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Article

Fe-Beta zeolite for selective catalytic reduction of NO_x with NH₃: Influence of Fe content

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ABSTRACT

Fe doped Beta zeolite with different Fe contents were prepared by ion exchange by changing the volume or the concentration of a Fe salt solution. For a particular mass of Fe salt precursor, the concentration of the metal salt solution during ion exchange influenced the ion exchange capacity of Fe, and resulted in different activities of the Fe-Beta catalyst. Fe-Beta catalysts with the Fe contents of (2.6, 6.3 and 9) wt% were synthesized using different amounts of 0.02 mol/L Fe salt solution. These catalysts were studied by various characterization techniques and their NH₃-SCR activities were evaluated. The Fe-Beta catalyst with the Fe content of 6.3 wt% exhibited the highest activity, with a temperature range of 202–616 °C where the NO_x conversion was > 80%. The Fe content in Beta zeolite did not influence the structure of Beta zeolite and valence state of Fe. Compared with the Fe-Beta catalysts with low Fe content (2.6 wt%), Fe-Beta catalysts with 6.3 wt% Fe content possessed more isolated Fe³⁺ active sites which led to its higher NH₃-SCR activity. A high capacity for NH₃ and NO adsorption, and a high activity for NO oxidation also contributed to the high NH₃-SCR activity of the Fe-Beta catalyst with 6.3 wt%. However, when the Fe content was further increased to 9.0 wt%, the amount of Fe₃O₄ nanoparticles increased while the amount of isolated Fe³⁺ active sites was unchanged, which promoted NH₃ oxidation and decreased the NH₃-SCR activity at high temperature.

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1. Introduction

With the rapid development of the automobile industry, automobile exhaust emission has become a source of air pollution, and causes dust haze, photochemical smog, acid rain, ozone depletion and the greenhouse effect [1–3]. Compared to gasoline cars, the content of O₂ in diesel exhaust is high, resulting in low HC and CO emission but high NO_x and PM emission. Many methods have been employed to reduce NO_x emission in

the presence of excess oxygen, such as by the direct decomposition of NO_x, NO_x storage and reduction (NSR) and selective catalytic reduction (SCR) of NO_x with ammonia. Among these techniques, the selective catalytic reduction of NO_x with NH₃ (NH₃-SCR) is regarded as the most efficient technology for the abatement of nitrogen oxide [4–7]. Zeolite catalysts have a large specific surface area and plentiful acid sites that adsorb NO and NH₃, leading to their outstanding catalytic performance for de-NO_x in the NH₃-SCR process. Many kinds of zeolite are

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used for the NH_3 -SCR reaction, such as ZSM-5, Beta, MOR, SAPO-34 and SSZ-13 [8–11], and transition metals, such as Cu [12–15], Fe [15–18], Mn [1,19] and Co [20] are used as the main active component in the modified zeolites. Among these, Cu-ZSM-5 and Fe-ZSM-5 catalysts are the most extensive researched. A series of Fe-ZSM-5 catalysts were prepared to find the correlation between Fe loading, preparation method and NH_3 -SCR activity [21].

Researchers have paid a lot of attention to the preparation of the zeolite catalysts with high NH_3 -SCR activity using the improvement of preparation conditions and proper selection of the metal salt precursor to control the sites of the active metal species in the zeolite [22,23], and the selection of the additives [24–26] as well as the optimization of the metal content to avoid the existence of large metal particles [21,27,28]. It is apparent that the primary parameter for determining the activity of the designated zeolites is the content of the active metal in the catalyst. On the other hand, in the preparation procedures of metal doped zeolite catalysts by impregnation and ion exchange methods, the metal salt is first dissolved in water to form the corresponding metal solution and then used to react with the zeolites matrix to load the active metal on the zeolite. According to our research, it was found that for a certain mass of Fe salt ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), the concentration of the Fe salt solution during ion exchange influenced the degree of ion exchange, leading to the different activities of the prepared Fe-Beta catalysts. That is, the relative value between the mass of the zeolite matrix and volume of metal salt solution during ion exchange should be taken into consideration to prepare a zeolite catalyst with high NH_3 -SCR activity.

Beta zeolite has a three dimensional channel structure with a 12-membered ring assembled from 4-, 5-, 6-membered rings [29], and is an attractive host material for metal loading. Furthermore, a metal-modified Beta zeolite has excellent hydrothermal stability compared to other NH_3 -SCR zeolite catalysts. Although SSZ-13 zeolite showed more outstanding activity and comparable thermal stability, the high price of the SSZ-13 zeolite originating from the use of templates limits its large scale application. Therefore, instead of exploiting novel zeolites, many researchers aim to improve the activity of conventional zeolite catalysts containing Beta zeolite.

