Fe-ZSM-5 for selective catalytic reduction of NO with NH$_3$: a comparative study of different preparation techniques

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Fe-ZSM-5 are prepared by using four different techniques: conventional aqueous ion-exchange (CA), improved aqueous ion-exchange (IA), solid-state ion-exchange (SS) and chemical vapor ion-exchange (CV). All of the catalysts show very high activities for selective catalytic reduction (SCR) of NO with ammonia. However, the activities are different and follow the sequence of Fe-ZSM-5 (IA) > Fe-ZSM-5 (CA), Fe-ZSM-5 (SS) > Fe-ZSM-5 (CV). ESR results indicate that Fe^{3+} ions with tetrahedral coordination are the active sites for the SCR reaction.

KEY WORDS: Fe-exchanged ZSM-5; selective catalytic reduction; SCR of NO with ammonia; ion-exchange; catalyst preparation

1. Introduction

Nitrogen oxides (NO, NO$_2$ and N$_2$O) generated by combustion processes remain to be a major source for air pollution. They contribute to photochemical smog, acid rain, ozone depletion and greenhouse effects. The current technology for reducing nitrogen oxides emissions from power plants is selective catalytic reduction (SCR) of NO$_x$ ($x =$ 1, 2) with ammonia. Many catalysts have been reported to be active for this reaction. They are mainly divided into two types: mixed oxides and ion-exchanged molecular sieves [1–3]. The commercial catalyst is vanadia and molybdena or tungsten oxide supported on titania.

In our previous work [4–7], we reported superior Fe-exchanged ZSM-5 and mordenite catalysts that show the highest activity among all known catalysts for ammonia SCR. Compared with the commercial vanadia catalyst, the Fe-ZSM-5 was 5–7 times more active; it also functioned in a broader temperature window, produced only N$_2$ (rather than N$_2$O) and H$_2$O, and showed a substantially lower activity for oxidation of SO$_2$ to SO$_3$ [4,5]. The SCR activity of the Fe-ZSM-5 was further increased by the presence of H$_2$O and SO$_2$ at high temperatures (>350 °C). The maximum activity was obtained on the Fe-ZSM-5 with a moderate exchange level (Fe/Al = 0.19–0.43).

It is known that Fe-ZSM-5 can be prepared using various techniques. The different methods will affect the states of iron and the ion-exchange level and thus result in different catalytic performance. Fe-ZSM-5 has also been extensively studied as a hydrocarbon SCR catalyst recently [8–13]. The results showed that the catalytic activity was very sensitive to sample preparation. Initially, Feng and Hall [8] reported an aqueous exchange method using FeC$_2$O$_4$ solution in an inert gas. An over-exchanged Fe-ZSM-5 (Fe/Al =

0.91) was synthesized and itshowed a much higher activity than an under-exchanged Fe-ZSM-5 (*i.e.*, Fe/Al < 0.33) for reducing NO with isobutane. Subsequently, they addressed a problem of reproducibility [9]. More recently, Prins and co-workers [14] investigated the preparation procedure by TG-DSC, FTIR and ^{27}Al MAS NMR and they concluded that iron is precipitated onto the zeolite mainly as an FeC$_2$O$_4$ complex, which blocks the pores and impedes complete exchange of the Na$^+$ cations. Most of the precipitate was removed by extensive washing of the zeolite, whereas most of the remaining iron species were transformed into iron oxide during subsequent thermal treatment. Therefore, it appears that over-exchanged Fe-ZSM-5 cannot be prepared easily using FeC$_2$O$_4$ aqueous solution. Chen and Sachtler prepared an over-exchanged Fe-ZSM-5 catalyst (Fe/Al = 1) using anaerobic sublimation of volatile FeCl$_3$ to H-ZSM-5 [10]. The resulting catalyst also showed a high activity and durability for hydrocarbon SCR reaction. It is clear that the preparation procedure will have a strong effect on the property of Fe-ZSM-5.

In this work, we prepare Fe-ZSM-5 using four different methods: conventional aqueous ion-exchange, improved aqueous ion-exchange, solid-state ion-exchange and chemical vapor ion-exchange. The iron-exchange level is controlled at Fe/Al = 0.17–0.22. The present results indicate that all of the catalysts are highly active for SCR of NO with ammonia at a very high space velocity (GHSV = 1.1×10^6 h^{-1}). Also the catalysts are characterized by electron spin resonance (ESR).

2. Experimental

Fe-ZSM-5 catalysts were prepared by using four different methods as follows:

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Table 1
Preparation conditions and iron contents of Fe-exchanged ZSM-5.

