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Effects of acid pretreatment on Fe-ZSM-5 and Fe-beta catalysts for N₂O decomposition

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ABSTRACT

Two series of ZSM-5 and beta zeolites were pretreated in 1.0 mol/L HNO₃ solution at room temperature for various time periods. The catalytic performances of their Fe-exchanged products in N₂O decomposition were evaluated. The Fe-zeolite catalysts were characterized using N₂ adsorption-desorption, inductively coupled plasma optical emission spectroscopy, X-ray diffraction, ultra-violet-visible spectroscopy, temperature-programmed desorption of NH₃, and scanning and transmission electron microscopies. For the ZSM-5 zeolite, acid leaching primarily takes place on the crystal surface and the particle size is reduced, therefore the pore channels are shortened. However, because of the good stability of MFI zeolites, the acid does not greatly penetrate the pore channels and new mesopores are not created. For the beta zeolite, because the amorphous material is inclined to dissolve (deagglomerate), some of the micropores are slightly dilated. The improved catalytic activities can be explained by the increased active Fe loading as a result of structural changes.

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1. Introduction

Nitrous oxide (N₂O) is a strong greenhouse gas, and its global warming potential is 310 and 21 times those of CO₂ and CH₄, respectively [1]. In addition, N₂O contributes to stratospheric ozone depletion. The global level of N₂O is increasing by 0.82 ppb/year [2]. Reduction of N₂O emissions is therefore urgent. Exhaust emissions from nitric acid plants and adipic acid installations are the largest industrial sources of N₂O. Conse-

quently, extensive efforts have been made to develop effective methods such as catalytic reduction, and thermal and catalytic N₂O decomposition, for controlling N₂O emissions in these exhausts. Among these methods, direct catalytic decomposition of N₂O to harmless N₂ and O₂ gases is the most effective and economical.

Various types of catalysts for N₂O decomposition have been designed, e.g., noble-metal catalysts, metal mixed oxides, and transition-metal (Fe, Co, Cu)-modified zeolite catalysts [3–8].

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Fe-containing zeolites are attractive catalysts for N_2O decomposition because of their high catalytic activities, good thermal stabilities, and low preparation costs [9–12]. Numerous studies have been performed to clarify the structures of active sites and reaction mechanism, to elucidate the relationship between the physicochemical properties and catalytic performance [13–16]. Fe-exchanged species located in the micropore channels, such as mono- and binuclear Fe species and small oligonuclear Fe_xO_y clusters, provide active sites for N_2O decomposition, but FeO_x nanoparticles supported inside and outside the pore channels are inert. A limited amount of active sites is deemed to be one of the key restrictions of catalytic performance. The amount and type of formed Fe species vary depending on the preparation method. Wet ion-exchange is the most popular method, because few steps are involved and the process is easily controlled. However, the main problem with this method is that complete exchange of the zeolite support cannot be achieved because the pore channels obstruct diffusion of Fe species precursors. The exchange degree can be improved by shortening the diffusion paths, e.g., by decreasing the zeolite crystal size or enlarging the pore channels, and this enhances the catalytic activity [17]. Melián-Cabrera et al. [18] reported that the deagglomeration of zeolite crystals caused by mild alkaline leaching treatment improved exchange, but the newly created mesopores did not enhance the catalytic activity. It has also been reported that the catalytic activities of Fe-ZSM-5 materials with hierarchical micro-mesopores are better than that of traditional microporous Fe-ZSM-5 [19–21]. Post-treatments such as alkaline or acid leaching are effective approaches to modify zeolite pore structures. Generally, alkaline treatment preferentially extracts Si from the zeolite framework and acid treatment removes Al [20]. Several works have focused on the effects of alkaline treatment on the catalytic performance in N_2O decomposition. However, few studies of the effects of acid treatment have been reported.

In this work, two typical parent zeolite supports, MFI and BEA, were treated in HNO_3 solution. Various characterization techniques were used to investigate the evolution of the porous structure, and the N_2O decomposition activity was evaluated. Possible explanations for the improved activities of the zeolite are proposed.

