

Steam Tolerance of Fe/ZSM-5 Catalyst for the Selective Catalytic Reduction of NO_x

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Abstract—This article reports the effects of steam on the activity and stability of Fe/ZSM-5 for the selective catalytic reduction of NO with *iso*-butane. When the feed contained 10% of H₂O, the de-NO_x activity was maintained if the temperature was above the maximum conversion temperature. However, when the temperature was below the maximum conversion temperature, the catalytic activity decreased. The effect of high temperature steam treatment on the stability was also examined. After the steam treatment, the activity of Fe/ZSM-5 decreased due to the dealumination of ZSM-5 and the migration of Fe ion isolated in the ion exchange site to form ferromagnetic iron agglomerate. The physico-chemical properties of the fresh and deactivated catalysts were monitored by ESR, ²⁷Al MAS NMR, XPS, XRD, TPR and FT-IR spectroscopy.

Key words: Fe/ZSM-5, De-NO_x, SCR, Steam Effect, Hydrothermal Aging, Deactivation, Stability

INTRODUCTION

Metal ion exchanged ZSM-5 catalysts have been extensively studied for the selective catalytic reduction (SCR) of NO_x under the net oxidizing condition by hydrocarbons. After all these efforts, it seems difficult to apply these materials to the practical exhaust after-treatment, since the catalysts are easily poisoned and irreversibly deactivated by steam present in the exhaust stream [Kim et al., 1999; Kim and Nam, 2001]. However, Feng and Hall [1997, 1998] have reported that they were able to prepare a remarkably durable catalyst, Fe/ZSM-5, that is highly stable up to 800 °C and insensitive to 20% steam. Nevertheless, the authors themselves were not successful in reproducing their results.

Chen and Sachtler [1998] proposed an easy-to-prepare Fe/ZSM-5, synthesized by subliming FeCl₃ into the cavities of H/ZSM-5. They reported that the performance of the catalyst was not impaired when 10% H₂O was added, but made no comment on the hydrothermal stability of the catalyst after a high temperature steam treatment.

More recently, we have studied the effects of iron loading and remaining Brønsted acid sites on the stability of Fe/ZSM-5 and found that the Fe/ZSM-5 sample prepared by sublimation followed by washing and calcination has about 30% of the original protons [Lee and Rhee, 1999]. The existence of these protons is considered to cause dealumination of zeolite, which triggers the migration of isolated copper ions in Cu/ZSM-5 [Tanabe et al., 1995; Yan et al., 1996; Budi et al., 1996].

Many studies have examined the nature of the active species in

Fe/ZSM-5, and a few structures have been reported in the literature. Kucherov and Slinkin [1988] reported that isolated Fe³⁺ ions were detected by ESR, while Joyner and Stockenhuber [1997, 1999] have proposed an oxygen containing nanoclusters with a structure similar to those of ferredoxin (Fe₂S₂). Sachtler et al. [1998, 2001] have proposed oxo-bridged binuclear complexes as active redox sites. More recently, Marturano et al. [2000] have shown that the final state of Fe depends on the hydrolysis processes upon washing after sublimation, the presence of extraframework Al species, and the crystallite size of the zeolite used.

The purpose of this study was to examine the effect of steam on the de-NO_x activity and structural stability of Fe/ZSM-5. We also examined the state of Fe and its changes during hydrothermal aging.

EXPERIMENTAL

1. Sample Preparation

The Fe/ZSM-5 catalyst was prepared by the sublimation method as described by Chen and Sachtler. Na/ZSM-5 (SiO₂/Al₂O₃=23.3), supplied by Tosoh Corp., was ion exchanged to NH₄/ZSM-5 and then calcined in an oxygen stream at 500 °C to give H/ZSM-5. Iron (III) chloride is sublimed into the cavities of the H/ZSM-5, in which it reacts chemically with protons at Brønsted acid sites. After sublimation the catalyst was washed three times and then calcined at 500 °C in an oxygen stream for 2 h. The Cu/ZSM-5 catalyst was prepared by the conventional aqueous ion exchange method at 80 °C by using Na/ZSM-5 and 0.01 M metal nitrate solution. Chemical analysis of the catalysts was undertaken by inductive-coupled

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[†]This paper is dedicated to Professor Wha Young Lee on the occasion of his retirement from Seoul National University.