Catalyst	Method	Fe content (wt%)	Ion-exchange level (%)	Preparation condition
Fe-ZSM-5 (CA)	Conventional aqueous ion-exchange	1.4	50	Exchanging NH_4-ZSM-5 with $FeCl_2$ solution for 24 h at room temperature
Fe-ZSM-5 (IA)	Improved aqueous ion-exchange	1.9	66	Exchanging NH_4-ZSM-5 with Fe + HCl solution at room temperature for 3 days in He
Fe-ZSM-5 (SS)	Solid-state ion-exchange	1.7	62	Exchanging H-ZSM-5 with $FeCl_2 \cdot 4H_2O$ solid at 550 °C for 6 h in He
Fe-ZSM-5 (CV)	Chemical vapor ion-exchange	1.7	62	Exchanging H-ZSM-5 with $FeCl_3$ vapor for 1 h at 350 °C

(a) *Conventional aqueous ion-exchange (CA).* 2 g NH_4-ZSM-5 (Si/Al $\approx$ 10) was added to 200 ml of 0.05 M $FeCl_2$ solution with constant stirring in air. After 24 h, the mixture was filtered and washed with deionized water. The NH_4-ZSM-5 was supplied by Alsi-Penta Zeolithe Gmbh (Germany). $FeCl_2 \cdot 4H_2O$ (99%) was obtained from Aldrich.

(b) *Improved aqueous ion-exchange (IA).* Because ferrous salts are easily oxidized to corresponding ferric salts by oxygen in air, normally there are some ferric impurities in $FeCl_2 \cdot 4H_2O$. However, pure ferrous solution can be obtained by reaction between excess iron powder and dilute hydrochloric acid solution under the atmosphere of an inert gas. In this method, Fe-ZSM-5 was obtained from exchanging 2 g NH_4-ZSM-5 with a mixed solution that contained 200 ml 0.1 M HCl and 0.73 g iron powder at room temperature for 3 days. Then, the mixture was filtered and washed with deionized water. During preparation of the catalyst, the hydrochloric acid reacted with the iron metal to generate ferrous ions and then the Fe^{2+} ions exchanged with NH_4-ZSM-5. In order to prevent oxidation of Fe^{2+} to Fe^{3+}, the ion-exchange was performed in flowing He (20 ml/min). The iron powder and the HCl solution (2.00 M) were supplied by Fisher.

(c) *Solid-state ion-exchange (SS).* 2 g H-ZSM-5, prepared by calcining NH_4-ZSM-5 at 500 °C for 3 h, was mechanically mixed with 0.12 g $FeCl_2 \cdot 4H_2O$ in a ball mill. The mixture was then transferred to a quartz tube and heated at 550 °C for 6 h in He (100 ml/min). The obtained sample was washed with water and filtered.

(d) *Chemical vapor ion-exchange (CV).* This method was similar to that proposed by Chen and Sachtler [10]. $FeCl_3$ (97%, Aldrich) was used as the iron source. During the experiment, 2 g H-ZSM-5 and 0.11 g $FeCl_3$, separated by glass wool, were loaded into a quartz reactor. Subsequently, the reactor was heated to 350 °C in flowing He (100 ml/min). $FeCl_3$ was evaporated and then exchanged with H-ZSM-5 according to the following equation:

$$\text{H-ZSM-5} + FeCl_3 \rightleftharpoons [FeCl_2]\text{-ZSM-5} + HCl \quad (1)$$

After 1 h, the sample was removed and then washed with deionized water to eliminate chlorine.

The catalysts obtained from the above four methods were dried at 120 °C overnight, then calcined at 500 °C for 6 h in air. Finally, the obtained samples were ground to 60–100 mesh. The Fe and Al contents in the samples were measured by neutron activation analysis. The iron-exchange level was calculated by 3 × (number of iron ions)/(number of aluminum ions) because almost all iron was present as Fe^{3+} [6,9]. The preparation of the catalysts and the resulting Fe contents are summarized in table 1. The Fe^{3+}-ion-exchange level was in the range of 50–66%, with errors of $\pm 3\%$, for the four Fe-ZSM-5 catalysts.

Since ESR is a powerful technique for analyzing the state of ferric ions [11,15–17], the obtained catalysts were subjected to characterization by ESR. ESR spectra were recorded on a Brucker EMX ESR spectrometer, under the conditions of a microwave power of 0.202 mW and a modulation amplitude of 5.0 G. Before the ESR experiment, the fresh and used Fe-ZSM-5 samples were first treated at 400 °C for 30 min in He to remove adsorbed gases, *e.g.*, H_2O and CO_2. When the samples were cooled to room temperature, they were sealed in Pyrex tubes under He atmosphere. The sealed samples were then transferred to the ESR sample holder and the ESR spectra were recorded at 20 °C.