2. Experimental

2.1. Catalyst preparation

Commercial H-ZSM-5 ($\text{Si}/\text{Al} = 27$) and H-beta ($\text{Si}/\text{Al} = 33$) zeolites with similar Si/Al molar ratios were purchased from the Nankai Zeolite Company (Tianjin, China). The zeolites were calcined in static air for 4 h at 600 °C before use, to remove organic impurities.

Acid treatment was performed as follows. The parent zeolite (3 g) was added to 1 mol/L HNO_3 solution (50 mL) at room temperature. The mixture was vigorously stirred for 2 or 24 h. We also performed acid treatment for 8 h, but this had no obvious effect on the catalytic activity (Fig. 1). We therefore only discuss the performances of the catalysts pretreated for 2 and 24 h. The sample was thoroughly washed with deionized water and dried at 120 °C overnight. The obtained zeolites were calcined in at 600 °C for 4 h.

Fe was incorporated into the original and modified zeolites using the wet ion-exchange method. All exchanges were performed using $\text{Fe}(\text{NO}_3)_3$ solution (50 mL) at room temperature for 24 h. The Fe^{3+} concentration in the precursor solution was fixed at 0.1 mol/L. After exchange, the samples were thoroughly washed with deionized water, dried at 120 °C overnight, and calcined in static air at 600 °C for 4 h, with a heating rate of 5 °C/min. The products are denoted by Fe-ZSM-5-*x* and Fe-beta-*x*, where *x* indicates the treatment time (h) or parent zeolite

2.2. Material characterization

X-ray diffraction (XRD) patterns of the samples were obtained using an Ultima IV X-ray powder diffractometer with $\text{Cu K}\alpha$ radiation; the working voltage and current were 40 kV and 40 mA, respectively.

N_2 adsorption-desorption experiments were performed at 350 °C using a Micromeritics TriStar II 3020 gas absorption analyzer after heat pretreatment at 200 °C for 6 h in a vacuum; the specific surface area was calculated using the Brunauer-Emmett-Teller (BET) equation.

Scanning electron microscopy (SEM) was performed using a

Fig. 1. XRD patterns of Fe-ZSM-5 (a) and Fe-beta (b) zeolites.

FEG-SEMJEOL microscope (JSM 7001 F model). The particle size was roughly measured using Nano Measurer. The microstructures were examined using high-resolution transmission electron microscopy (HRTEM; JEM 2100 instrument). Before the observations, the samples were ultrasonically dispersed in ethanol for 10 min and a drop of the suspension was placed on a copper grid.

Temperature-programmed desorption of NH_3 (NH_3 -TPD) experiments were performed in a fixed-bed reactor system equipped with a thermal conductivity detector. The sample (150 mg) was pretreated at 400 °C for 1 h under an Ar flow of 28.5 mL/min to remove water and other impurities. When the temperature had cooled to 100 °C, the gas was switched to pure NH_3 (10 mL/min) for 30 min. A flow of Ar (28.5 mL/min) was then passed through the reactor for 30 min to remove weakly physically adsorbed NH_3 . The TPD curves were recorded at a heating rate of 10 °C/min from 100 to 600 °C.

Ultraviolet-visible (UV-vis) spectra were obtained using a Hitachi UV-3000 spectrometer; diffuse reflectance (DR) spectra were recorded in air against BaSO_4 in the region 200–800 nm at a resolution of 1 nm. Deconvolution of the UV-vis absorbance bands into Gaussian sub-bands, followed by multiplication of the percentage of sub-bands with respect to the total area of the experimental spectrum by the total Fe content, gave the percentages of different Fe species in Fe-zeolite samples [22].

The Fe, Si, and Al contents of the catalysts were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES; Optima 8000 spectrometer).