In this study, we prepared Beta zeolite with different Fe contents by ion exchange under the condition of a specific concentration of Fe salt solution. Based on the characterization, such as X-ray diffraction (XRD), N_2 adsorption, ultraviolet-visible absorption spectroscopy (UV-Vis), X-ray photoelectron spectroscopy (XPS), hydrogen temperature programmed reduction (H_2 -TPR), temperature programmed desorption of NH_3 and $\text{NO}/\text{NO}+\text{O}_2$ (NH_3 -TPD and NO -TPD), and NH_3 -SCR activity of the catalysts, the significance of the relative value between the mass (g) of the Beta zeolite and the volume (mL) of iron salt solution during the preparation process and the content of Fe, surface structure and properties and the states of the Fe species, and the catalytic performance was discussed in detail.

2. Experimental

2.1. Preparation of catalyst

Fe doped Beta zeolite was prepared by ion exchange (IE) with different ratios of solid-to-liquid (S/L ratio), where solid is the mass (g) of Beta zeolite and liquid is the volume (mL) of iron salt solution. The starting zeolite was NH_4 -Beta with a Si/Al molar ratio of 25 from Nankai University Catalyst Co., Ltd. In the procedure of ion exchange, 2 g of NH_4 -Beta was added to a specific volume (40, 100 or 200 mL) of a fixed concentration $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution. The S/L ratio was 1:20, 1:50 and 1:100. The mixture was stirred for 24 h at 80 °C in an air atmosphere, and then the solid sample was filtered from the solution, dried overnight at 120 °C and calcined at 600 °C for 5 h in air. Finally, the sample was pelletized and crushed to 20–40 mesh. The Fe-Beta samples were marked as Fe-Beta-X(Y), where X and Y (mol/L) are the S/L ratio and the concentration of the Fe salt solution. If Y is not used, the concentration of the Fe salt solution was 0.02. The actual content of Fe in the samples was measured by the ICP method.

2.2. Characterization of catalyst

X-ray diffraction (XRD) was performed using a Rigaku D/MAX 2550 VB/PC X-ray diffractometer. The voltage and current were 40 kV and 40 mA, respectively. The Fe content in the sample was analyzed by an inductively coupled plasma optical emission spectrometer (ICP-AES, Thermo Elemental, IRIS 1000). The N_2 adsorption isotherms were measured on a Micromeritics ASAP 2020M surface area and pore size analyzer at –196 °C. Prior to the measurement, the sample was degassed at 180 °C until a stable vacuum of ~0.5 Pa was reached. The pore size distribution curves were calculated using the Horvath-Kawazoe (H-K) method. UV-Vis spectra were recorded on a Varian Cary 500 UV-Vis-NIR spectrophotometer at 200–800 nm with BaSO_4 as reference, and the spectra were converted with the Kubelka-Munk (K-M) function $F(R)$ for comparison. The XPS spectra were recorded on a Thermo ESCALAB 250 spectrometer with a monochromatized Al $K\alpha$ X-ray source (1486.6 eV) and a pass energy of 25 eV. C1s (binding energy 284.6 eV) of adventitious carbon was used as the reference.

Temperature programmed reduction of H_2 (H_2 -TPR) was carried out on a PX200 apparatus (Tianjin Pengxiang Technology Co. Ltd.) with a thermal conductivity detector (TCD). 100 mg of the sample was heated from room temperature to 800 °C at 10 °C/min in a mixed gas of 5% H_2 -95% N_2 (40 mL/min). The consumption of H_2 was monitored continuously with a TCD.

The acidity of the samples were measured by temperature programmed desorption of ammonia (NH_3 -TPD). Before the NH_3 -TPD experiment, 100 mg of the sample was pretreated in a flow of nitrogen (50 mL/min) at 600 °C for 1 h. After it was cooled down to 80 °C, the sample was saturated with a flow of 10% NH_3 -90% N_2 mixture (50 mL/min) for 1 h and flushed by N_2 (50 mL/min) for 1.5 h, and then the TPD was run in N_2 (50 mL/min) from 80 to 750 °C at 10 °C/min.

Temperature programmed desorption after adsorbing NO

(NO-TPD) or NO+O₂ (NO+O₂-TPD) was carried out on a custom-made equipment with a NO_x analyzer (Thermo Fisher Model 42i-HL NO-NO_x-chemiluminescence analyzer as detector). The sample was pretreated in Ar (300 mL/min) at 600 °C for 1 h and cooled down to room temperature. Then the sample was exposed to a flow of 500 ppm NO/Ar (300 mL/min) or 500 ppm NO + 5% O₂-95% Ar (300 mL/min) for 1 h to reach saturated adsorption of NO on the sample, followed by Ar (300 mL/min) purging for 30 min. Finally, NO-TPD and NO+O₂-TPD was carried out by heating the sample in Ar (300 mL/min) from room temperature to 600 °C at 10 °C/min.

