Iron-exchanged FAU zeolites: Preparation, characterization and catalytic properties for N₂O decomposition

Landong Li^a, Qun Shen^a, Jinjun Li^a, Zhengping Hao^{a,*}, Zhi Ping Xu^{b,**}, G.Q. Max Lu^b

^a Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, PR China

^b Australian Research Council (ARC) Centre of Excellence for Functional Nanomaterials, Australian Institute for Bioengineering and Nanotechnology and School of Engineering, The University of Queensland, Brisbane, QLD 4072, Australia

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ABSTRACT

New Fe-FAU zeolitic catalysts made from large channel zeolite matrix FAU by a simple wet ion exchange method show an excellent performance in N₂O catalytic decomposition. The ion exchange process was discussed in detail and the optimal conditions for wet ion exchange were proposed. The formation of various iron sites in Fe-FAU samples (isolated Fe ions, oligonuclear clusters and Fe₂O₃ nanoparticles) during preparation process was extensively investigated by means of UV–vis spectra, FTIR spectra of NO adsorption, TEM images, H₂-TPR and ²⁷Al MAS-NMR spectra. We have found that Fe(III)-FAU catalysts more effectively decompose N₂O with/out NO-assistance than other Fe-zeolite (such as Fe-MFI) catalysts prepared in the same way. Comprehensive understanding of the structure properties and the catalytic performance suggests that different iron sites in Fe-FAU make different contributions to N₂O thermal decomposition and that isolated/oligonuclear iron species contribute more due to their high accessibility towards N₂O. In addition, the high durability of Fe-FAU catalysts is proposed to account for the particular interactions between iron species and zeolite framework.

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1. Introduction

Incorporation of metal ions into a zeolite matrix brings about some special properties for heterogeneous catalysis. Iron zeolites, as an example, show high catalytic activity in many reactions, such as oxidation of benzene to phenol with nitrous oxide [1,2], selective catalytic reduction of nitrogen oxides [3–5], and direct decomposition of nitrous oxide [6–10]. As far as iron zeolite catalysts are concerned, the nature and distribution of active iron species are the key issue relevant to the catalytic activity. Some researchers have identified the iron species formed in the zeolites [11], however, their relationship with and contribution to the activity are not well demonstrated. It is well known that the formation of iron species in the zeolite matrix is directly related to the preparation procedure and conditions; thus in this research, we aim to illustrate the effects of preparation parameters on the formation of iron species in zeolite and to understand how their distribution is related to their catalytic performance.

In general, iron-zeolite catalysts were prepared by wet ion exchange with ferrous salt [12] or ferric salt [13], solid-state ion

exchange [14], chemical vapor decomposition (CVD) of FeCl₃ [15], and isomorphous substitution followed by extraction at elevated temperatures [16]. Wet ion exchange is simpler and more feasible for industrial applications as it involves fewer steps and the preparation parameters are more easily controlled. To evenly distribute the iron species into the channel by this method, one should assure that the channel dimension of the host zeolite is large enough for the hydrated/hydrolyzed iron ions to freely diffuse, so that FAU with a large channel dimension ([111] 0.74 × 0.74 nm) was chosen as the host to simplify the preparation parameters affecting the iron species formation in this research. In fact, Fe(III) ion exchanged FAU zeolites were examined as catalysts for several other reactions [17,18], while they did not show a good apparent catalytic activity for the N₂O decomposition [19]. However, our recent results indicated that Fe(III)-USY zeolite catalyst is very active in the direct N₂O decomposition, even better than any other Fe-zeolite catalysts [20]; we attributed this activity to the high and well dispersed Fe(III) loading in the channels. For comparison, a few other kinds of Fe(II) and Fe(III) zeolites were made in the same way. In brief, we have identified iron species formed in the zeolites by comprehensively analyzing the information revealed by the UV–vis spectra, the FTIR spectra of adsorbed probe molecule NO, the ²⁷Al NMR spectra and the TEM images. Our analysis relating the iron species and catalytic performance does not show that either the isolated Fe(III) species

* Corresponding author. Tel.: +86 10 62923564; fax: +86 10 62923564.

** Corresponding author. Tel.: +61 7 33463809; fax: +61 7 33363973.

E-mail addresses: zpinghao@rcees.ac.cn (Z. Hao), gordonxu@uq.edu.au (Z.P. Xu).

or the oligonuclear Fe(III)_xO_y cluster is more active for N₂O decomposition, but suggests that not all isolated/oligonuclear Fe(III) sites make the same (or similar) contributions to the activity, since the site accessibility is an important factor. Fe(III)-USY catalyst thus shows a potential in the end-of-pipe treatment of N₂O emission from a nitric acid plant both in the catalytic activity and the durability.

2. Experimental

2.1. Catalyst preparation

Commercial H-ZSM-5 (Si/Al = 11.8), Na-Y (Si/Al = 3.8), H-Y (Si/Al = 5.4) and ultra-stable Y (USY, Si/Al = 11.6) were purchased from Sinopec Co. and directly used as parent zeolites for ion exchange (Table 1). In general, various iron-containing zeolite catalysts were prepared by wet ion exchange using ferric salt or ferrous salt at room temperature for 48 h and subsequent calcination at 873 K for 4 h. For example, 2.0 g of the parent zeolite was exchanged with 200 ml 0.05 M FeCl₃ (pH ~1.8) for 48 h under vigorous stirring to load Fe(III). To load nominal Fe(II), we exchanged 2.0 g of the parent zeolite with 200 ml 0.05 M FeSO₄ (pH ~3.0) for 48 h under vigorous stirring in the flowing N₂ stream. The as-exchanged samples were then filtered, thoroughly washed, dried at 353 K and calcined at 873 K for 4 h in the air. In particular, as-obtained Fe(II)-USY and Fe(III)-USY were further treated with 0.01 M HCl at room temperature for 6 h, followed by filtration, through washing, drying at 353 K and calcination at 873 K for 4 h in the air (named as Fe(II)-USY-A and Fe(III)-USY-A, respectively). These iron zeolite catalysts, as denoted in Table 1, were then crushed and sized in 20–40 mesh, and kept in a desiccator for subsequent characterization and N₂O decomposition tests.

