Promotional effect of microwave hydrothermal treatment on the low-temperature NH₃-SCR activity over iron-based catalyst

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Abstract: Microwave hydrothermal was introduced into the preparation of iron-cerium-titanium mixed oxide catalyst for NH₃-SCR of NO_x. And the catalysts after microwave hydrothermal treatment or not are characterized by X-ray diffraction(XRD), Infrared spectrum(IR), Transmission Electron Microscope(TEM), nitrogen adsorption-desorption and temperature programmed desorption(NH₃/NO-TPD). Microwave hydrothermal treatment enhanced the low-temperature NH₃-SCR activity of iron-cerium-titanium mixed oxide catalyst, and made its NH₃-SCR reactive temperature window shift to the low-temperature region. Microwave hydrothermal treatment accelerated the crystallite rate of the precursors for iron-cerium-titanium mixed oxide catalysts, adjusted the microscopic pore structure of catalyst, and enlarged the pore diameter and the pore volume of catalyst. Microwave hydrothermal treatment increases Fe and Ce dispersion on the surface of catalyst, and the molar ratio of Ce³⁺/Ce⁴⁺ on the surface of mixed oxide catalyst could also be enhanced after microwave hydrothermal treatment, and improved the relative concentration of Ce³⁺, thereby enhanced the oxidation and reduction properties of catalyst. At the same time, microwave hydrothermal treatment enhanced the low-temperature adsorption

intensity of NH_3 over catalyst, thereby enhanced the low-temperature SCR activity of iron-cerium-titanium mixed oxide catalyst.

Keyword: Selective catalytic reduction(SCR), Iron-based catalyst, Low-temperature, Microwave hydrothermal treatment

1.Introduction

Selective catalytic reduction (SCR) with ammonia has been widely used for the abatement of NO_x emissions from stationary sources, especially for coal-fired power plants^[1-5]. The commercial catalyst system for NH_3 -SCR process is $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst promoted by MoO_3 or WO_3 ^[6-8] which showed higher activity of NO_x reduction and durability to sulfur compounds. However, this type of catalyst some of inevitable disadvantage in practical application such as the narrow operation temperature window with 300~400 °C, high conversion of SO_2 to SO_3 at high temperatures and the toxicity of vanadium pent-oxide to environment and human health^[9]. Therefore, it is of great significance and interest to develop novel active NH_3 -SCR catalysts working in the medium and/or low temperature as a potential substitution for the conventional $\text{V}_2\text{O}_5\text{-WO}_3(\text{MoO}_3)/\text{TiO}_2$ catalyst^[10-24]. Iron-based catalysts with iron oxides as catalytic component have attracted attention in NH_3 -SCR of NO_x owing to some advantages of high NH_3 -SCR activity, low cost and lack of toxicity compared to the conventional $\text{V}_2\text{O}_5\text{-WO}_3(\text{MoO}_3)/\text{TiO}_2$ catalyst. In our previous studies^[25], we have developed an environmentally friendly novel iron-based catalysts by doping cerium oxide and titanium oxide successively into iron oxide through co-precipitation method, which showed excellent NH_3 -SCR activity durability in the medium temperature range. However, the low-temperature NH_3 -SCR activity was not high enough for reducing the nitric oxide of the flue gas after dust removal and desulfurization from coal-fired power plants. Therefore, it is very

1 necessary to improve the low-temperature NH_3 -SCR activity of this iron-based catalyst.

2 Microwave can homogeneously heat the reaction medium rapidly, resulting in a blooming of
3 nucleation, which is favorable for small particle size and narrow particle size distribution^[26,27].

4 Microwave hydrothermal is a new technique to produce inorganic nano-compounds by
5 introducing the microwave into conventional hydrothermal system. Jiang et al. reported the
6 synthesis of low crystalline iron oxide nano-particles spheres with an average diameter of about 6
7 nm by microwave-hydrothermal method^[28]. Therefore, the particle size of iron-base mixed oxide
8 prepared by co-precipitation method could be refined by introducing microwave-hydrothermal
9 method with its surface area being enhanced, which contributed to improve the low-temperature
10 NH_3 -SCR activity of iron-based catalyst.