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Table 1. Chemical compositions of the catalyst samples

Sample	Metal loading (wt%)	Metal/Al ratio	Exchange level (%)
Cu/ZSM-5	3.8	0.57	114
Fe/ZSM-5	5.2	0.90	270

plasma atomic emission spectroscopy (ICP-AES). The chemical compositions of the samples are presented in Table 1.

2. Hydrothermal Aging

Hydrothermal aging was performed in a simulated wet exhaust stream of NO (500 ppm), *iso*-butane (500 ppm), O₂ (5%), H₂O (10%), and balance He. The catalysts were exposed to this stream at 500 °C, 600 °C, and 700 °C, respectively, for 10 h.

3. Reaction Studies

A typical inlet gas was composed of 500 ppm NO, 500 ppm *iso*-butane, 5% O₂, and balance He. To simulate the wet exhaust stream, 10% of H₂O was added to the dry feed. The total feed flow rate was 200 ml/min and the catalyst weight was 0.20 g, which gave a GHSV of 30,000 h⁻¹ based on the bulk density of 0.5 g/ml for the catalyst. The products were monitored by on-line gas chromatography (TCD detector, Porapak Q and Molecular sieve 5A columns in sequence reversal configuration) and chemiluminescence type NO_x analyzer (Rosemount model 951A). N₂O production was below detection limit for Fe/ZSM-5. CO₂ and CO were detected as carbon products.

For the activity data report, we used two quantities defined as follows:

$$\text{NO conversion (\%)} = [(\text{NO}_m - \text{NO}_{\text{out}}) / \text{NO}_m] \times 100 \quad (1)$$

$$\begin{aligned} \text{Competitiveness factor (\%)} \\ = [(\text{NO}_m - \text{NO}_{\text{out}}) / (13 \times i\text{-C}_4\text{H}_{10, \text{consumed}})] \times 100 \end{aligned} \quad (2)$$

The competitiveness factor is the ratio of the rate of hydrocarbon consumed to reduce NO to the rate of total hydrocarbon consumption.

4. Characterization

Electron spin resonance (ESR) spectra were taken in the X-band ($\lambda = 3.16$ cm) of the microwave region at 20 °C on a Bruker EMX spectrometer equipped with ST cavity. The spectra were recorded at a microwave power of 0.1 mW and modulation amplitude of 10 G in the field range of 400–4400 G. The sample (40 mg) was dehydrated in an oxygen stream at 500 °C for 2 h and transferred to the ESR sample tube. The tube was then sealed with gas torch under vacuum without exposure to air. Magic angle spinning (MAS) ²⁷Al nuclear magnetic resonance (NMR) spectra were taken on a Bruker DSX400 NMR spectrometer at 104.3 MHz with a rotor spinning rate of 14 kHz and a pulse length of 0.6 μ s.

X-ray photoelectron spectroscopy (XPS) was performed on the pressed wafer of catalysts by using a Kratos Model AXIS-HS spectrometer. X-ray powder diffraction (XRD) patterns were recorded on a Rigaku model D/Max-3C using CuK α X-ray tube at 35 kV and 25 mA with a scanning speed of 0.5°/min. Unit cell sizes of the

samples were compared qualitatively by the position of five strong peaks in ZSM-5 from 22.5° to 25°. Temperature programmed reduction (TPR) was done by using 12% H₂/N₂ mixture heated from 20 °C to 900 °C with a ramping rate of 20 °C /min and held at 900 °C for 20 min.

Table 2 shows the values for both bulk and surface concentration ratio of Fe/ZSM-5 after each treatment.