2.2. Catalyst characterization

The Si, Al and Fe contents in these iron-containing zeolites were analyzed by ICP-OES using an Optima 2000 spectrometer, and their specific surface area was determined through low temperature N₂ adsorption/desorption isotherms collected on a Quantachrome NOVA-1200 gas absorption analyzer. The X-ray diffraction (XRD) patterns of parent and iron-exchanging zeolites were recorded on a Rigaku powder diffractometer (D/MAX-RB) using Cu-K_α radiation ($\lambda = 0.15418$ nm) at a scanning rate of 4 °/min in $2\theta = 5$ –35°.

UV–vis measurements were carried out on a Hitachi UV-3000 spectrometer, and diffuse reflectance (DR) spectra were recorded in the air against BaSO₄ in the region of 190–800 nm at a resolution of 1 nm. The ²⁷Al MAS-NMR spectra were recorded on a Bruker DRX400 spectrometer (9.4 T). The samples were spun in the rotors. The r.f. pulse with the length of 0.3 μs was applied and the MAS frequency was fixed at 20 kHz. The spectrum was acquired after

2000 accumulations with the acquisition time of 0.1 s. A time interval of 1 s was selected between two successive accumulations to avoid saturation effects. Saturated Al(NO₃)₃ solution was used as the ²⁷Al chemical shift reference.

Transmission electron microscopy (TEM) images of the Fe-containing zeolite catalysts were acquired on a JEOL 3010 transmission electron microscope at an acceleration voltage of 300 kV. A few drops of alcohol suspension containing the catalyst sample were placed on a carbon-coated copper grid, followed by evaporation at ambient temperature.

The H₂ temperature-programmed reduction (TPR) of as-prepared catalysts was carried out in a microreactor using 5 vol% H₂/He at a heating rate of 5 K/min from 323 to 1173 K. Prior to reduction, the catalyst (50 mg) was treated in He at 873 K for 2 h. During the heating from 323 to 1173 K, the H₂ consumption was measured online with a gas chromatograph equipped with a TCD.

FTIR spectra of NO adsorption on these Fe-zeolite catalysts were collected on the spectrometer (Bruker Tensor 27) with 128 scans at a resolution of 4 cm^{−1}. A self-supporting pellet (about 50 mg) made of the catalyst sample was placed in the IR flow cell and the reference spectrum (i.e. background spectrum) was taken at room temperature (298 K). After the He stream was switched to a gas mixture containing 1% NO in He at a total flow rate of 30 ml/min, a series of time-dependent FTIR spectra of NO adsorption on the zeolite catalyst were sequentially recorded.

2.3. Activity measurements

N₂O decomposition experiments were performed in a fixed-bed flow microreactor at ambient pressure. In each run, 0.1 g catalyst (sieve fraction in 20–40 mesh) was placed in a quartz reactor (4 mm i.d.) and pretreated in He at 873 K for 1 h. After the reactor was cooled to 573 K, the reactant gas mixture (1500 ppm N₂O, with/out 5% O₂ or 200 ppm NO; He balance) was fed to the reactor. The total flow rate of the mixed gases was set at 60 ml/min, corresponding to GHSV = 30,000 h^{−1}. The outlet gas composition was analyzed online using a gas chromatograph (Agilent 6820 series) equipped with a TCD detector and two serial columns (a Porapak Q column served for the separation of N₂O and N₂/O₂, and a molecular sieve 5A column for the separation of N₂ and O₂). The steady-state N₂O conversion at a temperature ascending from 573 to 873 K at 25 K intervals was calculated based on the GC peak area. For the durability test of Fe(III)-USY sample, we chose a constant temperature (723 or 748 K) and monitored the conversion of N₂O for 100 h in a simulated gas mixture (1500 ppm N₂O, 5% O₂, 1% H₂O and 200 ppm NO; He balance).

3. Results and discussion

3.1. Solution behavior of ferric and ferrous ions

For hydrated ferric ions, the following stepwise hydrolyses occur in aqueous solution, accompanied by the condensation reaction [21,22]:

At pH ~1.8, the second hydrolysis reaction can be ignored. The main ferric ion species are Fe(H₂O)₆³⁺ (60%), Fe(H₂O)₅(OH)²⁺ (25%)

Table 1
Preparation and physicochemical properties of iron-zeolites

Sample	Fe source	Si/Al ^a	Fe/Al ^b	Fe (wt%)	S _{BET} (m ² /g)
Fe(II)-ZSM-5	FeSO ₄	12.4 (11.8)	0.24	1.81	418.7
Fe(III)-ZSM-5	FeCl ₃	12.1 (11.8)	0.04	0.30	422.8
Fe(II)-USY	FeSO ₄	11.9 (11.6)	0.36	2.79	534.3
Fe(II)-USY-A	Acid-treated	15.1 (11.9)	0.32	1.96	541.4
Fe(III)-USY	FeCl ₃	12.3 (11.6)	0.44	3.38	527.8
Fe(III)-USY-A	Acid-treated	16.8 (12.3)	0.37	2.06	535.8
Fe(III)-NaY	FeCl ₃	5.3 (3.8)	0.35	6.16	456.3
Fe(III)-HY	FeCl ₃	6.7 (5.4)	0.39	5.43	562.6

^a The number in parentheses is the Si/Al atomic ratio before iron exchange or acid treatment.

