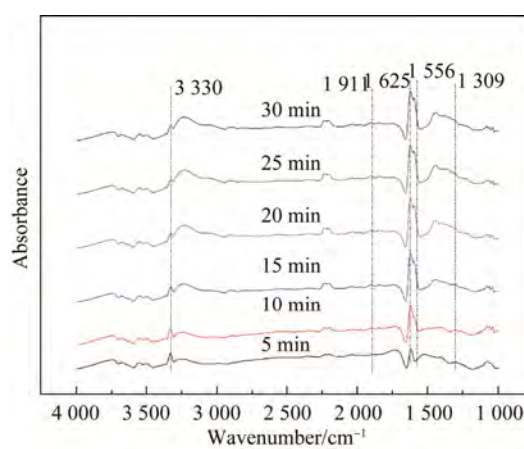


Fig. 15 DRIFT spectra of  $\text{NO}$  for the  $\text{MnO}_x/\text{TiO}_2$  catalyst modified with tourmaline and pre-adsorbed  $\text{NH}_3$  at  $200\text{ }^\circ\text{C}$

Fig. 14 shows the DRIFT spectra of  $\text{NH}_3$  for  $\text{MnO}_x/\text{TiO}_2$  catalyst modified with tourmaline at  $200\text{ }^\circ\text{C}$ . In Fig. 14, several characteristic peaks appear after introducing ammonia gas into the catalyst modified with tourmaline. At 10 min and 15 min, the peaks of  $\text{NH}_3$  adsorption at the Lewis acid sites at  $3330\text{ cm}^{-1}$  and  $1614\text{ cm}^{-1}$  appear, indicating that ammonia gas can be adsorbed on the surface of catalyst modified with tourmaline more quickly. The reaction rate is faster, and the absorption peak gradually becomes more intense with the continuous introduction of ammonia. The results above indicate that the ammonia adsorption capacity of the catalyst modified with tourmaline is greater than that of the catalyst without tourmaline. Fig. 15 shows the DRIFT spectra of  $\text{NO}$  for the  $\text{MnO}_x/\text{TiO}_2$  catalyst modified with tourmaline and pre-adsorbed  $\text{NH}_3$  at  $200\text{ }^\circ\text{C}$ . Clearly, the absorption peak area of ammonia decreases greatly after the introduction of  $\text{NO}$  and  $\text{O}_2$  into the catalyst modified with tourmaline. However, after the reaction for 30 min, there is still an obvious ammonia absorption peak at  $3330\text{ cm}^{-1}$ , further indicating that the catalyst modified with tourmaline has a greater adsorption capacity for ammonia<sup>[21]</sup>.

The results also indicate that the characteristic peak areas of  $\text{NO}$  adsorption of the catalyst modified with tourmaline are smaller than those of the catalyst without tourmaline due to the reaction of gaseous  $\text{NO}$  with adsorbed  $\text{NH}_3$ , resulting in more consumption and less  $\text{NO}$  adsorbed on the catalyst surface.

**3.3.2 Adsorption of  $\text{NO}$  and reaction between  $\text{NO}$  and  $\text{NH}_3$**  Fig. 16 shows the DRIFT spectra of  $\text{NO}$  for the pure  $\text{MnO}_x/\text{TiO}_2$  catalyst at  $200\text{ }^\circ\text{C}$ . Clearly, several adsorption peaks appear at  $1355$ ,  $1471$ ,  $1637\text{ cm}^{-1}$ ,  $3661\text{ cm}^{-1}$  and  $3731\text{ cm}^{-1}$  after adsorbing  $\text{NO}$  on the pure catalyst surface. According to the literature, the peaks at  $1355\text{ cm}^{-1}$  and  $1637\text{ cm}^{-1}$  correspond to the nitro group and weakly adsorbed  $\text{NO}_2$ , respectively. The peak at  $1471\text{ cm}^{-1}$  is assigned to the symmetric stretching and antisymmetric stretching vibration of monodentate nitrite, and the peaks at  $3661\text{ cm}^{-1}$  and  $3731\text{ cm}^{-1}$  are related to the telescopic vibration of  $\text{O-H}$ <sup>[22]</sup>. Consequently, the main adsorption products of  $\text{NO}$  on the surface of  $\text{MnO}_x/\text{TiO}_2$  catalyst are nitrate and nitrite, and there is merely a small amount of  $\text{NO}_2$ . During the transient adsorption of  $\text{NO}$ , the peak intensity of the spectrum

increases slowly with the adsorption time. Obviously, the reaction between NO and the lattice oxygen on the catalyst surface directly generates monodentate nitrite, and only a small amount of NO adsorbed to produce  $\text{NO}_2$ .