RESULTS AND DISCUSSION

1. Catalytic Activities of Copper and Iron Exchanged ZSM-5 Catalysts

The temperature dependence of de-NO_x reaction over copper and iron exchanged ZSM-5 catalysts is shown in Fig. 1. The NO conversion first increases with an increase in the temperature, reaches a maximum, and then decreases with an increase in the temperature. The temperature at which the NO conversion obtains its maximum depends on the kind of metal cations and is relatively lower for iron. Over the Cu/ZSM-5, no CO is observed as a product and *iso*-butane is completely oxidized to CO₂. On the other hand, a large amount of CO is formed as a product over Fe/ZSM-5. The conversion to CO shows a temperature dependence which is similar to that of the NO conversion.

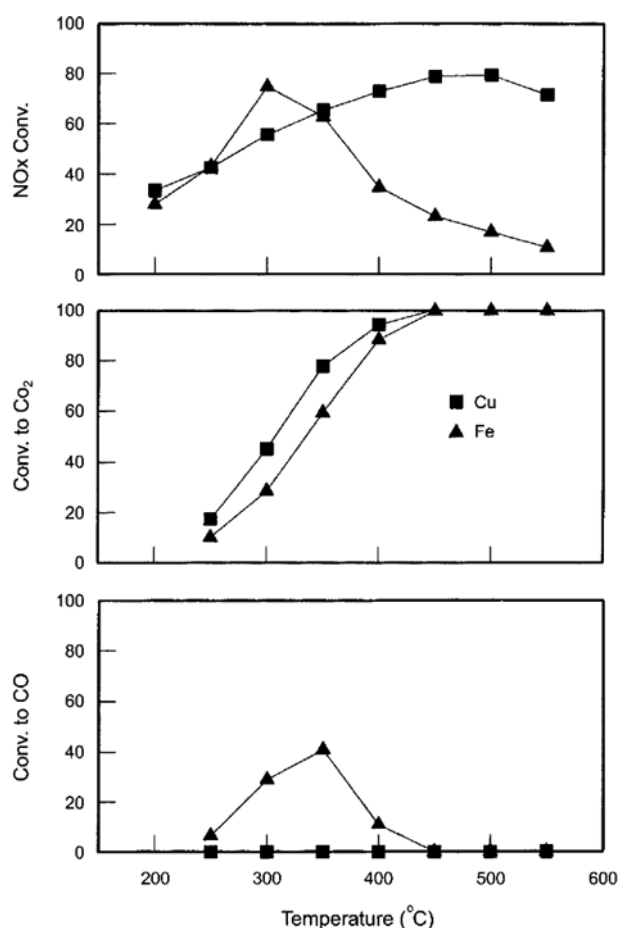


Fig. 1. Effect of the temperature on the SCR reaction over Cu/ZSM-5 and Fe/ZSM-5, respectively: (■) Cu/ZSM-5, (▲) Fe/ZSM-5.

Table 2. Bulk and surface concentration ratios of Fe-ZSM-5 catalysts after different treatments

Sample	Fe/Al		Si/Al	
	Surface ^a	Bulk ^b	Surface ^a	Bulk ^c
After sublimation	0.97		15.2	
Washed and calcined	0.60	0.9	15.9	12
Aged at 700 °C	0.38		15.1	

^aDetermined by XPS.

^bChemical composition determined by ICP analysis.

^cFramework atomic ratio determined by ²⁹Si MAS-NMR.

Table 3. Effect of H₂O addition on the SCR reaction over Cu/ and Fe/ZSM-5

Catalyst	H ₂ O addition	Rxn. temp. (°C)	NO conv. (%)	CO ₂ yield (%)	CO yield (%)	Compet. factor (%)
Cu/ZSM-5	Dry	350	65	78	0	6.5
	Wet	350	20	30	0	5.1
Fe/ZSM-5	Dry	350	63	55	42	4.8
	Wet	350	62	39	45	5.7
	Dry	300	75	29	29	10.0
	Wet	300	37	18	15	8.5