^b The Fe/Al atomic ratio should be 0.33 with ferric ions completely exchanging, while it should be 0.50 with ferrous ions fully exchanging.

and $\text{Fe}(\text{H}_2\text{O})_5(\text{O})\text{Fe}(\text{H}_2\text{O})_5^{4+}$ (15% Fe) if the total $[\text{Fe}^{3+}] = 0.05$ M. The Fe^{3+} –O distance is reported to be ca. 0.20 nm [23] and van der Waals' radius of water (or oxygen) is known to be 0.14 nm. Thus, the diameter of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ ion is estimated as ca. 0.68 nm and $\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ has almost the same diameter. The volume mean diameter of $\text{Fe}(\text{H}_2\text{O})_5(\text{O})\text{Fe}(\text{H}_2\text{O})_5^{4+}$ is calculated to be 0.90 nm. For ferrous ions, any hydrolysis reaction can be ignored under acid conditions (pH 3.0):

Thus the only aqueous iron species is the hydrated ferrous ion ($\text{Fe}(\text{H}_2\text{O})_6^{2+}$). As the Fe^{2+} –O distance is ca. 0.21 nm [24], the diameter of the $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ ion is thus 0.70 nm.

3.2. Factors affecting the Fe loading in zeolites

As listed in Table 1, the Si/Al atomic ratio in each Fe-zeolite is increased to some degree in comparison with its parent zeolite, due to dealumination (by 3–30%) from the framework at the acidic exchanging medium. The increase of the Si/Al ratio in the acid-treated USY samples (highlighted in bold in Table 1) suggests a further dealumination (by 20–25%) from the zeolite framework.

Theoretically, complete ion exchange in zeolites can give the Fe/Al ratio up to 0.50 in Fe(II)-zeolites and 0.33 in Fe(III)-zeolites. Table 1 shows that the Fe/Al ratio in Fe(II)-zeolites is 0.24–0.36, 50–70% of its maximum exchange amount. In contrast, this ratio in Fe(III)-zeolites is 0.35–0.44 (except for Fe(III)-ZSM-5), a bit more than the expected value (0.33). Note that the iron loading in USY is much higher than that in ZSM-5 for both Fe^{2+} and Fe^{3+} exchange (Table 1), probably due to the larger channel size in USY, as will be addressed shortly. In addition, different parent zeolites with the same faujasite (FAU) structure (Na-Y, H-Y and USY) were exchanged with Fe^{3+} where a similar Fe/Al ratio (0.35–0.44) was achieved. Therefore, the Fe loading is very much relevant to the Fe source and to the zeolite types.

In our opinion, the channel size of the zeolites and the iron ion species available for exchange play key roles in determining the Fe loading in zeolite. In the case of Fe^{2+} exchange, hydrated ferrous ion ($\text{Fe}(\text{H}_2\text{O})_6^{2+}$) is the only ion species in aqueous solution at room temperature and pH ~ 3 , having the size of 0.70 nm. Therefore, $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ can readily diffuse into USY faujasite with the channel size of $[1\ 1\ 1]\ 0.74 \times 0.74$ nm, and thus achieve a high ion exchange extent (Fe/Al = 0.36 for Fe(II)-USY). This is still much smaller than the full exchange (Fe/Al = 0.50), as also reported elsewhere [9,25], very likely due to oxidation of Fe(II) to Fe(III) during the exchange. However, ZSM-5 has the channel size of $[1\ 0\ 0]\ 0.51 \times 0.55$ nm $\leftrightarrow$ $[0\ 1\ 0]\ 0.53 \times 0.56$ nm, so it is difficult for $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ to diffuse into all the ZSM-5 channels, leading to a lower exchange degree (Fe/Al = 0.24 for Fe(II)-ZSM-5).

In comparison, the main ferric ion species are $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ (60%), $\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ (25%) and $\text{Fe}(\text{H}_2\text{O})_5(\text{O})\text{Fe}(\text{H}_2\text{O})_5^{4+}$ (15% Fe) in aqueous solution at pH ~ 1.8 and room temperature (total $[\text{Fe}] = 0.05$ M), with sizes being 0.68, 0.68 and 0.90 nm, respectively. Obviously, $\text{Fe}(\text{H}_2\text{O})_5(\text{O})\text{Fe}(\text{H}_2\text{O})_5^{4+}$ is much larger than the channel size of USY faujasite ($[1\ 1\ 1]\ 0.74 \times 0.74$ nm). Therefore it could be very difficult for this hydrolyzed ion to diffuse into the interior zeolite channel and join the proton exchange. $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and $\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ are smaller than the channel size of USY faujasite ($[1\ 1\ 1]\ 0.74 \times 0.74$ nm) and can readily diffuse into the channels to exchange. We believe that $\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ ion is more preferred, because the exchange of high positively charged ions $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ in silicon-rich zeolites is more difficult. Therefore, maximizing the $\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ concentration and minimizing the

Fig. 1. Distribution of Fe species and pH values as a function of Fe total concentration.

concentration of $\text{Fe}(\text{H}_2\text{O})_5(\text{O})\text{Fe}(\text{H}_2\text{O})_5^{4+}$ can lead to a higher Fe exchange degree. As shown in Fig. 1, the maximum concentration difference between $\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ and $\text{Fe}(\text{H}_2\text{O})_5(\text{O})\text{Fe}(\text{H}_2\text{O})_5^{4+}$ seems to occur at total $[\text{Fe}^{3+}] = 0.05$ –0.4 M, while $\text{Fe}(\text{H}_2\text{O})_5(\text{O})\text{Fe}(\text{H}_2\text{O})_5^{4+}$ starts to appear at $[\text{Fe}^{3+}] = 0.01$ M and exists with a considerable amount at $[\text{Fe}^{3+}] = 0.1$ M. So, considering the stability of the parent USY zeolite under acid conditions (pH > 1.5), we chose 0.05 M FeCl_3 solution with pH ~ 1.8 in this research for exchange, and achieved a higher Fe loading (Fe/Al = 0.44) in Fe(III)-USY. However, the steric hindrance may be the main reason that Fe(III)-ZSM-5 can only load small amounts of Fe(III) (Fe/Al = 0.04) because both $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and $\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ ions (0.68 nm) are much larger than ZSM-5 channel size ($[1\ 0\ 0]\ 0.51 \times 0.55$ nm $\leftrightarrow$ $[0\ 1\ 0]\ 0.53 \times 0.56$ nm).