Fig. 17 shows DRIFT spectra of  $\text{NH}_3$  over the pure  $\text{MnO}_x/\text{TiO}_2$  catalyst pre-adsorbed NO at 200 °C. In Fig. 17, the peak of nitro group at  $1355\text{ cm}^{-1}$  disappears, and the other peaks change rarely, indicating that the products generated after NO adsorption are difficult to desorb and decompose, and the adsorption is relatively tight. Meanwhile, gaseous  $\text{NH}_3$  can hardly react with NO, but  $\text{NH}_3$  continuously introduces, and there is thus no absorption peak of  $\text{NH}_3$ . It should be attributed to little active sites, and most of them are occupied by NO, resulting in the adsorption of a small quantity of  $\text{NH}_3$ .

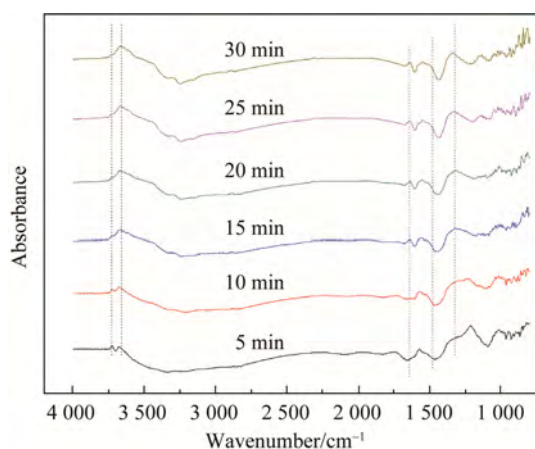


Fig. 16 DRIFT spectra of NO for the pure  $\text{MnO}_x/\text{TiO}_2$  catalyst at 200 °C

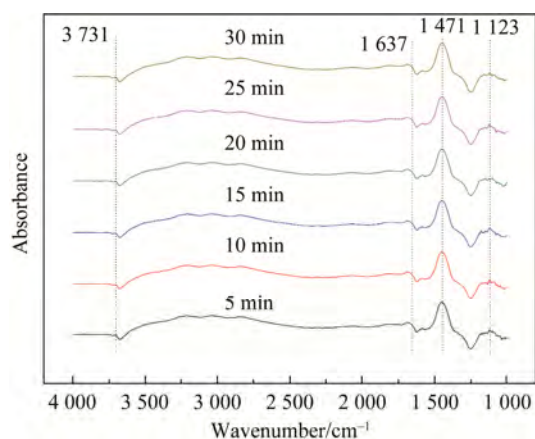


Fig. 17 DRIFT spectra of  $\text{NH}_3$  for the pure  $\text{MnO}_x/\text{TiO}_2$  catalyst pre-adsorbed NO at 200 °C

Fig. 18 shows the DRIFT spectra of NO for the  $\text{MnO}_x/\text{TiO}_2$  catalyst modified with tourmaline at 200 °C. In Fig. 18, there are several characteristic peaks at  $1028$ ,  $1471$ ,  $1637$ ,  $2334\text{ cm}^{-1}$  and  $3731\text{ cm}^{-1}$ , respectively. Among them, the peaks at  $1028\text{ cm}^{-1}$  and  $1471\text{ cm}^{-1}$  emerge an obvious synchronicity, which

should belong to the symmetric stretching and antisymmetric stretching vibration of the same species of monodentate nitrite, and the peak at  $1637\text{ cm}^{-1}$  represents weakly adsorbed  $\text{NO}_2$ <sup>[23]</sup>, due to mainly the reaction of NO with the lattice oxygen of the catalyst, and the peak at  $2334\text{ cm}^{-1}$  after adsorption for 15 min assigns to  $\text{N}_2\text{O}$ , which is attributed to the polarization effect of tourmaline reduced NO to a certain extent.

Fig. 19 shows the DRIFT spectra of  $\text{NH}_3$  for the  $\text{MnO}_x/\text{TiO}_2$  catalyst modified with tourmaline and pre-adsorbed NO at 200 °C. Clearly, the absorption peak at  $2334\text{ cm}^{-1}$  disappears, due to the reaction between the adsorbed  $\text{NH}_3$  and  $\text{N}_2\text{O}$ .  $\text{N}_2\text{O}$  tends to possess a high reaction activity with  $\text{NH}_3$  during denitrification, thus the characteristic peak disappears in the initial few minutes. The weakly  $\text{NH}_3$  absorption peaks appear at  $1689\text{ cm}^{-1}$  and  $3330\text{ cm}^{-1}$  with the continuous introduction of  $\text{NH}_3$ . The peak at  $1689\text{ cm}^{-1}$  corresponds to the antisymmetric angular vibration peak ( $\delta$  as  $(\text{NH}_4^+)$ ) of  $\text{NH}_4^+$  adsorbed on the B acid site, and the peak at  $3330\text{ cm}^{-1}$  is ascribed to the N-H symmetric stretching vibration (vs.  $\text{NH}_3$ ) of