2.3. Catalytic activity

N_2O decomposition experiments were performed using a fixed-bed flow microreactor (Φ 8 mm $\times$ 300 mm) at ambient pressure. In each run, the catalyst (0.4 g, 20–40 mesh) was placed in a quartz reactor. Before the experiment, the catalyst was pretreated in an Ar stream at 500 °C for 30 min to remove surface impurities. The reactor was cooled to 275 °C and a reactant gas mixture containing 5% O_2 , 5000 ppm N_2O , and balance Ar, at a total flow rate of 200 mL/min (gas hourly space velocity = 30000 h^{-1}), was fed into the reactor. The steady-state N_2O conversions at 25 °C intervals from 275 to 600 °C were calculated based on the gas chromatogram peak areas. The outlet gas compositions were analyzed online using a gas chromatography system (Shimadzu) equipped with a thermal

conductivity detector and two serial columns (a Porapak Q column for separation of N_2O and N_2/O_2 , and a 5 Å molecular sieve column for the separation of N_2 and O_2).

3. Results and discussion

3.1. Physicochemical properties of Fe-zeolites

Fig. 1 shows the XRD patterns of the Fe-ZSM-5 and Fe-beta zeolite catalysts. The MFI and BEA crystalline structures were well preserved after acid pretreatment and ion exchange, indicating that the crystalline structure was not invaded. Close examination of Fig. 1(a) shows slight reductions in the peak intensities of the Fe-ZSM-5 samples; this is consistent with the literature [23]. This may result from the reduced particle size after acid treatment. However, Fig. 1(b) shows that the diffraction peaks of the Fe-beta samples became sharper. No diffraction peaks from FeO_x nanoparticles were observed for any of the samples. However, the XRD resolution is insufficient to show FeO_x species evenly distributed over the internal/external pore channels, therefore the absence of FeO_x diffraction peaks is not hard evidence of the absence of FeO_x .

The relative crystallinities were estimated from the diffraction peak intensities, according to the literature method [24]. The crystallinities of the Fe-ZSM-5 and Fe-beta samples all improved after acid treatment, but the levels of improvement differed. For the Fe-ZSM-5 samples, the crystallinity increased slightly from 96% to 100% after acid treatment for 2 and 24 h. For the Fe-beta samples, the crystallinity increased from 81% to 92% and 100% after treatment for 2 and 24 h, respectively. These results suggest that the crystallinity of the parent beta zeolite was poorer, and it was more amorphous, than the parent ZSM-5 zeolite. The sample particle sizes were estimated from the SEM images; the Fe-ZSM-5 particle size decreased from 1.3 to 1.0 μm after acid treatment (Table 1). However, for the Fe-beta samples, the particle sizes were similar. During acid treatment, the amorphous material in the beta support may dissolve first in the acid solution, therefore the diffraction peak intensity increased. For the parent ZSM-5 support, because of its good crystallinity, corrosion mainly takes place on the zeolite surface, therefore the particle size gradually decreased. It is inferred that the etching locations on the ZSM-5 and beta zeolite structures may be different; this is confirmed by the following results.

Table 1
Physicochemical properties of Fe-ZSM-5 and Fe-beta samples.

Sample	Si/Al ^a	Fe (%)	Fe/Al ^a	Exchange ^b (%)	$S_{\text{BET}}/(\text{m}^2/\text{g})$	$V_{\text{total}}/(\text{cm}^3/\text{g})$	Crystallinity ^c (%)	Particle size ^d (μm)
Fe-ZSM-5-P	31.4	0.21	0.07	3.1	279	0.20	96	1.3
Fe-ZSM-5-2	34.3	0.20	0.06	2.6	296	0.21	100	1.1
Fe-ZSM-5-24	38.3	0.37	0.12	5.6	289	0.20	100	1.0
Fe-beta-P	35.0	1.07	0.45	22.1	438	0.46	81	0.1
Fe-beta-2	133.9	1.52	1.43	82.8	479	0.48	92	0.1
Fe-beta-24	192.8	1.21	1.62	100.0	496	0.53	100	0.1

^a Molar ratio.