In ZSM-5 we find much higher Fe(II) loading than Fe(III) loading (Fe/Al = 0.24 in Fe(II)-ZSM-5 vs. 0.04 in Fe(III)-ZSM-5). This result indicates that something happens to the hydrated $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ during the exchange. One possible process is dissociation of Fe^{2+} – H_2O ligand bonds, so $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ loses some water and the size is reduced, which thus promotes the ion exchange. The dissociation may be further driven by the increase of electrostatic interactions of smaller ferrous ions (less hydrated) with the zeolite matrix at the zeolite channel mouth [26]. In contrast, it is unlikely for $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and $\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ to break the Fe^{3+} – H_2O bond to lose water and reduce the ion size for exchange, because the hydrated enthalpy of ferric ions (ca. 4500 kJ mol $^{-1}$) is much greater than that of ferrous ions (ca. 2000 kJ mol $^{-1}$) [27] at room temperature. Therefore, in order for researchers to make fully-exchanged Fe(III)-ZSM-5, heating is required to facilitate the Fe^{3+} – H_2O bond dissociation, as reported by Melián-Cabrera et al. [28]. However, heating may promote the deep hydrolysis of ferric ions and may result in formation of the iron oxide on the outer surface of zeolite to block some channels.

As shown in Fig. 2, the framework of parent zeolites is well preserved after ion exchange and subsequent calcination. XRD patterns of Fe(II)-ZSM-5 and Fe(III)-ZSM-5 are the same, with the diffraction peaks being characteristic of the MFI structure [29]. Similarly, the XRD patterns of all other Fe-zeolites show typical diffraction peaks corresponding to the characteristic FAU structure [29] except for Fe(III)-NaY, whose XRD pattern has much weaker characteristic diffraction peaks at $2\theta > 10^\circ$. This difference may indicate some deterioration of FAU structure after the ion exchange and subsequent calcination, similar to that happening during

Fig. 2. XRD patterns of as-prepared iron-zeolites.

(NH_4) $_2\text{SO}_4$ ion exchange of Na-Y [30]. In addition, no obvious diffraction peaks corresponding to crystallized Fe_xO_y can be observed at the Fe loading up to 5–6 wt%, suggesting the good dispersion of iron species on the internal/external surface and the limited segregation of Fe_xO_y nanoparticles.

3.3. Fe species formed in zeolite

3.3.1. UV–vis DR spectra of Fe-zeolites

The nature and distribution of iron species in these Fe-zeolites can be identified by various techniques. One commonly used one is UV–vis DR spectroscopy. As shown in Fig. 3, Fe-zeolites exhibit strong absorbance in 200–800 nm, revealing the existence of various ferric ion species in these Fe-zeolite samples. After suitable spectral deconvolution for ion-exchanged Fe(III)-USY (Fig. 3A), several characteristic UV–vis absorption bands can be extracted and attributed to specific ferric ion species. In general, two bands at 215 and 285 nm are assigned to isolated Fe(III) in tetrahedral and octahedral coordination [31,32], respectively. These two bands are also assigned by Pirngruber et al. [33] to ferric ion dimers considering that the antiferromagnetic coupling is weak. Two bands located between 300 and 400 nm (at 335 and 385 nm) are ascribed to oligonuclear $\text{Fe(III)}_x\text{O}_y$ clusters in zeolite internal/external surfaces [16], and another two bands at above 400 nm (at 460 and 550 nm) are attributed to Fe_2O_3 nanoparticles (~ 1 nm) at the external surface of the zeolite crystal [34].

Spectral comparison of three Fe(III)-USY (exchanged, calcined and acid-treated, Fig. 3A–C and Table 2) reveals that (i) the two

bands corresponding to isolated Fe(III) are strongest in all three cases, showing high population of isolated Fe(III) in the zeolite; (ii) after calcination (Fig. 3B), two bands corresponding to the oligonuclear $\text{Fe(III)}_x\text{O}_y$ clusters become a bit stronger, while those bands to Fe_2O_3 nanoparticles are nearly unchanged, indicating slightly preferential formation of oligonuclear $\text{Fe(III)}_x\text{O}_y$ clusters upon calcination; (iii) acid treatment of calcined Fe(III)-USY dislodges Fe_2O_3 nanoparticles as well as isolated Fe(III), $\text{Fe(III)}_x\text{O}_y$ clusters and Al species, as clearly shown by the increase of Si/Al ratio, the lower Fe loading (Table 1) and the reduction of each iron species (Table 2).