11 In the present work, a combination of co-precipitation using NH_4OH as precipitant and
12 microwave hydrothermal treatment is employed to improve the low-temperature NH_3 -SCR
13 activity over iron-cerium-titanium mixed oxide catalyst. The results indicated that the
14 low-temperature NH_3 -SCR activity of iron-cerium-titanium mixed oxide catalyst could be
15 enhanced by introducing microwave hydrothermal treatment into the preparation of catalyst, and
16 made the NH_3 -SCR reactive temperature window shift to the low-temperature region,
17 $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ -MH could achieve 85.7~100% NO conversions in the temperature range of
18 125 ~ 250 °C. The structural properties and redox properties of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ and
19 $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ -MH were characterized using X-ray diffraction(XRD), Transmission Electron
20 Microscope(TEM), N_2 physisorption, Infrared(IR) and X-ray photoelectron spectra(XPS),
21 respectively. Finally, temperature programmed desorption of NH_3 and NO_x (NH_3 -TPD and
22 NO_x -TPD) was carried out to reveal the adsorption ability of reactants over $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ and

1 $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ -MH.

2 **2. Material and methods**

3 **2.1 The preparation of catalysts**

4 All the reagents used in the present work are of AR grade. $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ was
5 synthesized as Ref.^[25], which was prepared through co-precipitation method using $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$,
6 $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ti}(\text{SO}_4)_2$ as precursors and ammonium hydroxide as precipitator. Firstly, the
7 precursors of iron, cerium and titanium were dissolved in the distilled water to get the mixed
8 solution with the molar ratio of Fe^{3+} , Ce^{3+} and Ti^{4+} being 0.65:0.05:0.30, in which the total ion
9 concentration of Fe^{3+} , Ce^{3+} and Ti^{4+} was 0.2 mol/L. The solution was stirred for 1h at ambient
10 temperature to make sure the intensive mixing of Fe^{3+} , Ce^{3+} and Ti^{4+} , and then it was slowly
11 titrated into an certain 2 mol/L ammonia water until the pH of the solution reaching 9~10.
12 Without aging, the precipitate was filtered, and washed with distilled water for several times,
13 followed by desiccation at 105 °C for 12 h and calcined at 400 °C for 5 h in air(the heating rate
14 kept at 5 °C/min). The calcined samples were crushed and sieved to 40-60 mesh for tests.

15 The effect of microwave hydrothermal treatment on $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ was conducted using
16 a household microwave ovens(EG720FC8-NS(X), 2.45 GHz, 700 W). The aforementioned
17 precipitate of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ was placed under microwave irradiation for 15 min with 36.4%
18 power(microwave irradiation 8 s, 14 s suspended for a cycle with full power). Then, the
19 precipitate after microwave hydrothermal treatment was filtered and washed with distilled water
20 for several times, and the subsequent preparation was the same as the preparation of
21 $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$. The $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ catalyst after microwave hydrothermal treatment was
22 denoted as $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ -MH.