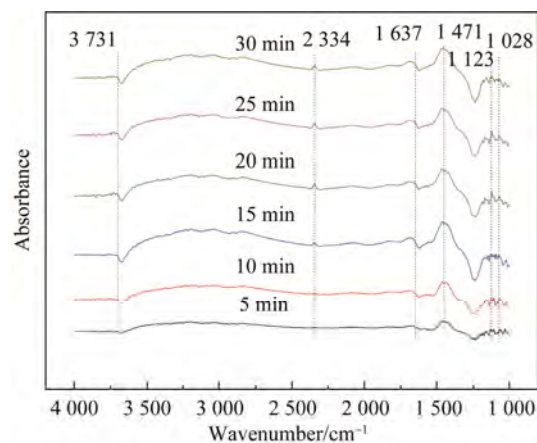


Fig. 18 DRIFT spectra of NO for the  $\text{MnO}_x/\text{TiO}_2$  catalyst modified with tourmaline at 200 °C

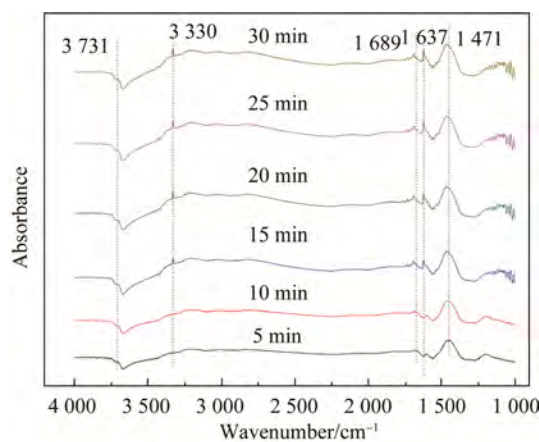


Fig. 19 DRIFT spectra of  $\text{NH}_3$  for the  $\text{MnO}_x/\text{TiO}_2$  catalyst modified with tourmaline and pre-adsorbed NO at 200 °C

coordinated  $\text{NH}_3^{[24]}$ , indicating that the active sites of the catalyst modified with tourmaline are increased to adsorb  $\text{NH}_3$  effectively. Furthermore, the absorption peaks of  $\text{NH}_3$  and  $\text{NO}$  tend to weaken gradually with

time, indicating that the adsorbed  $\text{NH}_3$  reacts with nitrite, and the reaction process follows the L-H reaction mechanism. Fig. 20 shows the flowchart for the reaction mechanism.

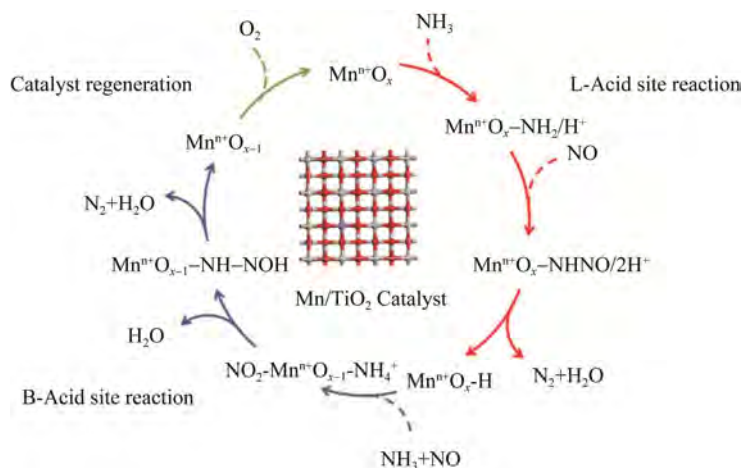


Fig. 20 Flowchart for denitration reaction of  $\text{MnO}_x/\text{TiO}_2$  catalyst

## 4 Conclusions

$\text{MnO}_x/\text{TiO}_2$  catalyst was modified with tourmaline, and the impact of polarization modification effect on the transient adsorption behavior and temperature-dependent quasi-steady adsorption behavior of reaction gas on the catalyst surface was investigated. The catalyst modified with tourmaline had superior denitration activity and stability, and the selectivity decreased with the increase of high valence manganese content.

The specific surface area of the catalyst modified with tourmaline increased and the number of acid sites increased. According to the *in-situ* FTIR characterization, the reaction mechanism of the catalyst surface before and after polarization modification with tourmaline mainly followed the L-H mechanism. The modification with tourmaline for  $\text{MnO}_x/\text{TiO}_2$  catalyst could increase the OH groups on the catalyst surface, thus having the more intense B acid sites, which was conducive to the adsorption and conversion of reaction gas on the surface, ammonia gas could be adsorbed on the surface of catalyst modified with tourmaline more quickly, and the reaction rate was faster. Nevertheless,  $\text{NO}$  could be adsorbed on the catalyst surface to generate nitrite, nitrate, weakly adsorbed  $\text{NO}_2$  and nitro, etc. The modification with tourmaline for  $\text{MnO}_x/\text{TiO}_2$  catalyst could promote the formation of  $\text{N}_2\text{O}$  with a high activity, and also the products could react with adsorbed  $\text{NH}_3$ , thus improving the catalytic activity and stability.

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