The effects of H₂O addition on the SCR reaction over Cu/ and Fe/ZSM-5 catalysts are summarized in Table 3. When 10% H₂O is added to the reactant feed, the activity of Cu/ZSM-5 is substantially reduced. Fe/ZSM-5, however, shows a different behavior with the increase in the temperature. In the descending branches above the maximum conversion temperature, the presence of H₂O has insignificant influence on the de-NO_x activity, while the combustion of hydrocarbon is slightly suppressed. This results in an increase in the competitiveness factor. Below or at the maximum conversion

temperature, H₂O addition decreases the de-NO_x activity significantly. This observation is in contrast to the results observed by Chen et al. [1998], in which H₂O addition slightly increased NO conversion when the temperature was below the maximum conversion temperature. Giles et al. [2000], however, reported that the activity for NO oxidation over Fe/ZSM-5 is inhibited by the presence of water, as it displaces the adsorbed NO and NO₂.

The effect of H₂O addition as discussed in the above cannot be clearly explained at the moment, and certainly requires further investigation. It is evident that the state of iron species in the catalysts and the hydrophobicity of the surface have to be examined to provide the reason why the catalyst deactivates under a wet condition. Temperature programmed desorption (TPD) of water and TPD of NO after simultaneous adsorption of NO and hydrocarbon with and without water may provide useful information for this purpose [Kim and Nam, 2001].

2. Effects of Hydrothermal Treatment

The catalytic activities of Fe/ZSM-5 catalyst before and after steam treatment are shown in Fig. 2. The reactions have been carried out under dry conditions. Upon aging at 500 °C, the active window of the catalyst slightly shifts to a higher temperature region. Steam treatment at above 600 °C, however, severely reduces the de-NO_x activity. When aged at 700 °C, the catalyst was almost completely deactivated. However, this catalyst is active for iso-butane combustion, and CO is further oxidized to CO₂.

The ESR spectra of fresh Fe/ZSM-5 show four different lines (see Fig. 3), which are similar to those reported by Kuchеров and

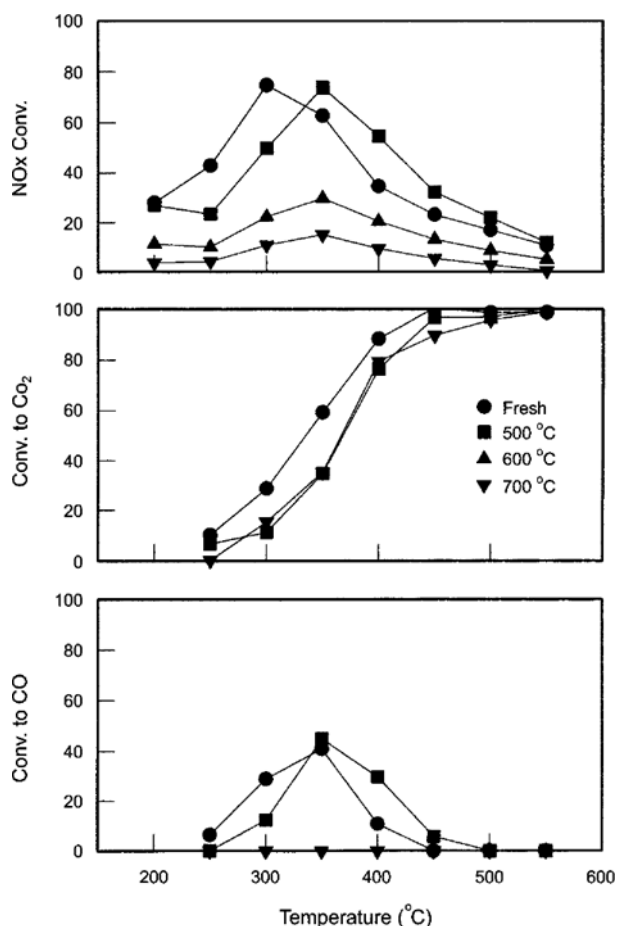


Fig. 2. Effect of the temperature on the SCR reaction over various Fe/ZSM-5 catalysts: (●) fresh, (■) aged at 500 °C, (▲) aged at 600 °C and (▼) aged at 700 °C.