2.2 Catalyst characterizations

Powder XRD measurements were carried out on D/MAX-2500PC X-ray diffraction Analyzer (Japan, Rigaku, Cu K α as radiation resource) and $\lambda=1.54$ Å. The data of 2θ from 10 to 80° were collected at 4°/min with the step-size of 0.02°. The morphology of samples was characterized by using transmission electron microscopes (TEM, Tecnai G2 F20 instrument, USA, FEI). N₂ adsorption-desorption isotherms were obtained at -196 °C using Micromeritics ASAP2020 Surface Area and Porosity Analyzer. Prior to N₂ physisorption, the samples were degassed at 300 °C for 5 h. Surface areas were determined by Brunauer-Emmertt-Teller (BET) equation in 0.05~0.35 partial pressure range. Pore volumes, average pore diameters and pore size distributions were determined by Barrett-Joyner-Halenda (BJH) method from the desorption branches of the isotherms. Infrared spectra of catalysts and their precursors were obtained using brucker VERTEX-70 infrared spectrometer by the accumulation of 32 scans with a spectral resolution of 4 cm⁻¹. A small amount of samples was milled with KBr, and a mixture of them was pressed into a disc for analysis. XPS were recorded on a Scanning X-ray Microprobe (ESCALAB-250, USA, ThermoFisher SCIENTIFIC) using Al Ka radiation (1486.7 eV). Binding energies of elements of samples were calibrated using C 1s peak (BE = 284.8 eV) as standard. The temperature programmed desorption(NH₃-TPD and NO_x-TPD) was carried out on a custom-made TCD setup using 50 mg catalysts. Prior to TPD experiments, the samples were also pretreated in helium at 500 °C for 1 h and cooled down to the room temperature(30 °C). Then the samples were saturated with 30 ml/min NO/NH₃ (3% in helium) at 30 °C for 1 h, following by helium purge for another 1 h. Finally, the temperature was raised to 500 °C in helium flow at the rate of 5 °C/min.

2.3 Activity measurement

1 The typical NH₃-SCR activity tests were carried out over 6 ml catalyst (40-60 mesh fraction)
 2 in a fixed-bed quartz tube reactor and the reaction conditions were controlled as follows: 1000
 3 ppm NO, 1000 ppm NH₃, 3% O₂ and balanced N₂ at the total flow rate of 3000 ml/min
 4 corresponding to gas hourly space velocity(GHSV) of 30,000 /h(ambient conditions). Different
 5 space velocities were obtained by tuning the volume of catalyst (if changing GHSV) without
 6 changing the total flow rate. During the measurement, the concentrations of NO, NO₂ and O₂ at
 7 the inlet and outlet of the reactor were monitored by Flue Gas Analyzer (Optima7.0, York
 8 Instruments Co. Ltd, Germany). NO_x conversion (η) was calculated as follows:

$$\eta = \frac{NO_x(in) - NO_x(out)}{NO_x(in)} \quad \frac{9}{10}$$

11 Where, $NO_x(in)$ and $NO_x(out)$ are the concentrations of NO_x at the inlet and the outlet
 12 of the reactor, respectively, NO_x represents NO+NO₂.

13 3. Results and discussion

14 3.1 NH₃-SCR activity

15 Fig.1 shows the NO_x conversion as a function of reaction temperature in the NH₃-SCR over
 16 Fe_{0.65}Ce_{0.05}Ti_{0.30}O_z and Fe_{0.65}Ce_{0.05}Ti_{0.30}O_z-MH. From the results we can see that
 17 Fe_{0.65}Ce_{0.05}Ti_{0.30}O_z-MH showed higher NH₃-SCR activity than Fe_{0.65}Ce_{0.05}Ti_{0.30}O_z at the
 18 low-temperature range of 125~175 °C, although its high-temperature NH₃-SCR activity was
 19 lower than Fe_{0.65}Ce_{0.05}Ti_{0.30}O_z at the temperature range of 350 ~ 400 °C. Therefore, the
 20 low-temperature NH₃-SCR activity of iron-cerium-titanium mixed oxide catalyst could be
 21 enhanced when its precursor was aged through microwave hydrothermal treatment, and made its
 22 reactive NH₃-SCR temperature window shift to the low-temperature region. In order to properly

1 test $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ -MH catalysts for NH_3 -SCR reaction, its NO_x conversion at higher GHSV
2 values of 60,000 /h and 120,000 /h are also given in Fig.1. From Fig.1 it can be found that GHSV
3 had a significant effect on the low-temperature NH_3 -SCR activity over $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ -MH
4 catalyst, and the NO_x conversion had an obvious decline in the relatively low temperature range of
5 100~250 °C with the GHSV increasing from 30,000 /h to 120,000 /h. Meanwhile, GHSV had little
6 effect on the NO_x conversion over $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ -MH catalyst at higher reaction temperatures.
7 Even at a high GHSV of 120,000 /h, $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ -MH catalyst showed good NO_x
8 conversion at medium-high reaction temperature and had more than 90% of NO_x conversion at
9 reaction temperature higher than 250 °C. In the following sections, we will fully investigate the
10 influence of microwave hydrothermal treatment on the microstructure, redox behavior and
11 reactant adsorption capability of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ catalyst using various characterization
12 methods.