For NO oxidation, the reactant gas was composed of 500 ppm NO + 5% O₂/95% Ar (300 mL/min). However, a mixed gas of 500 ppm NH₃ + 5% O₂/balanced Ar (300 mL/min) was used for the NH₃ oxidation. 200 mg of catalyst (20–40 mesh) was used and the gas hourly space velocity (GHSV) was 39000 h⁻¹. The concentration of NO and NO₂ in the tail gas was detected by a Thermo Fisher NO-NO_x-chemiluminescence analyzer. To avoid error caused by the oxidation of ammonia in the converter of the NO/NO_x analyzer, an ammonia trap containing phosphoric acid solution was installed in front of the chemiluminescence detector.

2.3. Activity test

Catalytic activities of the catalysts were evaluated in a fixed bed quartz tube reactor. 200 mg of the catalyst (20–40 mesh) was used in each run. The reactant gas was composed of 500 ppm NO, 500 ppm NH₃, 5%O₂ and balance Ar. The total flow rate was 300 mL/min and the GHSV was 39000 h⁻¹. The concentrations of NO and NO₂ were continually monitored by a chemiluminescent NO/NO_x analyzer (Thermo-Scientific, Model 42i-HL). The conversion of NO_x (X_{NO_x}) was calculated by

$$X_{\text{NO}_x} = (1 - ([\text{NO}] + [\text{NO}_2])_{\text{out}}/([\text{NO}] + [\text{NO}_2])_{\text{in}}) \times 100\%$$

3. Results and discussion

3.1. Catalytic performance

A series of Fe-Beta zeolites with different Fe content were first prepared by the ion exchange method in which a specific mass of Fe(NO₃)₃·9H₂O was dissolved into different volumes of

Fig. 1. Catalytic performance of the Fe-Beta catalysts for NH₃-SCR. Reaction conditions: 200 mg catalyst, 500 ppm NO, 500 ppm NH₃, 5% O₂, balance Ar, GHSV = 3.9 × 10⁴ h⁻¹.

H₂O to prepare different concentrations of the Fe salt solution. The Fe ion exchange capacity and NH₃-SCR activity of the catalysts are listed in Table 1. The results showed that the Fe ion exchange capacity decreased with the increase in the concentration of Fe salt solution when the mass of Fe(NO₃)₃·9H₂O precursor was 0.808 and 1.616 g compared with 2 g of Beta sample. For example, the Fe content was (5.3, 6.3 and 6.6) wt% in the Fe-Beta zeolite catalysts prepared with 0.05, 0.02 and 0.01 mol/L of Fe salt solution. In contrast, when the mass of the Fe(NO₃)₃·9H₂O precursor was low (0.3232 g), the concentration of the Fe salt solution did not influence the Fe ion exchange capacity. However, the activities for the NH₃-SCR reaction clearly changed. In summary, the concentration of the Fe salt solution markedly influenced the Fe ion exchange capacity and NH₃-SCR activity of the catalysts. The reason will be explored further in the future. In this work, the purpose was to study the effect of the content of Fe in the Fe-Beta catalysts on its surface structure and properties, state of the Fe species and NH₃-SCR activity based on the Fe-Beta-1/20 (0.02), Fe-Beta-1/50 (0.02) and Fe-Beta-1/100 (0.02) catalysts.

Fig. 1 further shows the NO_x conversion of the NH₃-SCR reaction as a function of reaction temperature over Fe-Beta-X(0.02) catalysts prepared with different S/L ratio. The

Table 1

Effect of the concentration of the Fe salt solution on Fe ion exchange capacity and NH₃-SCR activity of the catalysts.