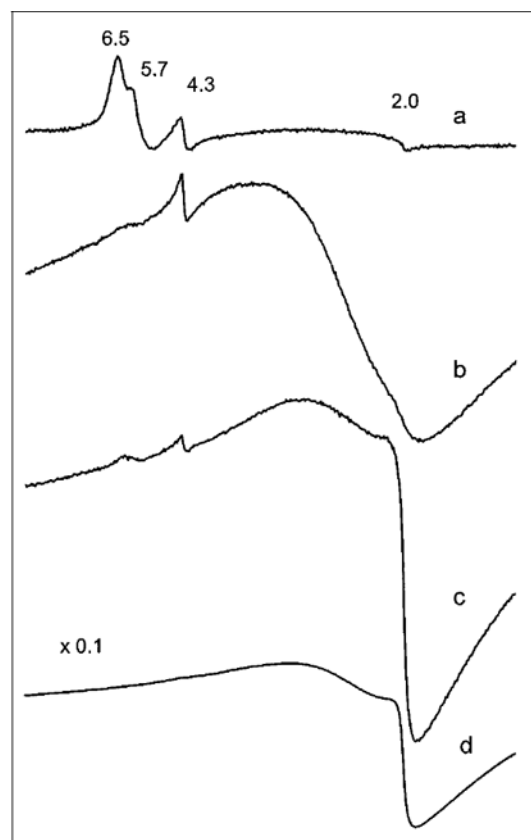


Fig. 3. ESR spectra of various Fe/ZSM-5 catalysts: (a) fresh, (b) aged at 500 °C, (c) aged at 600 °C and (d) aged at 700 °C.

Slinkin [1988]. They assigned these lines as follows: a weak line at $g=2.0$ originating from mutually interacting octahedral Fe³⁺ ions and intense narrow lines in a low-field region from Fe³⁺ ions in tetrahedral ($g=4.3$) and distorted tetrahedral ($g=5.7$ and 6.5) coordinations. Characteristics of iron oxide phase are represented by a very broad ESR line with $g=2.2$, which is commonly formed in samples prepared by an aqueous ion exchange method, but this is not observed in the fresh samples prepared in the present study.

Spectrum (a) of Fig. 3 indicates that in the fresh Fe/ZSM-5 most of the iron atoms are present as tetrahedral or distorted tetrahedral ion species in the cationic positions of ZSM-5. After the hydrothermal treatment at 500 °C, the low-field signals at $g=5.7$ and 6.5 weaken while a very broad line with $g=2.2$, typical characteristics of ferromagnetic iron oxide, appear. The signals at $g=5.6$ and 6.5 have been associated with highly reactive isolated Fe³⁺ cations in distorted tetrahedral coordination [Kucherov et al., 1998; Varga et al., 1998]. Therefore, the spectrum (b) indicates that the reactive isolated ferric ions in cationic site are migrated to form iron oxide agglomerate. More severe treatment at above 600 °C further reduces the low-field lines of tetrahedral coordination and generates an overwhelmingly intense line at $g=2.0$, which represents the octahedral coordination. Almost all the low-field species disappear after aging at 700 °C.