13 3.2 Structure property

14 3.2.1 IR

15 The IR spectral of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$, $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ -MH and their precursors are
16 recorded between 400 and 1800 cm^{-1} , which are shown in Fig.2. From Fig.2, it can be seen that
17 compared to the precursor of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ -MH, there existed the additional IR bands at
18 around 422、474 and 1353 cm^{-1} in the precursor of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$. According to the reports^[29],
19 the IR bands at around 422 and 474 cm^{-1} are attributed to the adsorption peak of FeOOH.
20 Meanwhile, the IR band at around 1353 cm^{-1} is due to bending vibration bands of O-H group.
21 Therefore, Microwave hydrothermal treatment induced FeOOH in the precursor of
22 $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ decomposing into some water. From Fig.2 we can also find that compared to

1 $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z\text{-MH}$, there exist some IR bands at 984、1048、1127 and 1198 cm^{-1} due to the
2 adsorption peak of SO_4^{2-} on $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$, which might be assigned to a small amount of
3 SO_4^{2-} absorbed on FeOOH surface in the precursor of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ ^[30,31]. Meanwhile, SO_4^{2-}
4 absorbed on $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ catalyst could enhance its Brønsted acid strength, which
5 contributed to improve the high-temperature $\text{NH}_3\text{-SCR}$ activity on $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ ^[32]. From
6 Fig.1, it can be found that the high-temperature $\text{NH}_3\text{-SCR}$ activity of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ decreased
7 when its precursor was aged by microwave hydrothermal treatment. Therefore, we can induce that
8 microwave hydrothermal treatment made FeOOH in the precursor of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$
9 decomposing, and depressed the adsorption of SO_4^{2-} on its surface, which caused the
10 high-temperature $\text{NH}_3\text{-SCR}$ activity on $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ decreased.

11 **3.2.2 XRD and TEM**

12 Fig.3 shows the XRD results of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$, $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z\text{-MH}$ and their
13 precursors. The samples expect $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z\text{-MH}$ showed no obvious diffraction patterns
14 besides some broad bumps, implying that the samples were in poor crystallization. The interaction
15 between iron, cerium and titanium species led to a high dispersive state of active phases, without
16 forming iron oxides, cerium oxides or titanium oxide particles. Compared to $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$,
17 there existed some little XRD diffraction peaks due to $\text{Fe}_9\text{TiO}_{15}$ mixed oxide(JCPDS). Fig.4 is the
18 TEM images of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ and $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z\text{-TEM}$ catalysts. From Fig.4, it can be
19 found that the sizes of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ and $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z\text{-MH}$ catalysts are very small, and
20 they both exist serious surface agglomeration. However, compared with $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$
21 catalyst, the particle agglomeration degree of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z\text{-MH}$ catalyst is poor and its
22 particle size distribution is more uniform. Therefore, microwave hydrothermal treatment could

strengthen the reaction of forming iron-titanium mixed oxides between iron species and titanium species and made its particle size distribution more uniform, which might contribute to improve the low-temperature NH_3 -SCR activity on $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ ^[33].

3.2.3 N_2 physisorption

Fig.5. shows the N_2 adsorption-desorption curve and the pore size distribution of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ and $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ -MH. The BET surface areas, BJH desorption pore volumes, average pore diameters are given in Tab.1. Microwave hydrothermal treatment could made P/P_0 at N_2 adsorption-desorption curve hysteresis loop closure point of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ shift to right, implying that microwave hydrothermal treatment led some of micro-pores in $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ collapsed, and enlarged its average pore diameter, which decreased its BET surface area. However, microwave hydrothermal treatment could enlarge the pore volume of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$.