Sample	The mass of Fe(NO ₃) ₃ ·9H ₂ O (g/2g Beta)	Concentration of iron salt solution (mol/L)	pH value of iron salt solution	Fe content (wt%) ^a	Al content (wt%) ^a	Fe/Al	Temperature range (NO _x conversion above 80%)
Fe-Beta-1/20(0.02)	0.3232	0.02	1.7	2.6	2.4	0.52	217–536
Fe-Beta-1/50(0.008)	0.3232	0.008	2.0	2.5	2.4	0.50	260–631
Fe-Beta-1/100(0.004)	0.3232	0.004	2.2	2.7	2.7	0.48	220–567
Fe-Beta-1/20(0.05)	0.808	0.05	1.3	5.3	1.6	1.60	190–553
Fe-Beta-1/50(0.02)	0.808	0.02	1.7	6.3	1.8	1.69	202–616
Fe-Beta-1/100(0.01)	0.808	0.01	1.9	6.6	1.9	1.67	185–587
Fe-Beta-1/20(0.125)	1.616	0.125	1.1	5.2	1.5	1.67	205–588
Fe-Beta-1/50(0.04)	1.616	0.04	1.5	9.1	1.2	3.66	195–595
Fe-Beta-1/100(0.02)	1.616	0.02	1.7	9	1.2	3.62	212–559

^a detected by ICP.

Fig. 2. XRD patterns of the Fe-Beta catalysts.

Fe-Beta catalyst prepared with S/L = 50 (Fe-Beta-1/50) exhibited the best SCR activity, while that prepared with S/L=20 (Fe-Beta-1/20) displayed the worst SCR activity. The content of Fe in the catalysts are shown in Table 1 and increased when increasing the volume of Fe salt solution during the preparation process. Based on the content of Fe in the catalysts, it can be deduced that the activity of the Fe-Beta-X(0.02) catalysts prepared with different S/L ratio exhibited a volcano curve with the increase in Fe content in the catalysts.

3.2. Structural characterization of the catalysts

Fig. 2 shows the XRD patterns of the different Fe-Beta catalysts. All samples exhibited the diffraction peaks corresponding to Beta zeolite, revealing that the introduction of Fe ion into Beta zeolite did not destroy the structure of Beta zeolite. In addition, the intensity of the diffraction peaks of Beta zeolite decreased with the increase in Fe content. Furthermore, compared with the pristine Beta zeolite, the diffraction peaks at 35.6°, 40.9° and 49.5° assigned to the α -Fe₂O₃ species appeared for the Fe-Beta-1/100 catalyst [30–32]. This means that the Fe species was highly dispersed in the Fe-Beta-1/20 and Fe-Beta-1/50 catalysts or the amount of Fe oxide was below the detection limit. However, α -Fe₂O₃ particles existed in the Fe-Beta-1/100 catalyst due to its high Fe content.

Fig. 3 shows N₂ adsorption isotherms of the different catalysts. The BET surface area, pore size and pore volume of the catalysts are shown in Table 2. The N₂ adsorption isotherms of all the catalysts can be classified as Type I [33], which is typical of microporous materials such as zeolites [34,35]. The surface

Fig. 3. N₂ adsorption isotherms (inset: pore size distribution) of the Fe-Beta catalysts.

Fig. 4. Fe 2p XPS spectra of the Fe-Beta catalysts.

area and pore size of the Fe-Beta catalysts did not obviously change after the introduction of Fe into the Beta zeolite, but the corresponding pore volume increased gradually with the increase in the Fe content of the Fe-Beta catalysts. This may be due to dealumination in the Fe ion exchange process.

Fig. 4 shows the XPS spectra of Fe 2p_{3/2} and Fe 2p_{1/2} for the different Fe-Beta catalysts. The binding energies of the Fe 2p_{3/2} and Fe 2p_{1/2} peaks were 711.2 and 724.5 eV, respectively, and a satellite peak of Fe 2p_{3/2} was located at 719.0 eV [36,37]. The deconvolution of the Fe 2p_{3/2} peak for the Fe-Beta catalysts was performed by Lorentzian-Gaussian functions with a Shirley background. The two distinct peaks centered at 710.7 and 712.4 eV can be assigned to Fe 2p_{3/2} peaks of Fe²⁺ and Fe³⁺

Table 2

Nitrogen adsorption data and surface compositions of the Fe-Beta catalysts determined by XPS.

Sample	S_{BET} (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)	Fe ²⁺		Fe ³⁺		Fe ³⁺ /Fe ²⁺
				Binding energy (eV)	Peak area	Binding energy (eV)	Peak area	
Beta	478	0.36	0.39	—	—	—	—	—
Fe-Beta-1/20	490	0.35	0.41	710.7	7706	712.4	10071	1.31
Fe-Beta-1/50	497	0.35	0.45	710.8	14901	712.5	20286	1.36
Fe-Beta-1/100	490	0.35	0.49	710.6	10148	712.2	13788	1.36

Fig. 5. UV-Vis spectra of the Fe-Beta catalysts.

[38,39]. The relative amounts of Fe^{2+} and Fe^{3+} on the surface of the different catalysts are listed in Table 2. The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios of the catalysts are very close [40].