The SCR activity measurements were carried out in a fixed-bed quartz reactor. 20 mg catalyst was used in this work. The flue gas was simulated by blending different gaseous reactants. The typical reactant gas composition was as follows: 1000 ppm NO, 1000 ppm NH_3, 2% O_2 and balance He. The total flow rate was 500 ml/min (ambient conditions) and thus a very high GHSV (gas hourly space velocity) was obtained (1.1×10^6 h^{-1}). The premixed gases (1.01% NO in He and 1.00% NH_3 in He) were supplied by Matheson. The NO and NO_2 concentrations were continually monitored by a chemiluminescent NO/NO_x analyzer (model 42C, Thermo Environmental Instruments Inc.). To avoid errors caused by the oxidation of ammonia in the converter of the NO/NO_x analyzer, an ammonia trap containing phosphoric acid solution was installed before the sample inlet to the chemiluminescent analyzer. Since N_2O formation was not detected with Fe-ZSM-5 in our previous work [4–7],

Table 2
Catalytic performance of Fe-ZSM-5 catalysts.[a]

Catalyst[b]	Temperature (°C)	NO conversion to N_2 (%)	$k^c/10^3$ (cm^3/g s)
Fe-ZSM-5 (CA)	300	16.8	0.147
	350	22.4	0.221
	400	63.5	0.948
	450	79.0	1.58
	500	74.5	1.48
Fe-ZSM-5 (IA)	300	17.4	0.153
	350	35.4	0.381
	400	76.8	1.37
	450	83.2	1.80
	500	72.0	1.38
Fe-ZSM-5 (SS)	300	19.0	0.169
	350	38.5	0.423
	400	71.4	1.17
	450	79.1	1.58
	500	74.6	1.48
Fe-ZSM-5 (CV)	300	9.0	0.076
	350	20.0	0.194
	400	35.0	0.405
	450	70.0	1.22
	500	73.0	1.41
	550	62.0	1.11

[a] Reaction conditions: 20 mg catalyst, [NO] = [NH_3] = 1000 ppm, [O_2] = 2%, He balance, total flow rate = 500 ml/min and GHSV = 1.1×10^6 h^{-1}.
[b] Definition of catalysts is seen in table 1.
[c] First-order rate constant, as defined in the text, calculated by equation (2).

N_2O was not analyzed in this work. The data were obtained after 10 min when the SCR reaction reached steady state.

3. Results and discussion

The catalytic performance for SCR of NO with ammonia is summarized in table 2. Under a very high space velocity (GHSV = 1.1×10^6 h^{-1}), these Fe-ZSM-5 catalysts still showed high NO conversions to N_2. With increasing temperature, the NO conversion was found to increase first, passing through a maximum, then decreased at higher temperatures. The maximum NO conversion decreased in the sequence of Fe-ZSM-5 (IA) > Fe-ZSM-5 (CA), Fe-ZSM-5 (SS) > Fe-ZSM-5 (CV). Since the reaction was reported to be first order with respect to NO (under stoichiometric NH_3 conditions) for most catalysts [1–3], the SCR activity can also be represented quantitatively by an apparent first-order rate constant (k). By assuming plug-flow reactor (in a fixed bed of catalyst) and free of diffusion limitation, the apparent first-order rate constant can be calculated from NO conversion (X) by

$$k = -\frac{F_0}{[NO]_0 W} \ln(1 - X), \qquad (2)$$

where F_0 is the molar NO feed rate, $[NO]_0$ is the molar NO concentration at the inlet (at the reaction temperature), and W is the catalyst amount (g). According to the NO conversions and reaction conditions, the apparent first-order
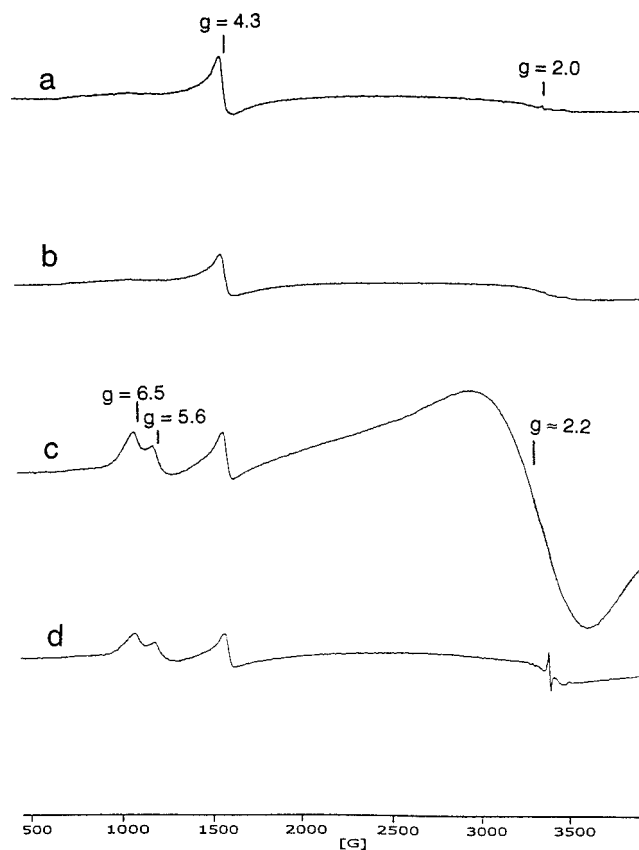