The TPR profiles of the fresh and deactivated samples are pre-

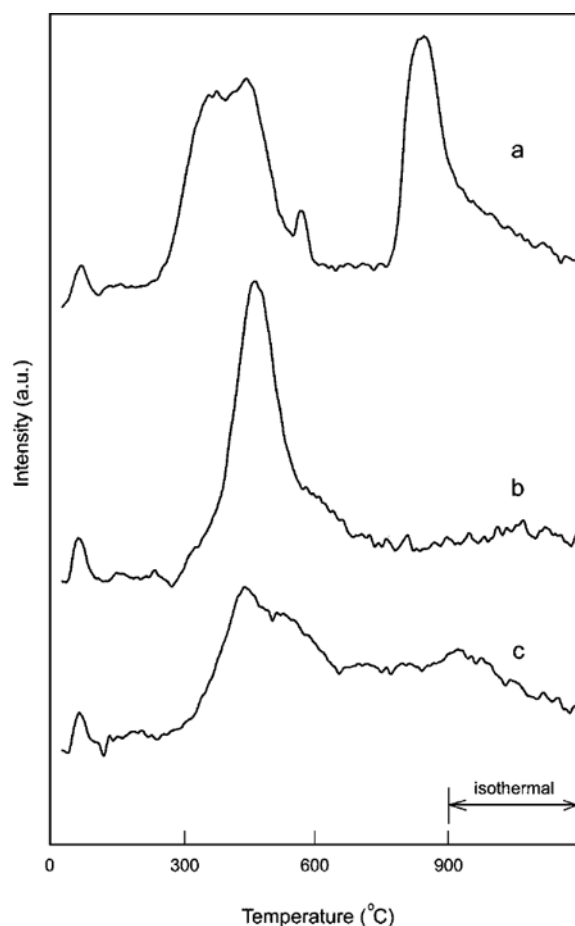


Fig. 4. TPR profiles of various Fe/ZSM-5 catalysts: (a) fresh, (b) aged at 500 °C and (c) aged at 700 °C.

sented in Fig. 4. The profile of the fresh one shows three H₂-consumption peaks at around 450 °C, 600 °C, and >800 °C, respectively. The first peak is assigned as the reduction of Fe³⁺ ion in the ion exchange sites of ZSM-5 to Fe²⁺ as well as the reduction of Fe₂O₃ oxide to Fe₃O₄. The second peak corresponds to the reduction of Fe₃O₄ to Fe⁰. Some of Fe²⁺ ions are irreversibly reduced to Fe⁰ to give the last reduction peak [Lee and Rhee, 1999]. The molar ratio of the hydrogen consumption to Fe (H/Fe) is about unity for the peak at 450 °C, which indicates that almost all the iron is reduced from Fe³⁺ to Fe²⁺. The profile of the sample aged at 500 °C shows the peak around 450 °C and a broad high temperature peak above 700 °C. The broad high temperature peak can be attributed to the reduction of iron agglomerate. Aging at 700 °C changes the profile to the one with broader high temperature peaks, which indicates that the iron ions in the ion exchange sites of ZSM-5 have migrated to form iron agglomerates.

The ²⁷Al MAS NMR spectra of the samples are shown in Fig. 5. Two signals at about 50 ppm and 10 ppm have been assigned to framework and non-framework aluminum, respectively. Though it has a small peak at about 10 ppm, the spectrum of the fresh sample shows that most of the aluminum is in the tetrahedral sites of zeolite framework. The spectrum (b) clearly shows a much larger signal at 10 ppm, and this indicates that the sample was severely dealuminated after hydrothermal treatment at 600 °C.

According to our previous report on the infrared spectra of the hydroxyl stretching region [Lee and Rhee, 1999], the fresh Fe/ZSM-5 showed a peak at 3,610 cm⁻¹, which has been assigned to the protons of the Brønsted acid site. The intensity of the peak was about 30% of that observed in the parent H/ZSM-5. The proton is known to have detrimental effects on the hydrothermal stability of zeolite because it causes dealumination when the zeolite is exposed to mois-