^b As (Fe/Al) ICP $\times$ 46.5.

^c Based on the intensity of the reflection at $2\theta = 7.94^\circ$ for ZSM-5. Based on the intensity of the reflection at $2\theta = 7.6^\circ$ for beta.

^d Based on the estimation from the SEM images.

Fig. 2. N_2 adsorption-desorption curves (a, b) and pore distribution curves (c, d) of Fe-ZSM-5 and Fe-beta samples.

The N_2 adsorption-desorption isotherms and the pore distributions are shown in Fig. 2. The Fe-ZSM-5 and Fe-beta samples predominantly show type I isotherms, indicating inherent microporous structures. The pore distribution curves also show that no mesopores were created in the Fe-ZSM-5 or Fe-beta samples by mild acid treatment. However, Abelló et al. [25] reported that alkaline leaching of ZSM-5 zeolite could form new mesopore channels. The Si/Al ratio of the ZSM-5 zeolite suggests that Al removal is less extensive than Si removal. It is therefore more difficult to build mesoporous structures in a ZSM-5 support by acid treatment. Close inspection of the pore distribution curves shows that the distribution of half pore diameters in the ZSM-5 zeolite was almost unchanged. However, for the Fe-beta samples, the micropore sizes increased slightly; the number of micropores of radius 0.4 nm decreased and the number of micropores of radius 0.5 nm increased. These results suggest that acid treatment did not create new mesopores, but the micropores in the Fe-beta samples were widened to a certain extent.

Table 1 lists the textural parameters of the Fe-ZSM-5 and Fe-beta samples. The BET surface area of the Fe-beta-P sample is high ($438 \text{ m}^2/\text{g}$), and that of the Fe-ZSM-5-P zeolite is low ($279 \text{ m}^2/\text{g}$). Acid treatment for various times increased the BET surface area of Fe-ZSM-5 from 279 to $296 \text{ m}^2/\text{g}$. The BET surface areas of the Fe-beta samples were significantly higher than those of Fe-ZSM-5, increasing from 438 to $496 \text{ m}^2/\text{g}$; a similar trend was observed for the total pore volumes. It is suggested that the acid treatment removes some of the amorphous mate-

rial in the zeolite support, which opens the pore channels. The sharp increase in the textural parameters of the beta series may indicate the increased presence of amorphous structures; this is consistent with the XRD results.

The chemical compositions of the synthesized Fe-ZSM-5 and Fe-beta zeolites were determined using ICP-OES; the data are listed in Table 1. The original Si/Al ratios of the Fe-ZSM-5-P and Fe-beta-P zeolites are around 31 and 35, respectively; these are a little higher than the nominal value for H-zeolite-P. Some Al could be leached out during the wet ion-exchange process, because the metal precursor solution is acidic ($\text{pH} \approx 2.5$). The Si/Al ratio increased with pretreatment time. For the Fe-ZSM-5 samples, the Si/Al ratios increased from 31.4 to 38.3, whereas for the Fe-beta samples, they increased from 35.0 to 192.8. The stability of the ZSM-5 zeolite in acid solution is therefore better than those of beta supports. Only external Al is removed from the surface of Fe-ZSM-5, therefore its structure is retained; this is supported by the results of the N_2 adsorption-desorption tests. In contrast, for the beta zeolites, the amorphous structure and framework Al can be leached out, which causes the pore to widen, as indicated by the pore distribution curves.

The Fe loadings in the Fe-ZSM-5-P, Fe-ZSM-5-2, and Fe-ZSM-5-24 samples were 0.21%, 0.20%, and 0.37%, respectively. Lengthy acid-leaching treatment (24 h) of the ZSM-5 support affected the Fe loading. The Fe contents of the Fe-beta samples increased from 1.07% in Fe-beta-P to 1.52% and 1.21% in Fe-beta-2 and Fe-beta-24, respectively. The slight increase in the Fe loading on the ZSM-5 support may be caused

Fig. 3. Representative SEM images of various catalysts. (a) Fe-ZSM-5-P; (b) Fe-ZSM-5-24; (c) Fe-beta-P; (d) Fe-beta-2.

by the limited cutting of diffusion channels in ZSM-5. The apparent enhanced Fe loading in the beta zeolite is caused by the increased micropore size and elimination of the amorphous structure.

