Wet ion exchanged Fe-USY catalyst for effective N₂O decomposition

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Abstract

Zeolite matrix FAU with large channel dimension is applied as good host for iron species and Fe-USY sample is prepared by wet ion exchange method using ferric salt as the iron source. The as-prepared Fe-USY catalyst exhibits quite good activity for N₂O decomposition and a 100% conversion (to N₂ and O₂) can be achieved at above 748 K. Besides, Fe-USY shows good durability for N₂O decomposition under simulated conditions at a typical nitric acid plant, which demonstrates its potential for future application.

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1. Introduction

Nitrous oxide (N₂O) is a greenhouse gas that greatly contributes to the green house effect and severely destructs the ozone layer in the stratosphere [1]. An effective way to minimize the impact of N₂O on the environment is to catalytically decompose N₂O to environment-friendly N₂ and O₂ on the sites of anthropogenic activities, e.g. adipic acid production, nitric acid manufacture, fossil fuel and biomass combustion prior to N₂O emission to the air. The basic requirement for effective decomposition of N₂O is that the catalyst employed possesses high activity and sufficient durability.

Currently, zeolite-supports catalysts, particularly, iron zeolites have attracted much attention because of their good catalytic performance for this decomposition, even in the presence of other components (O₂, H₂O, and SO₂ etc.) in the stream [2]. Since the preparation process affects the catalyst activity and durability, many investigations have been carried out to reveal the relationship to make

high-performance iron zeolite catalysts [2–9]. The widely used methods include solid state ion exchange [3], chemical vapor decomposition (CVD) of FeCl₃ [4,5], and isomorphous substitution followed by extraction [6]. Compared with these methods, wet ion exchange is simpler and more feasible for industrial manufacture since it involves fewer steps and the process parameters are easily controlled. In general, iron zeolites were made via ferrous ion exchange [7], while the oxidation of Fe²⁺ to Fe³⁺ during the ion exchange process renders the process non-repeatable [8]. Ferric ion exchange appears an ideal method to prepare iron zeolites, however, the ion diffusion is very much limited and the ion exchange degree is very low due to the long diffusion path and the relatively larger size of hydrated ferric ions in comparison with the pore size of zeolite.

To achieve high ion exchange degree, we can either shorten the diffusion path or choose a zeolite with larger pore size. The former was demonstrated by Melián-Cabrera et al. by decreasing the diffusion path upon a mild alkaline treatment [9]. The latter has now been demonstrated in this study that we selected a special zeolite matrix (FAU) with a larger channel dimension ([111] 0.74 × 0.74 nm), as the support to load ferric ions to make iron zeolite. We have found that the wet ion exchange of FeCl₃ with FAU can readily lead to an over-exchanged Fe-USY with

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reliable reproducibility. The as-prepared Fe-USY shows good activity and durability for the catalytic decomposition of N₂O.

2. Experiment

2.1. Materials preparation

Commercial H-ZSM-5, H-Beta and H-USY (Sinopec Co.) with a similar Si/Al ratio (ca. 12) were used as the parent zeolites in this study. Ferric ions were introduced to zeolites by wet ion exchange in 0.05 M FeCl₃ aqueous solution with an initial pH of 2 at room temperature. After ion exchange for 48 h, the sample was filtered, thoroughly washed, dried and then calcined in the air at 873 K for 4 h.

2.2. Materials characterization

The Si, Al and Fe contents of iron zeolites were determined by ICP-OES using an Optima 2000 spectrometer.

Low temperature N₂ adsorption/desorption experiments were carried out in a Quantachrome NOVA-1200 gas absorption analyzer and the specific surface area was calculated with BET equation.

UV–vis measurements were carried out on a Hitachi UV-3000 spectrometer, and diffuse reflectance spectra were recorded in the air against BaSO₄ in the region of 190–800 nm.

Transmission electron microscopy images of samples were acquired on a JEOL 3010 transmission electron microscope at an accelerate voltage of 300 kV.