3.2.4 XPS

The surface atomic concentrations and valence states of Fe, Ce, Ti and O elements in $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ and $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ -MH catalysts were characterized by XPS, and the results are shown in Tab.2 and Fig.5, respectively.

As shown in Fig. 6(A), The binding energies of $\text{Fe}2p_{3/2}$ and $\text{Fe}2p_{1/2}$ in $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ and $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ -MH were about 710.6 and 724.1 eV, respectively, which attributed to Fe^{3+} . And the spectra of $\text{Fe}2p_{3/2}$ was asymmetrical in samples, indicating that there existed some species of Fe^{2+} in $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ and $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ -MH. However, a slight decrease in binding energies of $\text{Fe}2p_{3/2}$ and $\text{Fe}2p_{1/2}$ was observed when the precursor of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ was under microwave hydrothermal treatment, which implied that microwave hydrothermal treatment could

1 affect the interaction between iron and other elements in $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$, thereby changed the
2 electron cloud distribution of Fe over catalysts. The XPS spectra peaks of Ce 3d over
3 $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ and $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z\text{-MH}$ could be fitted into eight peaks with being labeled
4 as u(u, u', u'', u''') and v(v, v', v'', v''') which attributed to Ce 3d_{5/2} and Ce 3d_{3/2}, respectively.
5 According to literatures^[34], u(about 882.3 eV) belonged to the characteristic peak of Ce⁴⁺ with
6 u'(about 885.1 eV) attributed to the characteristic peak of Ce³⁺, which indicated the coexistence of
7 both Ce³⁺ and Ce⁴⁺ oxidation states over $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ and $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z\text{-MH}$. At the
8 same time, microwave hydrothermal treatment caused the intensities of the characteristic peaks
9 attributed to Ce⁴⁺ to decrease, while caused those of u' and v' peaks attributed to Ce³⁺ to increase.
10 Thereby, microwave hydrothermal treatment enhanced the molar ratio of Ce³⁺/Ce⁴⁺ which
11 improved the low-temperature NH₃-SCR activity of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ through enhancing its
12 low-temperature catalytic oxidation performance of NO to NO₂. From Tab.2 we can see that
13 microwave hydrothermal treatment could decrease the concentrations of iron and cerium elements,
14 and enhanced their dispersion in the surface of iron-cerium-titanium mixed oxide. Fig.5(C)
15 showed that the binding energies of 530.8 and 529.8 eV were attributed to the adsorption oxygen
16 and the lattice oxygen over the surface of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$, respectively. And microwave
17 hydrothermal treatment catalysts caused the binding energy of its surface adsorption oxygen
18 shifted to 529.6 eV and its oxygen lattice binding energy shifted to 531.2 eV. Many researchers
19 have suggested that a high ratio of surface adsorption oxygen($\text{O}_\alpha/\text{O}_\text{t}$) is beneficial for the NO
20 oxidation to NO₂ in the NH₃-SCR reaction at low temperatures and thereafter facilitates the "fast
21 SCR" reaction^[35-37]. However, a high ratio of surface lattice oxygen($\text{O}_\beta/\text{O}_\text{t}$) might promote the
22 high-temperature oxidation activity of NH₃ to NO_x, which might be harm to the NH₃-SCR activity