Four representative catalysts were selected and their morphological changes were directly investigated using SEM; the results are shown in Fig. 3. Fig. 3(a) and 3(b) show that after acid etching for 24 h, the bulk structure was maintained, but the particle surfaces of Fe-ZSM-5-24 were more ragged than those of Fe-ZSM-5-P; this is confirmed by the TEM images. Some hollows caused by acid corrosion are observed. The morphologies of the Fe-beta samples (Fig. 3(c) and 3(d)) changed. In the Fe-beta-P sample, large amorphous blocks are mixed with small particles. However, for the Fe-beta-2 sample, the particle size distribution is more uniform. The large blocks disappear and the amount of small cubic crystals increases. The SEM results indicate that for the Fe-ZSM-5 samples acid leaching occurs preferentially on the zeolite surface and the particle size is reduced; this is in line with the XRD results. However, for the Fe-beta samples, acid erosion tends to occur on the large particles with amorphous structures. The small zeolite crystalline particles are difficult to dissolve in a short acid-treatment time, therefore in the XRD results, the crystalline size of the beta support is almost unchanged after acid treatment.

The four typical catalysts were further studied using TEM (Fig. 4). The Fe-ZSM-5-P pore channels can be seen in its TEM image, indicating good preservation of the zeolite structure after Fe exchange. The ICP-OES results show that the Fe loading is low, therefore the crystalline surface is clean with almost no FeO_x nanoparticles. The pore channels of Fe-ZSM-5-24 (Fig. 4(b)) are still well preserved. FeO_x nanoparticles of size 5–40

nm can be seen because of the increased Fe loading, confirmed by ICP-OES. The cubic structure of the Fe-beta zeolite is well preserved after acid treatment and the FeO_x nanoparticles of size 4–9 nm are present in both the Fe-beta-P and Fe-beta-2 samples. However, the amount and particle size of FeO_x do not vary much. These results confirm that serious aggregation of FeO_x nanoparticles occurs during ion exchange and calcination. FeO_x particle growth was not eliminated by acid treatment.

The acidic properties of H-zeolites and Fe-zeolites were investigated using NH₃-TPD; the results are shown in Fig. 5. The

Fig. 4. Representative TEM images of various catalysts. (a) Fe-ZSM-5-P; (b) Fe-ZSM-5-24; (c) Fe-beta-P; (d) Fe-beta-2.

Fig. 5. NH_3 -TPD profiles of ZSM-5 (a) and beta (b) zeolites.

profiles of the ZSM-5 series show two major types of NH_3 desorption peaks for commercial H-ZSM-5. According to the literature, the peak centered at around 150 °C corresponds to weak acid sites such as NH_3 hydrogen bonded to silanol groups, and the peak centered at around 450 °C corresponds to strong acid sites, which are formed through reaction of NH_3 with zeolite $\text{SiOH}(\text{Al})$ or Fe binuclear hydroxo species [26–29]. The introduction of Fe species into H-ZSM-5 by wet ion exchange results in a distinct decrease in the amount of Brønsted acid sites, because the protons in Brønsted acid hydroxyl groups are replaced by cationic Fe species. When the acid post-treatment time was prolonged, the amount of Brønsted acid sites in Fe-ZSM-5 decreased slightly. It is supposed that continuous dealumination of the zeolite framework removes some of the exchanged Al in the zeolite matrix. In addition, after acid treatment, the diffusion channels become more open; this promotes

exchange of protons in Brønsted acid sites by cationic Fe species, which decreases the amount of Brønsted acid sites. The situation is more complex for beta zeolites. Fig. 5(b) shows that the numbers of weak and strong acid sites both decrease after acid post-treatment and Fe exchange. However, at >400 °C, in addition to the acid sites, a new peak centered at around 300 °C appears after ion exchange; this is not observed for the ZSM-5 series. Sugawara et al. [29] observed a similar NH_3 desorption peak at 300 °C after Fe ion exchange. They ascribed it to NH_3 desorption from Fe binuclear species. The presence of a larger number of binuclear Fe species in the Fe-beta samples was therefore verified by the NH_3 -TPD results.