Fig. 5 shows UV-Vis spectra of the Fe-Beta catalysts. It is widely accepted that based on the UV-Vis spectra, the Fe species in a Fe-doped zeolite can be distinguished as isolated Fe^{3+} in tetrahedral sites (<250 nm) [41,42] and higher coordination octahedral sites ($250\text{--}300$ nm) [8,43], small oligonuclear Fe_xO_y (between 300 and 400 nm) [44], and Fe_xO_y nanoparticles on the zeolite surface (above 400 nm) [27,45,46]. In order to calculate the relative amounts of the different Fe species, the UV-Vis spectra of the Fe-Beta catalysts were subject to peak resolution and fitting according to the references [47–49]. There were seven peaks in the UV-Vis spectrum of the Fe-Beta catalysts assigned as peaks I, II, III, IV, V, VI and VII. The first two peaks were attributed to isolated Fe^{3+} in tetrahedral sites and higher coordination octahedral sites, respectively. Peaks III and IV were attributed to small oligonuclear Fe_xO_y , while peaks V, VI and VII were due to Fe_xO_y nanoparticles on the zeolite surface. Subsequently, the percentage of the total area of the peaks related to the different Fe species and wt% Fe of the corresponding species by quantitative analysis of the UV-Vis spectra for the Fe-Beta catalysts (Fig. 5) are shown in Table 3. F_1 , F_2 , F_3 and F_4 represented the area (%) of the fitted peaks (I), (II), (III and IV) and (V, VI and VII), respectively.

As shown in Table 3, with the decrease in S/L ratio, the percentage of the area of the fitted peaks ($A\%$) related to isolated Fe^{3+} in tetrahedral sites (F_1) hardly changed (12, 10 and 11)%, indicating that the relative amount of isolated Fe^{3+} in tetrahedral sites in the Fe-Beta catalysts can be maintained. Similarly, this phenomenon also existed for the small oligonuclear Fe_xO_y (F_3). However, $A\%$ related to isolated Fe^{3+} in octahedral sites (F_2) decreased markedly with the increase in S/L ratio. In contrast, $A\%$ related to Fe_xO_y nanoparticles (F_4) increased with the increase in S/L ratio. These results revealed that the Fe species tended to aggregate to form Fe_xO_y nanoparticles on the surface of the Fe-Beta catalysts when more Fe atoms were introduced into the catalysts, accompanied with the considerable decrease in the relative amount of isolated Fe^{3+} species. This situation also existed in the $A\%$ of the different Fe species for each

Table 3

Percentage of the area of the sub-bands and wt% Fe of the corresponding species by quantitative analysis of the UV-Vis spectra (Fig. 3) of the Fe-Beta catalysts.

Fe Species	Fe-Beta-1/20		Fe-Beta-1/50		Fe-Beta-1/100	
	wt% ^e	A (%) ^f	wt%	A (%)	wt%	A (%)
F_1^a	0.31	12	0.59	10	0.96	11
F_2^b	0.87	33	1.39	22	1.17	13
$F_1 + F_2$	1.18		1.98		2.13	
F_3^c	0.69	27	2.12	34	2.70	30
F_4^d	0.73	28	2.09	34	4.17	46

^a Isolated Fe^{3+} in tetrahedral sites (<250 nm)

^b Isolated Fe^{3+} in octahedral sites ($250\text{--}300$ nm)

^c Small oligonuclear Fe_xO_y ($300\text{--}400$ nm)

^d Fe_xO_y nanoparticles (>400 nm)

^e Content of different Fe species was calculated by $A(\%)/100 \times$ the total content of Fe in the catalyst

^f Percentage of the area of the sub-bands in the UV-Vis spectra.

Fe-Beta catalysts. For examples, the $A\%$ related to F_2 , F_3 and F_4 were close for the Fe-Beta-1/20 catalyst (33%, 27%, 28%), which were higher than those of F_1 . However, compared with the Fe-Beta-1/20 catalyst, the $A\%$ related to F_3 and F_4 for the Fe-Beta-1/50 catalyst obviously increased (34 and 34)%, accompanied by the large decrease in the $A\%$ of F_2 . When the Fe content in the catalyst increased, the $A\%$ related to F_4 for the Fe-Beta-1/100 catalyst was further increased to 46%. These changes also indicated that the Fe species tended to aggregation when more Fe species were introduced into the Beta zeolite.