2.3. Catalytic testing

N₂O decomposition experiments were performed in a fixed-bed flow microreactor at atmospheric pressure. Typically, 0.1 g sample (sieve fraction, 0.25–0.5 mm) 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 (He balance) was fed to the reactor. The steady-state tests were conducted isothermally every 25 K at ascending temperature from 573 K to

Table 1
Physicochemical properties of iron zeolites

Sample	Si/Al	Fe/Al ^a	Fe (wt%)	S _{BET} (m ² g ^{−1}) ^b
Fe-ZSM-5	11.8	0.04	0.30	422 (423)
Fe-Beta	10.8	0.06	0.52	512 (516)
Fe-USY	11.6	0.42	3.38	528 (512)

^a The theoretical Fe/Al ratio for full exchange is 0.33.

^b The data in bracket are the S_{BET} for parent zeolites.

3. Results and discussion

As shown in Table 1, the Si/Al ratio of three zeolites is 10.8–11.8 and their surface area is 423–516 m²/g. After introduction of Fe species by ion exchange, the surface areas do not show obvious changes and the structure of zeolite are well preserved (confirmed by XRD patterns, not shown here). The Fe/Al ratio in USY (0.42) is 6–10 times higher than the other two (0.04 and 0.06). The stoichiometric exchange of the acidic zeolite with Fe³⁺ will results in an Fe/Al ratio of 0.33. Therefore, Fe-ZSM-5 and Fe-Beta are very much under-exchanged, while Fe-USY seems to be over-exchanged.

The nature and distribution of Fe species in USY are assessed by UV–vis spectra, as shown in Fig. 1. After suitable deconvolution, several UV–vis absorption bands can be assigned to characteristic Fe species. For example, the two bands between 200 and 300 nm (215 nm and 285 nm) are assigned to isolated Fe³⁺ ions (hydrated), the two bands between 300 and 400 nm (335 nm and 385 nm) to small oligonuclear Fe³⁺_xO_y clusters in zeolite channels and the two bands at above 400 nm (460 nm and 540 nm) to Fe₂O₃ nanoparticles on the external surface [6]. Although the uncalcined and calcined Fe-USY show similar UV–vis characteristics, the high-resolution TEM images in Fig. 2 reveals that Fe₂O₃ particles in uncalcined Fe-USY are small (<1 nm) while in calcined Fe-USY they are large (1–4 nm) on the external surface, suggesting aggregation of Fe₂O₃ nanoparticles upon calcination. The formation of multiple iron species in uncalcined Fe-USY is supposedly related to the ferric ion hydration and ion exchange process.

Hydrolysis of ferric salt occurs in aqueous solution, accompanied by the condensation reaction [10,11]:

873 K and the gas products were analyzed on-line 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).

Therefore, the ferric ion species in 0.05 M FeCl₃ aqueous solution (pH 2.0) are Fe(H₂O)₆³⁺ (ca. 44%) and Fe(H₂O)₅(OH)²⁺ (ca. 32%), and the rest is [Fe(H₂O)₅O-Fe(H₂O)₅]⁴⁺ (ca. 24% Fe). The effective van der Waals diameter of hydrated monomer ions is 0.67–0.69 nm [12], just smaller than the pore size of USY ([111]

Fig. 1. UV-vis/DRS spectra of ion-exchanged and calcined Fe-USY.

Fig. 2. TEM images of ion-exchanged and calcined Fe-USY. Inlet are the images enlarged for 5 times and the iron species are marked by circles.

0.74×0.74 nm), so that the monomer ions can readily diffuse in USY channels and achieve the high exchange degree, but $[\text{Fe}(\text{H}_2\text{O})_5\text{OFe}(\text{H}_2\text{O})_5]^{4+}$ is large ($0.86\text{--}0.88$ nm) and cannot easily enter the channel. It should be mentioned that $\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ is the preferred monomer for ion exchange due to electronic restraint in high-silicon zeolites during ion exchange process. However, even the diameter of monomer ions is larger than the pore size of ZSM-5 ($[100]$ 0.51×0.55 nm $\leftrightarrow$ $[010]$ 0.53×0.56 nm) and beta ($[010]$ 0.66×0.67 nm $\leftrightarrow$ $[001]$ 0.56×0.56 nm), which makes it very difficult for the ferric species to diffuse into the channel in any way. So we believe that ferric ions mainly exchange the surface protons in the case of Fe-ZSM-5 and Fe-Beta. In addition, when the monomer ions diffuse into USY channels, some may react with the Brønsted acid sites to produce oligonuclear $\text{Fe}^{3+}_x\text{O}_y$ clusters, which seemingly results in an over-exchange.