On the other hand, the UV–vis spectra of Fe(II)-USY after ion exchange (dried at 353 K overnight) and calcination (873 K, 4 h) show the existence of a considerable amount of isolated Fe(III), oligonuclear $\text{Fe(III)}_x\text{O}_y$ clusters and Fe_2O_3 nanoparticles. The oxidation of Fe(II) to Fe(III) presumably occurs after exchange, perhaps during drying and/or calcination. In particular, calcination gives many more oligonuclear $\text{Fe(III)}_x\text{O}_y$ clusters and Fe_2O_3 nanoparticles (Fig. 3E and Table 2). This is in sharp contrast with the fact that Fe(III)-USY exhibits the similar UV–vis spectra before and after calcination, which reflects the higher thermal stability of iron species in Fe(III)-USY. In addition, calcined Fe(III)-HY and Fe(III)-NaY samples (Fig. 3G–H and Table 2) were found to contain a considerable amount of isolated Fe(III) ions, oligonuclear $\text{Fe(III)}_x\text{O}_y$ clusters and Fe_2O_3 nanoparticles, while calcined Fe(III)-NaY contains more Fe_2O_3 nanoparticles.

3.3.2. TEM images and H_2 TPR of Fe-zeolites

In line with the results of UV–vis spectra, the TEM image (Fig. 4A) has indicated that iron oxides/clusters in ion-exchanged Fe(III)-USY are so very small (<1 nm) that they are hard to observe. Such iron oxides/clusters probably come from the aggregation and dehydration of iron-containing species on the zeolite surface during the drying process. After calcination, larger Fe_2O_3 nanoparticles (1–4 nm) can be observed (Fig. 4B), suggesting the aggregation of small iron oxides/clusters and isolated Fe(III) species upon calcination. However, such an aggregation of small iron oxides from <1 to 1–4 nm does not result in any obvious change in the intensity of corresponding UV–vis bands, meaning that the formed Fe_2O_3 nanoparticles (1–4 nm) contribute relatively little weight. After acid treatment (Fe(III)-USY-A), a majority of larger Fe_2O_3 nanoparticles (1–4 nm) is dislodged, with fewer small iron oxides left (Fig. 4C). The black spots in the TEM image of calcined Fe(III)-HY (Fig. 4D) are similar to those of calcined Fe(III)-USY both in darkness and spot size. However, the TEM image of calcined Fe(III)-NaY shows much larger Fe_2O_3 nanoparticles with much darker background, probably due to more Fe_2O_3 nanoparticles and to some deterioration of the FAU structure.

The H_2 -TPR profiles of Fe-zeolites reveal the existence of reducible Fe_2O_3 nanoparticles in some cases. As shown in Fig. 5, H_2 consumption (e.g. Fe reduction) starts at 400–450 K and continues to over 1100 K. Previous investigations [3,13,35,36] demonstrate

Table 2
Percentage of subband areas (I_1 at $\lambda < 300$ nm, I_2 at $300 < \lambda < 400$ nm, and I_3 at $\lambda > 400$ nm) derived by deconvoluting UV–vis spectra and corresponding Fe species loading

Samples	I_1^a (%)	I_2^a (%)	I_3^a (%)	Isolated ^b (%)	Oligonuclear ^b (%)	Nanoparticles ^b (%)
Fe(III)-USY ion exchanged	54.2	34.1	11.7	1.83	1.15	0.39
Fe(III)-USY	50.4	38.3	11.4	1.70	1.29	0.39
Fe(III)-USY-A	57.9	33.8	8.3	1.19	0.69	0.17
Fe(II)-USY ion exchanged	59.3	31.2	9.5	1.65	0.87	0.27
Fe(II)-USY	44.3	35.0	20.7	1.23	0.98	0.58
Fe(II)-USY-A	53.0	35.5	11.5	1.04	0.71	0.23
Fe(III)-HY	51.9	38.4	9.7	2.82	2.08	0.53
Fe(III)-NaY	51.8	35.1	13.1	3.19	2.16	0.81

^a Calculated from the data in Fig. 3.

^b In wt%.

Fig. 3. UV-vis spectra of Fe(III)-USY (A–C), Fe(II)-USY (D–F), Fe(III)-HY (G) and Fe(III)-NaY (H).

Fig. 4. TEM images of ion-exchanged Fe(III)-USY (A), calcined Fe(III)-USY (B), acid-treated Fe(III)-USY (C), calcined Fe(III)-HY (D) and calcined Fe(III)-NaY (E).

that (i) H_2 consumption up to 750 K corresponds to reduction of Fe(III) to Fe(II) (isolated, oligonuclear and nanoparticle), (ii) reaction in 750–1000 K is due to reduction of FeO (from nanoparticles) to Fe^0 , and (iii) H_2 consumption over 1000 K is due to reduction of Fe(II) to Fe^0 in oligonuclear/isolated form, with collapse of the zeolite framework. Compared with acid-treated Fe(III)-USY-A, the calcined Fe(III)-USY has an extra reduction bump at ~ 900 K. This means that the latter contains more reducible Fe_2O_3 nanoparticles, in agreement with observations from UV-vis spectra and TEM images. In particular, the H_2 -TPR profiles of Fe(II)-

USY and Fe(III)-NaY show a broad band in 800–1000 K, indicating the existence of much more reducible Fe_2O_3 nanoparticles, in line with the UV-vis and TEM observations.

3.3.3. FTIR spectra of NO adsorbed on Fe-zeolites

Fig. 6 presents the time-dependent FTIR spectra of NO adsorbed on some iron-zeolites at room temperature. In the normal nitrosyl region (1700 – 1970 cm^{-1}) [37], two very weak bands at 1910 and 1850 cm^{-1} are observed, without significant change with time in intensity for the ion-exchanged Fe(III)-USY (bottom lines, Fig. 6A).

Fig. 5. H_2 -TPR profiles of selected Fe-zeolite samples.