As for the content of the different Fe species in the Fe-Beta catalysts, the situation is different from that for the relative amount of the different Fe species. As shown in Table 3, the content of each kind of Fe species increased with the increase in the content of Fe in the Fe-Beta catalysts, except F_2 for the Fe-Beta-1/100 catalyst. On the other hand, when the content of Fe was low in the Fe-Beta-1/20 catalyst, the contents of F_1 , F_2 , F_3 and F_4 were (0.31, 0.87, 0.69 and 0.73)%, respectively. With the increase in the S/L relative value to 1/100 for the Fe-Beta-1/100 catalyst, the content of different Fe species changed to (0.96, 1.17, 2.70 and 4.17)% respectively, due to the aggregation of Fe in the catalysts. In other words, the Fe-beta-1/100 catalyst has a relatively high content of Fe_xO_y nanoparticles, which is consistent with the XRD results.

It was reported that the different Fe species have quite different NH_3 -SCR activity and some species are considered unfavorable for NO reduction [50]. When the reaction temperature was lower than 300°C , the active center is mainly isolated Fe^{3+} species, including those in tetrahedral (F_1) and octahedral sites (F_2). While the reaction temperature was $300\text{--}500^\circ\text{C}$, the activity of oligonuclear Fe_xO_y increased. When the temperature reached over 500°C , Fe_2O_3 nanoparticles favor NH_3 -SCR activity. On the other hand, it should be noted that Fe_2O_3 nanoparticles also has good activity for ammonia oxidation, while for the isolated Fe^{3+} species and oligonuclear Fe_xO_y , nonselective oxidation of ammonia occurred at $>500^\circ\text{C}$. As shown in Table 3, the Fe-Beta-1/20 catalyst possessed a lower content of all the

Fe species than the Fe-Beta-1/50 and Fe-Beta-1/100 catalysts because of the low content of Fe in the Fe-Beta-1/20 catalyst, leading to its lower SCR activity in the whole temperature range. In contrast, compared with the Fe-Beta-1/50 catalyst, more Fe_xO_y oligomers and nano-particles that have high activity for nonselective oxidation of NH_3 at high temperature existed on the Fe-Beta-1/100 catalyst, resulting in the lower SCR activity of the Fe-Beta-1/100 catalyst at high temperature ($\geq 450^\circ\text{C}$). These results indicated that to obtain a high SCR activity, the concentration of isolated Fe^{3+} species should be improved on the Fe-Beta catalyst for a given condition of high Fe content in the catalyst.

3.3. H_2 -TPR

Fig. 6 shows the H_2 -TPR profiles of the different Fe-Beta catalysts. There were three reduction peaks below 700°C in the profiles of all the catalysts. The overlapped reduction peaks centered at 395 and 504°C were attributed to the reduction of isolated Fe^{3+} and oligomeric iron oxo species or tiny Fe_2O_3 into Fe_3O_4 [51,52], while the peak at 655°C was due to the reduction of Fe_3O_4 to FeO [41,52]. On the other hand, the intensities of the reduction peaks at 395°C for Fe-Beta-1/50 and Fe-Beta-1/100 catalysts were very close, and much stronger than that for the Fe-Beta-1/20 catalyst, which was consistent with the UV-Vis results that the contents of isolated Fe^{3+} species (F_1+F_2) were (1.18, 1.98 and 2.13) wt% in the Fe-Beta-1/20, Fe-Beta-1/50 and Fe-Beta-1/100, respectively. However, the intensities of the reduction peaks at 504 and 655°C increased with the increase in the Fe content of the Fe-Beta catalysts. As shown in Fig. 6, the intensity of the reduction peaks at 504°C for the Fe-Beta-1/50 catalyst was much stronger than that for the Fe-Beta-1/20 catalyst, but was lower than that for the Fe-Beta-1/100 catalyst as the Fe contents related to small oligonuclear Fe_xO_y were 0.69, 2.12 and 2.70 wt% respectively (Table 3). Similarly, the intensity of the reduction peaks at 655°C for the Fe-Beta-1/50 catalyst was a little stronger than that for the Fe-Beta-1/20 catalyst, but was much lower than that for the Fe-Beta-1/100 catalyst, due to the large increase in the content of Fe_2O_3 nanoparticles in the Fe-Beta-1/100 catalyst (4.17 wt%).

Fig. 6. H_2 -TPR profiles of the Fe-Beta catalysts.