3.2. Characterization of Fe species

UV-vis DR spectroscopy is an effective and common method

Fig. 6. Deconvoluted UV-vis spectra of Fe-ZSM-5 (a, b, c) and Fe-beta (d, e, f) zeolites before and after acid post-treatment.

Table 2

Sub-band area percentages (I_1 at $\lambda < 300$ nm, I_2 at $300 < \lambda < 400$ nm, and I_3 at $\lambda > 400$ nm) derived from deconvoluted UV-vis spectra and corresponding Fe species loading.

Catalyst	I_1^a	I_2^a	I_3^a	Isolated ^b	Oligonuclear ^b	Nanoparticle ^b
Fe-ZSM-5-P	55	32	13	0.12	0.07	0.03
Fe-ZSM-5-2	49	28	23	0.01	0.06	0.05
Fe-ZSM-5-24	42	32	26	0.15	0.12	0.10
Fe-beta-P	47	27	26	0.50	0.29	0.27
Fe-beta-2	61	24	15	0.93	0.37	0.22
Fe-beta-24	68	24	8	0.82	0.30	0.09

^a Percentage of sub-band areas.

^b Fe species loading (%).

for determining the nature and distribution of Fe species in Fe-zeolites [30,31]. We used UV-vis DR spectroscopy to investigate the Fe species in different Fe-zeolites. Fig. 6 shows the UV-vis spectra of the Fe-ZSM-5 and Fe-beta samples deconvoluted into sub-bands, which can be attributed to specific Fe species in the Fe-zeolites. The bands at 215 and 285 nm are respectively assigned to isolated Fe^{3+} ions in tetrahedral and octahedral coordination environments [32,33]. The bands at 335 and 385 nm indicate the presence of small oligonuclear $\text{Fe}_x^{3+}\text{O}_y$ clusters [22], and the absorption bands at 460 and 540 nm are attributed to the presence of bulky FeO_x crystallites on the external surfaces of the zeolite crystals [34]. Various Fe species are therefore present in all the Fe-zeolites samples. However, the distributions of Fe species differ.

The amounts of Fe species were estimated semi-quantitatively based on the relative intensities of these sub-bands and the total Fe loading in the zeolite. The data in Table 2 show that isolated Fe^{3+} ions are the predominant species in all the Fe-zeolites. However, for the Fe-ZSM-5 samples, the percentage of isolated Fe^{3+} on the exchanged sites decreased, and the percentage of oligonuclear $\text{Fe}_x^{3+}\text{O}_y$ clusters and FeO_x nanoparticles increased, with increasing acid-treatment time. For the Fe-ZSM-5-24 sample, the oligonuclear and FeO_x nanoparticle populations were 32% and 26%, respectively. TEM observations show a large amount of FeO_x nanoparticles in the Fe-ZSM-5-24 samples; this is a result of the high Fe loading after calcination and aggregation. The opposite trend is observed for the Fe-beta series, i.e., the percentage of mono- Fe^{3+} species increased, and the percentage of oligonu-

clear $\text{Fe}_x^{3+}\text{O}_y$ clusters and Fe nanoparticles decreased, with increasing acid-treatment time. For the Fe-beta-24 sample, the percentages of oligonuclear $\text{Fe}_x^{3+}\text{O}_y$ clusters and nanoparticles FeO_x decreased to 24% and 8%, respectively. However, if the Fe loadings are taken into account, the Fe-ZSM-5-24 and Fe-beta-2 samples have the largest contents of isolated Fe^{3+} ions and oligonuclear $\text{Fe}_x^{3+}\text{O}_y$ clusters. In terms of active sites for N_2O decomposition, it is believed that the absolute amount of isolated Fe^{3+} and oligonuclear $\text{Fe}_x^{3+}\text{O}_y$ clusters on the exchanged sites affects the catalytic performance.