The band at 1850 cm^{-1} is attributed to the mononitrosyl group while that at 1910 cm^{-1} is attributed to dinitrosyl group on isolated iron sites in zeolites [38–40]. Some other weak peaks at 1550 , 1425 , 1360 , 1230 , 1130 and 1100 cm^{-1} are due to nitrites/nitrates oxidized from NO and stored on the surface [37], which slightly increase in intensity with the adsorption time. The strongest band at 1715 cm^{-1} , obviously intensifying with the adsorption time, in our opinion, could be assigned to the mononitrosyl group on dinuclear oxygen-bridged Fe ions (discussed in Section 3.3.5), while a similar band at 1700 – 1750 cm^{-1} was assigned to mononitrosyl on Fe(II) clusters in Fe/ZrO₂ [41] and Fe/SnO₂ [42], and on Feⁿ⁺ clusters in Fe/Al₂O₃ and Fe/TiO₂ [43]. Surprisingly, such an intense band almost completely disappears on calcined Fe(III)-USY, indicating the disappearance of the dinuclear oxygen bridged Fe ions. Note that peaks at 1550 , 1230 and 1130 cm^{-1} due to nitrites/nitrates become more intense with the adsorption time. This shows that adsorption of NO on calcined Fe(III)-USY is mainly a process involving oxidation of NO and storage as nitrites/nitrates. More surprisingly, acid treatment/calcination brings back the dinuclear oxygen-bridged Fe ions, as indicated by the reappearance of the intense band at 1715 cm^{-1} (top lines, Fig. 6A).

In the case of ion-exchanged Fe(II)-USY, NO is adsorbed in some other way. As shown in Fig. 6B, although weak bands at 1910 , 1850 , and 1765 cm^{-1} (corresponding to mono- and di-nitrosyl groups) are also observed, the strongest bands are located at 1360 and 1400 cm^{-1} , then shift to 1340 and 1425 cm^{-1} over the calcined Fe(II)-USY, corresponding to various nitrates [37]. The formation of nitrates is probably a result of NO oxidation over Fe(II,III) mixed oxide clusters/nanoparticles. We believe that the exchanged Fe(II) ions are partly oxidized to Fe(III) ions in isolated, cluster, and particle form during drying and calcination. After acid treatment, the band at 1715 cm^{-1} becomes obvious, indicating the formation of the dinuclear oxygen bridged Fe ions, as in the case of acid-treated Fe(III)-USY.

The FTIR spectra of NO adsorbed on Fe(III)-HY (Fig. 6C) indicate that NO adsorbs over ion-exchanged and calcined Fe(III)-HY in a way similar to that over Fe(III)-USY. The predominant adsorption occurs over the dinuclear oxygen-bridged Fe ions in the Fe(III)-exchanged sample while such species disappear after calcination.

In the case of Fe(III)-NaY (Fig. 6D), the exchanged and calcined samples show the similar NO adsorption behavior, i.e. adsorption at isolated Fe(III) sites (bands at 1910 , 1850 , 1765 and 1715 cm^{-1}) [38–40], and formation of nitrates (broad peak at 1425 cm^{-1}). However, this behavior is much different from that over Fe(III)-USY and Fe(III)-HY, probably related to deterioration of the FAU structure, as shown by the XRD and TEM images.

3.3.4. ^{27}Al MAS-NMR spectra of Fe-zeolites

The ^{27}Al MAS-NMR spectra in Fig. 7 provide useful information regarding the transformation of tetrahedral and octahedral Al species during various treatments of Fe(III)-USY sample, and show the formation of various forms of iron species as well. As seen in the spectrum for the parent H-USY, there are two ^{27}Al resonances, a strong one at 55 ppm and a weak one at -5 ppm , corresponding to two kinds of Al species in USY zeolite. In general, the resonance at 55 ppm is attributed to tetrahedrally coordinated Al (Al^{IV}) in the zeolite lattice [44] and that at -5 to 0 ppm is due to framework-connected octahedral Al species (Al^{VI}) [45]. After wet ion exchange/drying, the resonance peak at 55 ppm is narrower, while the weak peak at -5 ppm corresponding to Al^{VI} does not change. After calcination, however, the peak at -5 ppm relevant to Al^{VI} species becomes much stronger, indicating the transform of lattice Al^{IV} to extra-lattice Al^{VI} during calcination. Further acid treatment of calcined Fe(III)-USY weakens the responses both at 55 and -5 ppm , with the latter weakened much more, showing that more extra-lattice Al^{VI} species are dislodged.

3.3.5. Transformation of iron species in Fe(III)-USY

Based on the above observations, we draw a schematic diagram (Fig. 8) to outline the formation of various iron species and the transformation of Al species in sample Fe(III)-USY during exchange/drying, calcination and acid treatment. After ion exchange (Step 1), most protons are substituted with iron species, to form isolated Fe(III) ions (species **a**, normally with some coordinated H₂O but not shown here), dinuclear oxygen-bridged Fe ions (species **b**, coordinated H₂O or OH not shown), oligonuclear Fe(III)_xO_y clusters (species **c**) and Fe₂O₃ nanoparticles (not shown in the figure). The existence of dinuclear oxygen-bridged Fe species has been very recently reported by Nam and co-workers for the solid-exchange Fe-ZSM-5 catalysts with Fe/Al > 0.2 [46]. In this process, the iron species replace almost all protons and are bound to the lattice. Meanwhile, the lattice Al^{IV} species remain unchanged, as suggested by the ^{27}Al NMR spectrum.

The calcination at 873 K (Step 2), in our opinion, brings about a few new species, such as isolated Al^{VI}-O-Fe(III) (not shown here), Al^{IV}-O-Fe(III)_mO_n complex (species **d**), and Al^{VI}-O-Fe(III)_pO_q complex (species **e**). As the dinuclear oxygen bridged Fe ions are now transformed to larger oligonuclear Fe(III)_mO_n clusters (from species **b** Al^{IV}-O-Fe(III)OFe(III) to species **d** Al^{IV}-O-Fe(III)_mO_n), thus calcined Fe(III)-USY does not show the characteristic NO adsorption band at 1715 cm^{-1} . In addition, the transformation of tetrahedral Al^{IV} to octahedral Al^{VI} is also in line with the intense ^{27}Al NMR resonance peak at -5 ppm .