3.4. NH_3 -TPD

Fig. 7 shows the NH_3 -TPD profiles of the different Fe-Beta catalysts. Beta zeolite showed two desorption peaks at 165 and 385°C , assigned to the desorption of ammonia species from weak acid site (weak Lewis acid sites) and strong acid site (Brönsted acid sites) [52,53]. In addition, the intensity of the desorption peak at the low temperature was much stronger than that at the high temperature, indicating that Beta zeolite has more Lewis acid sites because of its structural defects caused by the unsaturated bonding of silicon [11]. When Fe was introduced into Beta zeolite, the intensity of the desorption peak at low temperature decreased, while the intensity of the desorption peak at high temperature increased due to the appearance of the strong Lewis acid sites derived from Fe species. At the same time, two new desorption peaks at 285 and 330°C assigned to strong Lewis acid site appeared [18,54,55]. Although it is difficult to assign the desorption peaks of the strong Lewis acidic sites to specific Fe species, it was noticed that the Fe-Beta-1/50 catalyst has the highest amount of strong acid sites ($250\text{--}450^\circ\text{C}$). In the SCR reaction, the acid sites of the SCR catalyst is essential to adsorb and activate NH_3 . Therefore, the large amount of strong acid sites on the Fe-Beta-1/50 catalyst is beneficial to its NH_3 -SCR activity.

3.5. NO -TPD and $\text{NO}+\text{O}_2$ -TPD

Fig. 8 shows the NO -TPD profiles of the Fe-Beta catalysts. Two desorption peaks existed at 130 and 330°C for all the Fe-Beta catalysts. The former can be attributed to physisorbed NO_x and decomposition of monodentate nitrate species [56], while the strong desorption peak at 330°C was assigned to the decomposition of bidentate and bridged nitrate species with higher thermal stability [57,58]. For the different Fe-Beta catalysts, the areas of the desorption peaks at high temperature were close. However, the areas of the desorption peaks at low temperature was larger for the Fe-Beta-1/50 catalyst compared with the other two catalysts. In other words, the Fe-Beta-1/50 catalyst exhibited more NO adsorption compared

Fig. 7. NH_3 -TPD profiles of the Fe-Beta catalysts.

Fig. 8. NO-TPD (a) and NO+O₂-TPD (b) profiles of the (1) Fe-Beta-1/20, (2) Fe-Beta-1/50 and (3) Fe-Beta-1/100 catalysts.

with Fe-Beta-1/20 and Fe-Beta-1/100 catalysts, which is beneficial to its NH₃-SCR activity.

When the co-adsorption of NO and O₂ was carried out, the NO+O₂-TPD profiles of all catalysts were different from the corresponding NO-TPD profiles, as shown in Fig. 8(b). There is just one strong desorption peak at 285 °C assigned to the decomposition of nitrate species, and the amount of desorbed NO_x was much higher than that in the NO-TPD profiles. The reason for this difference between the NO-TPD and NO+O₂-TPD profiles is that the presence of O₂ in the gas promoted the generation of nitrate species, leading to the improvement of the adsorption of NO_x. At the same time, more nitrate species adsorbed on the catalyst surface weakened the physisorption of NO_x, resulting in the disappearance of the desorption peak at low temperature. On the other hand, the amount of desorbed NO_x on Fe-Beta-1/20 catalyst was slightly lower than that on Fe-Beta-1/50 and Fe-Beta-1/100 catalysts, but the desorption temperature was similar for the three catalysts.

3.6. NH₃ Oxidation and NO Oxidation

It is well known that NH₃ oxidation is one of the reasons for a low SCR activity of a catalyst at high temperatures. Hence the catalytic activities of the Fe-Beta catalysts for the NH₃ oxidation were tested and shown in Fig. 9. There is hardly any NO_x produced below 450 °C, but the NO_x concentration increased quickly at temperatures above 450 °C. Furthermore, the activity of the Fe-Beta catalysts for NH₃ oxidation increased with the increase in Fe content. As shown in the results of UV-Vis and H₂-TPR, the content of Fe₂O₃ nanoparticles in the catalysts increased with the increase in the Fe content, leading to the improvement of NH₃ oxidation, since NH₃ oxidation primarily occurred on the Fe₂O₃ nanoparticles [59–61].

It is widely accepted that improving the activity of a SCR catalyst for NO oxidation can promote its low temperature activity, due to the occurrence of “fast SCR”. Therefore, the activity of the Fe-Beta catalysts for NO oxidation to NO₂ was also investigated. As shown in Fig. 10, NO oxidation occurred at the low temperature of 100 °C and reached the highest conversion

at 320 °C [58]. At higher temperature, the conversion decreased rapidly due to thermodynamic limit [62]. Furthermore, the Fe-Beta-1/50 catalyst showed the highest activity for NO oxidation, which is beneficial to its NH₃-SCR activity at low temperature. In contrast, the Fe-Beta-1/20 catalyst had the lowest activity due to the low content of Fe in this catalyst [63].