3.3. Catalytic performances of Fe-zeolites

The catalytic activities of the Fe-zeolite samples in direct N_2O decomposition were evaluated (Fig. 7). Prolonged acid treatment affected the catalytic properties of the Fe-ZSM-5 samples. The activity improved slightly with increasing acid-treatment time. The catalytic activity curve for the Fe-ZSM-5-24 sample moved to a temperature 10–15 °C lower than that for the Fe-ZSM-5-P sample; for example, at 500 °C, N_2O conversion over conventional Fe-ZSM-5-P was 58%, whereas for the Fe-ZSM-5-2 and Fe-ZSM-5-24 samples, the conversions increased to 59% and 75%, respectively. The improvements in the catalytic performances of the Fe-beta samples are more pronounced. The Fe-beta-2 sample gave the best catalytic performance. At 425 °C, N_2O conversion over Fe-beta-2 was 90%, whereas only 57% conversion was achieved with Fe-beta-P. The order of the activities of the Fe-exchanged beta zeolites is Fe-beta-2 > Fe-beta-24 > Fe-beta-P. A longer acid treatment time did not improve the catalytic activity.

3.4. Discussion

The relationship between the catalytic performance and amount of Fe active sites on different Fe-zeolites is linear (Fig. 8). Regardless of changes in the physicochemical properties, the factor that directly affects the activity is the amount of Fe active sites. The morphological and structural evolution caused by acid treatment are shown in Fig. 9. The parent ZSM-5 has large particles (1.3 μm) and a small amount of impurities. Acid leaching dissolves the amorphous material inside and outside

Fig. 7. N_2O conversions over Fe-zeolites at different temperatures. (a) Fe-ZSM-5; (b) Fe-beta.

Fig. 8. Relationship between N₂O conversion and active Fe content. (a) Fe-ZSM-5 at 525 °C; (b) Fe-beta at 450 °C.

the pore channels and 100% crystallinity is obtained. The BET surface area and total pore volume increase slightly as a result of the open pore channels. When the treatment is prolonged, corrosion strips the zeolite surface layer by layer, which reduces the crystal size (1.0 μm) and roughens the surfaces. The Si/Al ratio is close to the value for the untreated zeolite, indicating that dealumination involves similar dissolution of both Si and Al. In this situation, it is difficult to reform the pore channels of the Fe-ZSM-5 samples. The narrow pore channels and large crystals result in pore blocking during exchange in the Fe-ZSM-5-24 sample. The ICP-OES results show that the Fe loading increases. However, narrow pore channels with a higher Fe loading promote aggregation, which leads to formation of larger amounts of unwanted FeO_x nanoparticles [35]. These two factors inhibit the formation of Fe active sites, and this could explain the slight improvement in the catalytic performances of the Fe-ZSM-5 samples. For the Fe-beta series, the original amorphous material generally dissolves first, as shown by the greatly improved crystallinity. The large differences among the Si/Al ratios imply that Al is removed from the beta support, with retention of most of the Si. The BET surface area and total pore volume are therefore greatly increased, and the micropores widen slightly. These positive factors enhance the Fe loading. The Fe loading decreases with increasing treatment time, because of the lack of Brønsted sites for exchange as a result of excessive dealumination. These results confirm that acid pretreatment of the zeolite support can improve the catalytic activities of Fe-containing zeolite catalysts. However, the most appropriate treatment conditions depend on the physicochemical properties of the zeolite support. It is difficult to design a catalyst containing only the most active Fe species by adjusting the treatment conditions.

Fig. 9. Evolution of sample morphology upon mild acid leaching.