After acid treatment at room temperature and calcination at 873 K (Step 3), some Al^{VI}, isolated Fe(III), Fe(III)_pO_q clusters and most Fe₂O₃ nanoparticles are removed from the zeolite surface by dissolution. The leaching of Fe and Al from the zeolite is supported by element analysis (Table 1). Based on UV-vis spectra (Fig. 3), TEM images (Fig. 4) and ^{27}Al NMR spectra (Fig. 7), we presume that the acid treatment induces a series of reactions, such as dissolution of Al^{VI} and removal of oligonuclear Fe(III)_pO_q (from species **e** to **f**). Another possible reaction is the re-deposition of leached Fe³⁺ ions to form species **a** and **b** as there is a large enough amount of Fe³⁺ in the solution. Therefore, the dinuclear oxygen-bridged Fe ions

Fig. 6. FTIR spectra of NO adsorption on Fe(III)-USY (A), Fe(II)-USY (B), Fe(III)-HY (C) and Fe(III)-NaY (D) at 298 K. From light to dark: NO interacted with sample for 5, 10, 20 and 30 min.

(species **b**) are re-generated and can adsorb NO with the characteristic IR absorption at 1715 cm^{-1} (Fig. 6A).

3.4. Catalytic performances of Fe-zeolites

The temperature dependence of steady-state N_2O decomposition over Fe-USY and Fe-ZSM-5 catalysts is shown in Fig. 9A. Fe(III)-USY exhibits the highest N_2O decomposition activity while Fe(III)-ZSM-5 gives the lowest activity, which can be first ascribed to the difference in Fe(III) loading. As listed in Table 1, Fe(III)-USY has much higher Fe(III) loading than in Fe(III)-ZSM-5 (3.38 vs. 0.30 wt%) and thus possesses proportionally more active Fe species. Due to the same reason, both Fe(II)-USY (2.79 wt% Fe) and Fe(II)-ZSM-5 (1.81 wt% Fe) have activity lower than that of Fe(III)-USY but higher than that of Fe(III)-ZSM-5. The figure also shows that Fe(III)-USY catalyst starts N_2O decomposition at ca. 600 K, and the 50% and 100% N_2O conversion occurs at 670 and 750 K, respectively. This activity for N_2O decomposition is comparable with or even better than the best iron-zeolite catalysts

reported elsewhere, e.g. Fe-Ferrierite [13,28]. Compared with ferrierite, much cheaper USY appears to be a more economical zeolite-hosting iron species for N_2O decomposition.

The Fe loading is not the only factor that determines catalytic activity for N_2O decomposition. As shown in Fig. 9B, Fe(III)-USY and Fe(III)-USY-A perform very similarly in term of N_2O conversion at the same temperature. However, their Fe loadings are quite different, being 3.38 wt% in Fe(III)-USY and 2.06 wt% in the acid-treated Fe(III)-USY-A. Similarly, Fe(III)-HY has 5.43 wt% Fe(III), yet it only shows an activity a bit higher than Fe(III)-USY and Fe(III)-USY-A. To the contrary, Fe(III)-NaY has the highest Fe(III) loading (6.16 wt%), but exhibits a much lower activity (Fig. 8B). Similar finding has been reported by Segawa and co-workers [47] that low Fe loading in Fe-MFI exhibited a rather high N_2O conversion. These observations suggest that the active Fe species is the other important factor that determines the catalytic activity for N_2O decomposition.

It has been proposed that both isolated Fe(III) species and oligonuclear $\text{Fe(III)}_x\text{O}_y$ cluster are active, but the latter is more

Fig. 7. ^{27}Al MAS-NMR spectra of parent H-USY, ion exchanged Fe(III)-USY, calcined Fe(III)-USY, acid-treated Fe(III)-USY-t and Fe(III)-USY used for 100 h.

active for N_2O decomposition [6,10,48]. Based on the current research, however, it is difficult to judge which one is more active. We noted that Fe(III)-USY, Fe(III)-USY-A and Fe(III)-HY have very similar activity values, but the fractionated isolated and oligonuclear Fe(III) species vary in loading from 1.13 to 2.82 wt% and from 0.69 to 2.08 wt% (Table 2), respectively. Thus we cannot simply say that isolated or oligonuclear Fe(III) sites are more active than the other, but we could infer that only a small fraction of isolated or oligonuclear Fe(III) sites are active for N_2O decomposition.

The site accessibility is probably the other important factor that determines the activity contribution of isolated or oligonuclear Fe(III) sites. For example, the iron sites near the channel mouth are more easily accessed by N_2O than those sitting in sodalite cavities, which have highly hindered access to the N_2O molecule and thus

show a higher apparent activity. The accessibility is also affected by the presence of Fe_2O_3 nanoparticles. Once Fe_2O_3 nanoparticles block the channel mouth, the channel is not accessible to N_2O and does not contribute to the N_2O decomposition. This may be the reason why Fe(III)-USY-A has an activity value similar to those of Fe(III)-USY and Fe(III)-HY. The latter two have much higher isolated/oligonuclear Fe(III) sites, but they also contain more Fe_2O_3 nanoparticles (TEM in Fig. 4 and Table 2), so their total accessible active Fe(III) sites may be similar to those of Fe(III)-USY-A. Similarly, Fe(II)-USY contains a similar amount of isolated/oligonuclear Fe(III) sites, but the fact that its Fe_2O_3 nanoparticle amount (Table 2) is higher than that of Fe(III)-USY-A (0.58 vs. 0.17 wt%) causes its apparent activity value to be lower than that of Fe(III)-USY-A (Fig. 9). An even worse case is Fe(III)-NaY. Fe(III)-NaY contains a quite high amount of isolated/oligonuclear Fe(III) sites, but its larger amount of Fe_2O_3 nanoparticles blocks many channels, leading to a much lower activity.