4. Conclusions

For a specific mass of Fe salt precursor, the concentration of the Fe salt solution during ion exchange affected the degree of ion exchange, and consequently the SCR activity of the prepared Fe-Beta catalysts. Using the same concentration of the Fe salt solution, three Fe-Beta catalysts with the Fe content of (2.6, 6.3 and 9) wt% were prepared with solid-to-liquid ratio of 1/20, 1/50 and 1/100, respectively. The Fe-Beta-1/50 catalyst displayed the highest activity, with a temperature range where the NO_x was >80% of 202–616 °C. Although there was no obvious difference in the surface area, pore size and valence state of Fe among the different Fe-Beta catalysts, the Fe-Beta-1/50 catalyst had a high amount of isolated Fe³⁺ active sites accompanied with a relatively high Fe content, and good NH₃ and NO

Fig. 9. NO_x concentration produced in NH₃ oxidation over (1) Fe-Beta-1/20, (2) Fe-Beta-1/50 and (3) Fe-Beta-1/100.

Fig. 10. NO oxidation over the (1) Fe-Beta-1/20, (2) Fe-Beta-1/50 and (3) Fe-Beta-1/100 catalysts.

adsorption and high activity for NO oxidation. All these advantages resulted in its higher NH_3 -SCR activity than the other two Fe-Beta catalysts. Fe-Beta catalysts with the same Fe content prepared by different concentrations of the Fe salt solution would be explored further. These results provide a valuable guide for preparing a zeolite catalysts with a high NH_3 -SCR activity.

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Graphical Abstract

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Fe-Beta zeolite for selective catalytic reduction of NO_x with NH_3 : Influence of Fe content

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Fe-Beta catalysts with different Fe content were prepared by ion exchange method through modulating the volume of Fe salt solution with a certain concentration. The catalyst with 6.3 wt% Fe content possessed the high amount of strong acidic sites, and high ability to NO adsorption and the high activity for NO oxidation, leading to the high NH_3 -SCR activity at low temperature.

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Fe-Beta 分子筛催化剂在选择催化还原氮氧化物反应中的活性: Fe 含量的影响

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摘要: NO_x 是主要的大气污染物之一, 对环境和人体健康具有极大的危害。其主要来源之一是柴油机尾气排放, V₂O₅-WO₃/TiO₂ 催化剂是现阶段大规模商用的 SCR 催化剂, 但 V₂O₅-WO₃/TiO₂ 催化剂相对较窄的温度窗口和 V₂O₅ 的生物毒性使得迫切需要新型的环境友好的高效 SCR 催化剂, 其中分子筛因其特殊的孔道结构和催化性能受到广泛的关注。用于 SCR 过程的分子筛主要包括 ZSM-5, Beta, MOR, SAPO-34 和 SSZ-13 等, 通常采用 Cu, Fe, Mn 和 Co 等过渡金属对其进行改性, 通过调变分子筛的表面酸性和氧化还原性能, 提高催化剂的 SCR 活性。Beta 分子筛具有三维 12 元环孔道结构, 相对其它分子筛具有较好的水热稳定性, 而且制备工艺成熟, 价格低廉, 因此该类分子筛催化剂在 SCR 过程中具有很好的应

用前景.

我们采用离子交换法制备了系列 Fe-Beta 催化剂,发现将相同质量硝酸铁溶解在不同体积去离子水中,配制成不同浓度的硝酸铁溶液后与分子筛进行离子交换反应,制备得到的 Fe-Beta 催化剂中 Fe 的含量和 NH₃-SCR 催化活性均存在显著差别.在此基础上,我们固定硝酸铁溶液浓度 (0.02mol/L),通过增加溶液的体积,分别制备了 Fe 含量为 (2.6, 6.3 和 9) wt% 的 Fe-Beta 分子筛.结果表明,Fe 负载量为 6.3 wt% 时,Fe-Beta 催化剂表现出最好的催化活性,NO_x 转化率大于 80% 的温度窗口为 202–616 °C.虽然三个催化剂在比表面积,孔径和 Fe 的价态上没有明显的差别,但 Fe 含量为 6.3 wt% 的催化剂在保持相对较高的 Fe 负载量的同时具有更多的孤立 Fe³⁺物种,同时具有较好的 NH₃ 和 NO 吸附性能以及 NO 氧化能力,这些特性使得该催化剂相对于其它两个催化剂表现出更高的 NH₃-SCR 催化活性.当 Fe 含量增加到 9 wt% 时,催化剂中 Fe_xO_y 纳米颗粒的含量大幅增加,使得 NH₃ 非选择性氧化能力加强,从而导致高温 NH₃-SCR 反应活性大幅下降.

关键词: β 分子筛; 选择催化还原; 铁含量; 铁物种; 离子交换

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