1 at high temperatures^[35]. In this paper, it was found that microwave hydrothermal treatment
 2 promoted the low-temperature NH₃-SCR activity over Fe_{0.65}Ce_{0.05}Ti_{0.30}O_z catalysts and decreased
 3 its high-temperature NH₃-SCR activity(Fig.1). Meanwhile, microwave hydrothermal treatment
 4 slightly decreased the concentration of the adsorption oxygen over Fe_{0.65}Ce_{0.05}Ti_{0.30}O_z, but
 5 enhanced its lattice oxygen concentration(O_β), and increased its total surface oxygen
 6 concentration(Tab.2). Therefore, although microwave hydrothermal treatment slightly decreased
 7 the surface adsorption oxygen concentration of Fe_{0.65}Ce_{0.05}Ti_{0.30}O_z catalysts,
 8 Fe_{0.65}Ce_{0.05}Ti_{0.30}O_z-MH catalysts showed higher low-temperature NH₃-SCR activity. Compared
 9 with Fe_{0.65}Ce_{0.05}Ti_{0.30}O_z-MW, there existed some sulfur element on the surface of
 10 Fe_{0.65}Ce_{0.05}Ti_{0.30}O_z, which attributed to SO₄²⁺ adsorbed in the precursor of Fe_{0.65}Ce_{0.05}Ti_{0.30}O_z.
 11 Therefore, it indicated that microwave hydrothermal treatment made the precursors of catalyst
 12 crystallized, thereby, decreased the adsorption of SO₄²⁺ over Fe_{0.65}Ce_{0.05}Ti_{0.30}O_z. As shown in
 13 Fig.6(D) and Tab.2, the binding energies of 458 and 463.7 or 463.8 eV in Fe_{0.65}Ce_{0.05}Ti_{0.30}O_z and
 14 Fe_{0.65}Ce_{0.05}Ti_{0.30}O_z-MH corresponded well with Ti⁴⁺. Microwave hydrothermal treatment made the
 15 surface concentration of Ti⁴⁺ slightly increase from 12.02% to 12.11%, and decreased the molar
 16 ratios of Fe/Ti and Ce/Ti on the surface of Fe_{0.65}Ce_{0.05}Ti_{0.30}O_z.

17 In conclusion, microwave hydrothermal treatment made the precursor of Fe_{0.65}Ce_{0.05}Ti_{0.30}O_z
 18 crystallized, which influenced the interaction of elements in catalysts and the dispersion of iron
 19 and cerium element. Moreover, microwave hydrothermal treatment enhanced the molar ratio of
 20 Ce³⁺/Ce⁴⁺ and the surface lattice oxygen(O_β) concentration of Fe_{0.65}Ce_{0.05}Ti_{0.30}O_z, and decreased
 21 its surface adsorption oxygen concentration and surface adsorption SO₄²⁺ concentration.

22 **3.2.5 NH₃/NO-TPD**

The adsorption/desorption capacity of NH_3 and NO over $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ and $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z\text{-MH}$ catalysts was investigated by TPD methods. As the NH_3 -TPD results shown in Fig.7(A), two samples had one broad NH_3 desorption peak from 100 to 500 °C with the peak temperature lower than 200 °C, which indicated that there existed both low-temperature Lewis acid sites and high-temperature Brønsted acid sites. Compared with $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$, $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z\text{-MH}$ showed stronger NH_3 desorption peak at the temperature range of 150~350 °C. Therefore, microwave hydrothermal treatment could enhance the adsorption of NH_3 reducing agent over $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$, especially the low-temperature adsorption of NH_3 . From Fig.7(B) we can see that two samples had two NO desorption peaks at 100~200 and 300~400 °C, which could be ascribed to the decomposition of monodentate nitrate at low-temperature and the decomposition of bridging nitrate and bidentate nitrate at high-temperature^[38], respectively. Microwave hydrothermal treatment enhanced the low/medium-temperature adsorption of NO over $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$, but decreased its surface high-temperature adsorption of NO . Therefore, microwave hydrothermal treatment could change the surface structure of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$, and enhanced the low-temperature adsorption of NH_3 -SCR reactants over catalysts.

4 Conclusion

The low-temperature NH_3 -SCR activity of iron-cerium-titanium mixed oxide catalyst could be enhanced when its precursor was treated after microwave hydrothermal, which made its NH_3 -SCR reactive temperature window shift to the low-temperature region. Microwave hydrothermal treatment accelerated the crystallite rate of the precursors for iron-cerium-titanium mixed oxide catalysts, adjusted the microscopic pore structure of catalyst, and enlarged the pore diameter and the pore volume of iron-cerium-titanium mixed oxide catalyst. Microwave