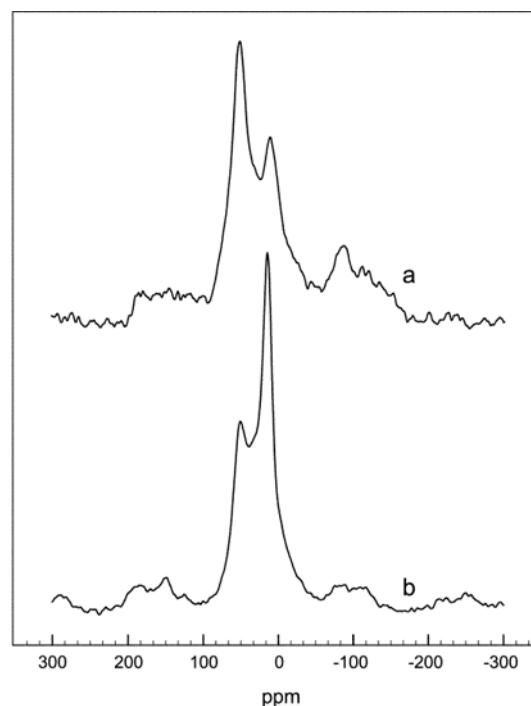


Fig. 5. ²⁷Al MAS NMR spectra of Fe/ZSM-5 catalysts: (a) fresh and (b) aged at 600 °C.

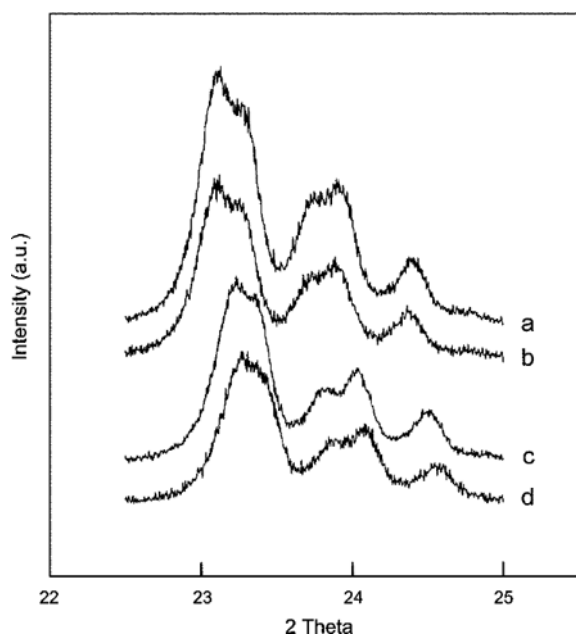


Fig. 6. XRD patterns of (a) Na/ZSM-5, (b) fresh Fe/ZSM-5, (c) Fe/ZSM-5 aged at 500 °C, and (d) Fe/ZSM-5 aged at 700 °C.

ture at a high temperature.

Presented in Fig. 6 are the XRD patterns of fresh and deactivated samples. One can observe from the patterns that the peaks are shifted to the right as the degree of aging increases. This shift may be attributed to the shrinking of the unit cell of ZSM-5 as the dealumination proceeds. The XRD analysis does not show any signs of the presence of FeO, Fe₂O₃, or Fe₃O₄ crystallites, which suggests that the iron agglomerate is different from these three crystallite phases or is very fine if they are formed.

The relative surface concentration of iron, analyzed by XPS spectroscopy, also supports the formation of iron agglomerate phase. The Fe/Al ratio in the catalyst surface is reduced from 0.60 for the fresh sample to 0.38 for the sample hydrothermally aged at 700 °C. This is strong evidence of the formation of iron agglomerates.

CONCLUSIONS

Iron-exchanged ZSM-5 shows a better de-NO_x activity than copper exchanged ones at a temperature below 300 °C, at which the NO conversion obtains a maximum. In the temperature range above the maximum conversion temperature, the addition of 10% H₂O to the feed has negligible influence on the de-NO_x activity but increases the competitiveness factor.

When the Fe/ZSM-5 is treated with steam at high temperatures, its de-NO_x activity tends to decrease. The decrease in the activity becomes significant if aged at a temperature above 600 °C. This hydrothermally induced deactivation of the Fe/ZSM-5 catalyst is attributed to the dealumination of zeolite and the agglomeration of iron ions. Dealumination is likely to occur at the remaining Brønsted acid site, *i.e.*, Al site which is charge-balanced by protons. Hydrothermal aging also causes the highly reactive iron species in the ion exchange sites of zeolite to migrate and form iron agglomerates, which is not effective for NO_x reduction but active for the direct

combustion of hydrocarbons.

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