4. Conclusions

After acid leaching of the parent zeolites (1.0 mol/L HNO₃ solution at room temperature for different periods of time) Fe-zeolites were prepared and used in N₂O decomposition. Characterization using various methods showed that the patterns of acid corrosion on ZSM-5 and beta zeolite support are different. Only a small amount of Al on the ZSM-5 surface is dissolved in mild acid treatment. In contrast, the amorphous material in the beta support is first dissolved and some of the micropores are widened. Catalytic tests showed that acid pretreatments of Fe-ZSM-5 and Fe-beta had positive effects on the catalytic activities, as shown by the curves shifting to lower temperatures by about 10–15 and 30 °C, respectively. The activity improvements suggest that only a fraction of the extra Fe is activated when the degree of exchange increases.

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Graphical Abstract

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Effects of acid pretreatment on Fe-ZSM-5 and Fe-beta catalysts for N₂O decomposition

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For ZSM-5, acid leaching first occurs on the crystal surface and the crystal size is reduced; for beta, the amorphous material is first dissolved and some micropores are widened.

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酸预处理对于 Fe-ZSM-5 和 Fe-beta 分子筛催化消除 N₂O 的影响

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摘要: 作为六大温室气体之一, N₂O 的增温潜能是 CO₂ 的 310 倍, 甲烷的 21 倍, 目前仍然以 0.80 ppb/年的速度增长, 但是减排成本很低, 因此对 N₂O 的消除具有重要意义. 在工业中金属修饰的微孔分子筛因其优良的催化活性, 高水热稳定性, 低成本等优点而成为研究重点. 但是微孔分子筛狭窄的微孔孔道限制了金属前驱体的进入, 导致活性金属含量低, 进而限

制了活性的提高. 因此采用一定的改性手段减小分子筛颗粒尺寸, 缩短微孔孔道长度或者扩大微孔孔道来增加活性铁物种的含量进而提高分子筛催化活性.

本文选用商用的 ZSM-5 和 beta 分子筛作为母板分子筛, 按照 3 g : 50 mL 比例将分子筛母板与 1.0 mol/L 的 HNO_3 在室温下混合, 分别搅拌 0, 2 和 24 h, 然后采用液相离子交换法负载金属铁制备得到 Fe-ZSM-5 和 Fe-beta. 通过 X 射线衍射、 N_2 物理吸附脱附、电感耦合等离子原子发射光谱仪、扫描电镜、透射电镜、 NH_3 程序升温脱附及紫外漫反射 (UV-vis) 等手段对不同时间处理的分子筛的形貌、酸性和铁物种等物理化学性质进行表征. 对两种催化剂催化消除 N_2O 的反应性能进行了测试. 结果显示, 温和的酸处理下分子筛脱除了部分 Al, 其中, ZSM-5 分子筛的表现为由外向内逐层刻蚀, 颗粒尺寸减小, 孔道长度缩短, 但是由于 MFI 型分子筛较高的稳定性, 酸处理对分子筛孔道大小的改变并不明显, 而对于 beta 分子筛, 首先是其中大量无定形物种的去除, 然后对孔道进行修饰, 使之略微扩大, 但是对颗粒尺寸的影响不大.

ICP 结果显示, 商用 ZSM-5 和 beta 分子筛经过温和的酸处理改性后, Si/Al 比增大, 负载 Fe 的含量明显增加, 各催化剂催化消除 N_2O 的活性也出现了不同程度的提高. Fe-ZSM-5 和 Fe-beta 分子筛上 N_2O 完全转化温度分别向低温段移动了 10–15 和 30 °C. UV-vis 谱图显示, 分子筛中存在着不同种类的铁物种, 通过分峰计算发现, 孤立的 Fe^{3+} 铁离子和低聚态的 $\text{Fe}_x^{3+}\text{O}_y$ 均是催化活性铁物种, 其含量的增加部分也解释了活性提高的原因.

关键词: 金属铁修饰的分子筛; 氧化亚氮; 催化性能; 酸浸; 活性位

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