hydrothermal treatment strengthened the interaction between iron oxide and titanium oxide and promoted the formation of iron-titanium composite oxide. The molar ratio of $\text{Ce}^{3+}/\text{Ce}^{4+}$ on the surface of mixed oxide catalyst could be enhanced after microwave hydrothermal treatment, and improved the relative concentration of Ce^{3+} on the surface of catalyst which enhanced the reduction and oxidation conversion between Ce^{3+} and Ce^{4+} . At the same time, microwave hydrothermal treatment enhanced the Lewis acid of mixed oxide catalyst, and improved the low-temperature adsorption of NH_3 over catalyst, thereby enhanced the low-temperature SCR activity over iron-cerium-titanium mixed oxide catalyst.

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Tab.1 Microstructure of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ and $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z\text{-MH}$

Samples	$S_{\text{BET}}(\text{m}^2/\text{g})^{\text{a}}$	Pore volume(cm^3/g) ^b	Pore diameter(nm) ^c
$\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$	252.83	0.451	5.2
$\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z\text{-MH}$	239.77	0.472	5.7

^a BET surface area. ^b BJH desorption pore volume. ^c Average pore diameter.

Tab.2. XPS results of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ and $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z\text{-MH}$

Samples	Fe (%)	Ce (%)	Ti (%)	S (%)	Fe/Ti	Ce/Ti	$\text{O}_i(\%)$		
							$\text{O}_f(\%)$	$\text{O}_a(\%)$	$\text{O}_\beta(\%)$
$\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$	12.41	2.17	12.02	0.12	1.03	0.18	73.28	23.27	50.01
$\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z\text{-MW}$	10.16	1.94	12.11	0.00	0.84	0.16	75.79	22.85	52.94

Figure1

Figure2

Figure3

Figure4-Fe_{0.65}Ce_{0.05}Ti_{0.60}O₃-200nm

Figure4-Fe_{0.65}Ce_{0.05}Ti_{0.60}O_z-100nm

Figure4-Fe_{0.65}Ce_{0.05}Ti_{0.60}O_z-50nm

Figure4-Fe_{0.65}Ce_{0.05}Ti_{0.60}O₃-20nm

Figure4-Fe_{0.65}Ce_{0.05}Ti_{0.60}O₂-MH-200nm

Figure4-Fe_{0.65}Ce_{0.05}Ti_{0.60}O_z-MH-100nm

Figure4-Fe_{0.65}Ce_{0.05}Ti_{0.60}O₃-MH-50nm

Figure4-Fe_{0.65}Ce_{0.05}Ti_{0.60}O₂-MH-20nm

Figure5(A)

Figure5(B)

Figure6(A)

Figure6(B)

Figure6(C)

Figure6(D)

Figure7(A)

Figure7(B)

Fig.1. Effect of microwave hydrothermal treatment on the NH_3 -SCR activity over iron-based catalyst, reaction conditions: 6 mL of catalyst, $[\text{NO}]=[\text{NH}_3]=0.1\%$, $[\text{O}_2]=3.0\%$ and 3000 mL/min of total flow rate, gas hourly space velocity(GHSV)=30,000 /h

Fig.2 Effect of microwave hydrothermal treatment on IR results of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ and its precursor (a the precursor of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$, b the precursor of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z\text{-MH}$, c $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$, d $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z\text{-MH}$)

Fig.3 Effect of microwave hydrothermal treatment on XRD results of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ and its precursor (a the precursor of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$, b the precursor of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z\text{-MH}$, c $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$, d $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z\text{-MH}$)

Fig.4 TEM images of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ and $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z\text{-MH}$ catalysts

Fig.5 Effect of microwave hydrothermal treatment on the microstructure of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ (a $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$, b $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z\text{-MH}$)

Fig.6 Effect of microwave hydrothermal treatment on XPS results of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$ (a $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$, b $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z\text{-MH}$)

Fig.7 Effect of microwave hydrothermal treatment on NH_3/NO -TPD results of $\text{Fe}_{0.65}\text{Ce}_{0.05}\text{Ti}_{0.30}\text{O}_z$