Thus we can easily prepare Fe-USY with high Fe^{3+} loading and good Fe-species dispersion via wet ion exchange and subsequent calcination. The high loading and good dispersion of Fe-species are critical to the effective thermal decomposition of N_2O , since both isolated Fe^{3+} sites and oligonuclear iron oxides contribute to the high catalytic activities, and more Fe-species can produce more catalytic sites [13–15]. Our tests indicate that the as prepared Fe-USY performs excellently in N_2O thermal

decomposition. As presented in Fig. 3, Fe-USY exhibits the highest activity. More remarkably, the activity of Fe-USY catalyst is comparable with that of the best iron zeolite reported elsewhere [16–18]. Note that the 90% and 50% N_2O conversion occurs at 723 K and 673 K, respectively, ca. 80 K lower than those when using Fe-Beta and Fe-ZSM-5 prepared in the same way. In addition, Arrhenius plots give the apparent activation energy E_a of

Fig. 3. Catalytic activities for N_2O decomposition on Fe-zeolites. Reaction conditions: 0.1 g catalyst, 1500 ppm N_2O , and the balance He, GHSV = $30,000 \text{ h}^{-1}$.

129.9 kJ mol⁻¹ for Fe-USY, much lower than that of Fe-Beta (150.8 kJ mol⁻¹) and Fe-ZSM-5 (155.9 kJ mol⁻¹). The catalytic activity of Fe-USY for N₂O decomposition is studied under different reaction conditions and the results are summarized in Table 2. Generally, the existence of NO in reaction system shows distinct positive effect on N₂O decomposition while H₂O and O₂ shows mild negative effects, in consistent with those reported for iron-zeolites [19,20].

We have further tested the durability of Fe-USY catalyst under simulated conditions at the typical nitric acid plant, including NO, O₂ and H₂O in the stream. Time-on-stream profiles of Fe-USY in Fig. 4 show that there is no loss of the activity over 100 h, indicating the catalyst is highly durable under these conditions. This is in contrast with Fe-ZSM-5 catalysts that suffered from severe activity lost in the presence of water vapor [21], although they were prepared by wet ion exchange and exhibited high activity for N₂O decomposition in spite of the low iron loading. In this study, good activity and high durability are simultaneously achieved in Fe-USY catalyst. The good durability of Fe-USY catalyst can be attributed to the replacement of most protons by Fe in zeolite matrix, so that the frame-

work aluminum is stabilized through combination with Fe species in wet exhaust at elevated temperatures [22].

4. Conclusion

In summary, zeolite matrix FAU, as a new support of iron species, can be readily loaded with a multiple iron species in the channels simply by one-pot wet ion exchange. The as-prepared Fe-USY catalyst exhibits superior activity and durability for N₂O catalytic decomposition, which is a potential catalyst for N₂O abatement at the nitric acid production plants.

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Table 2

Catalytic results and calculated apparent activation energy for N₂O decomposition on Fe-USY under different reaction conditions

Reactant composition (He balance)	GHSV (h ⁻¹)	T ₅₀ (K)	T ₉₀ (K)	E _a (kJ/mol)
1500 ppm N ₂ O	30,000	675	727	129.9
1500 ppm N ₂ O	15,000	671	720	129.2
1500 ppm N ₂ O	60,000	692	743	130.4
5000 ppm N ₂ O	30,000	683	732	132.1
10,000 ppm N ₂ O	30,000	685	733	132.7
1500 ppm N ₂ O – 200 ppm NO	30,000	642	688	98.7
1500 ppm N ₂ O – 2.5% O ₂	30,000	689	731	144.7
1500 ppm N ₂ O – 1% H ₂ O	30,000	702	736	150.6
5000 ppm N ₂ O – 200 ppm NO – 2.5% O ₂ – 1% H ₂ O	30,000	677	719	140.2

Fig. 4. Time-on-stream behaviour of Fe-USY catalyst for N₂O decomposition. Reaction conditions: 0.1 g catalyst, 1500 ppm N₂O, 200 ppm NO, 2.5% O₂, 1% H₂O, balance He, GHSV = 30,000 h⁻¹.