It is worth mentioning that the larger channel dimension can enhance the accessibility of iron sites sitting in zeolite channels, so FAU ([1 1 1] $0.74 \times 0.74 \text{ nm}$) appears to be a better host of active iron species than MFI ([1 0 0] $0.51 \times 0.55 \text{ nm} \leftrightarrow [0 1 0]$ $0.53 \times 0.56 \text{ nm}$) and a better catalyst for N_2O decomposition.

3.5. Durability of Fe(III)-USY zeolite catalyst

The high catalytic activity of Fe(III)-USY for N_2O decomposition motivates us to investigate the performance under simulated situations, such as with O_2 (5%) and NO (150–200 ppm) in the exhaust stream, in order to clarify their effects on N_2O decomposition. As seen in Fig. 10, the presence of 5% O_2 in the reaction system shows some negative effect on N_2O decomposition. For example, N_2O conversion was decreased by 5–10% at 650–725 K. The inhibition effect of O_2 on N_2O decomposition is presumably related to the N_2O decomposition mechanism. Since O_2 can occupy the active sites to reduce N_2O chemisorption and can inhibit the release of chemisorbed oxygen on the surface, the total conversion rate is thus partially prohibited.

In contrast, the existence of low concentration NO facilitates N_2O decomposition. For example, the temperature at which

Fig. 8. Schematic diagram for the formation of various iron species and the transformation of Al species in Fe(III)-USY.

Fig. 9. Catalytic activities for N₂O decomposition on Fe(II)-ZSM-5, Fe(III)-ZSM-5, Fe(II)-USY, Fe(III)-USY (A); catalytic activities for N₂O decomposition on Fe(III)-NaY, Fe(III)-HY, Fe(III)-USY and Fe(III)-USY-A (B). Reaction conditions: 0.1 g catalyst, 1500 ppm N₂O and the balance He, GHSV = 30,000 h⁻¹.

15–90% N₂O conversion occurs is about 50 K lower after adding 200 ppm NO (Fig. 10). The positive effect of NO on N₂O decomposition over Fe(III)-USY catalyst is consistent with the results reported for other iron-zeolites [49–51], and can basically be ascribed to promoting oxygen desorption from the active sites. When O₂ (5%) and NO (200 ppm) coexist in the reaction system, a composite function operates; as a result, a moderate positive effect is observed on N₂O decomposition (Fig. 10).

We further tested the durability of Fe(III)-USY catalyst under simulated conditions for a typical nitric acid plant, i.e. 1500 ppm N₂O, 200 ppm NO, 5% O₂ and 1% H₂O in He. Time-on-stream profiles in Fig. 11 show that the N₂O conversion is 90–91% and 98–99% at 723 and 748 K, respectively, and remained almost unchanged for 100 h, indicating that the catalyst is highly durable under these conditions. It is well known that Fe-ZSM-5 catalyst performs very well for N₂O decomposition, but suffers from severe activity loss in the presence of water vapor. The deactivation of Fe-ZSM-5 catalysts is due to the dealumination of zeolite framework and subsequent clustering of iron species [52]. As for Fe(III)-USY catalyst, the exchange of most protons in USY matrix with ferric ions reduces the proton-induced dealumination at higher temperatures. Moreover, formation of chemically bound Al–O–Fe species can protect Fe(III)-USY against dealumination, preserving a

Fig. 10. Catalytic activities for N₂O decomposition on Fe(III)-USY under different conditions. Reaction conditions: 0.1 g catalyst, 1500 ppm N₂O, 0 or 200 ppm NO, 0 or 5% O₂ and the balance He, GHSV = 30,000 h⁻¹.

Fig. 11. Time-on-stream behavior of Fe(III)-USY catalyst for N₂O decomposition. Reaction conditions: 0.1 g catalyst, 1500 ppm N₂O, 200 ppm NO, 5% O₂, 1% H₂O, balance He, GHSV = 30,000 h⁻¹.

high durability of Fe(III)-USY catalyst. This durability has been also revealed by the ²⁷Al NMR of calcined Fe(III)-USY catalyst (Fig. 7), which shows that there is no obvious change in intensity of peaks at 55 and –5 ppm before and after 100-h usage under the simulated conditions.

4. Conclusions

We prepared several Fe-zeolites with MFI and FAU structure via simple wet ion exchange, characterized their structural features and tested their catalytic performance for N₂O decomposition. Thanks to the large channel dimension of FAU, Fe(H₂O)₆²⁺ or Fe(H₂O)₅(OH)²⁺ directly diffuses into the channels and exchanges all protons, leading to a higher Fe loading. Multiple Fe(III) species, including isolated Fe(III) species (mononuclear or dinuclear oxygen bridged), oligonuclear Fe(III)_xO_y clusters and Fe₂O₃ nanoparticles, were identified in all Fe-zeolites by means of UV-vis, TEM, H₂ TPR and FTIR of adsorbed NO. Formation of these various iron species was proposed on the basis of these

observations and of ^{27}Al NMR spectra taken for each step of the preparation process. Fe-FAU catalysts exhibited a higher activity and a good durability for N_2O decomposition under simulated conditions. Based on the structural characterization and catalytic performance, we propose that only the isolated/oligonuclear iron species with ready access to N_2O molecules could have more contribution to N_2O decomposition. Fe_2O_3 nanoparticles in catalysts played a negative role since they might block the channel of zeolites and reduce the accessibility of isolated/oligonuclear iron species in the channels.

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