Figure 1. ESR spectra at 20 °C of fresh catalysts: (a) Fe-ZSM-5 (CA: conventional aqueous ion-exchange), (b) Fe-ZSM-5 (IA: improved aqueous ion-exchange), (c) Fe-ZSM-5 (SS: solid-state ion-exchange) and (d) Fe-ZSM-5 (CV: chemical vapor ion-exchange). Detailed preparation conditions of the catalysts are given in table 1.

rate constants on the above catalysts were calculated and compared in table 2. The maxima of first-order rate constants also varied with the same sequence of NO conversions, i.e., Fe-ZSM-5 (IA) showed the highest SCR activity ($k = 1800$ cm^3/g s at 450 °C) and Fe-ZSM-5 (CV) showed the lowest activity ($k = 1410$ cm^3/g s at 500 °C).

The ESR spectra of the fresh Fe-ZSM-5 are shown in figure 1. After the fresh Fe-ZSM-5 (CA) was treated in He at 400 °C for 30 min and then cooled to room temperature, a strong narrow line at $g = 4.3$ was observed (figure 1(a)). This signal can be assigned to Fe^{3+} ions in tetrahedral coordination [6,11,15–17]. Also, two very weak signals were detected on the spectrum. One was broad ($g \approx 2.2$ and $\Delta H \approx 800$ G), which probably comes from aggregated Fe^{3+} ions in the extraframework α-Fe_2O_3 and/or Fe_3O_4 species exhibiting ferromagnetic behavior [11]. The iron oxides might come from hydrolysis and oxidation of $FeCl_2$. The other signal was narrow ($g = 2.0$), originating from Fe^{3+} complexes with octahedral symmetry [11]. It is noted that the sample was sealed in a Pyrex tube and the empty Pyrex tube also showed a signal at $g = 4.3$, but the intensity was only one quarter as strong as that of Fe-ZSM-5. The above ESR results are in agreement with our previous XPS and H_2-TPR results that iron was present mainly as ferric form in the Fe-ZSM-5 [6]. Oxygen oxidized Fe^{2+} to Fe^{3+} during
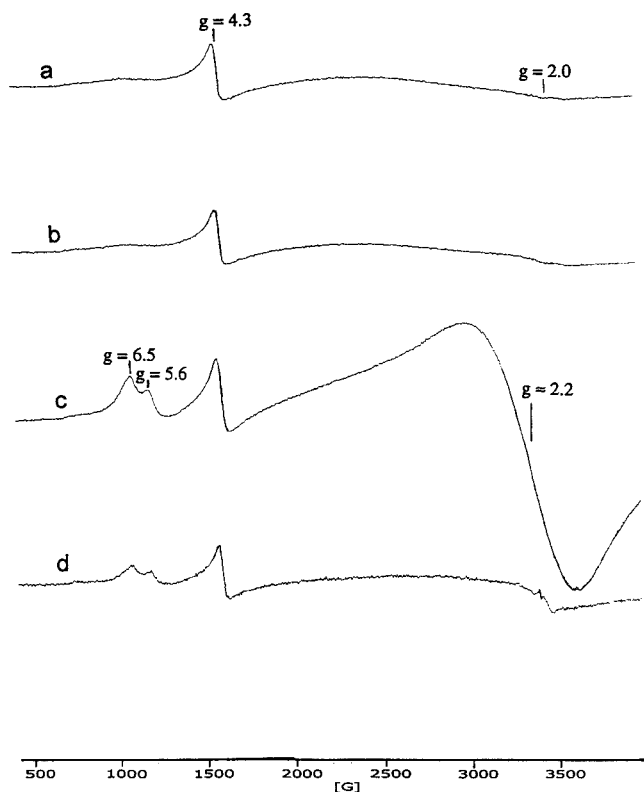
Figure 2. ESR spectra at $20\,^\circ$C of used catalysts: (a) Fe-ZSM-5 (CA: conventional aqueous ion-exchange), (b) Fe-ZSM-5 (IA: improved aqueous ion-exchange), (c) Fe-ZSM-5 (SS: solid-state ion-exchange) and (d) Fe-ZSM-5 (CV: chemical vapor ion-exchange). Detailed preparation conditions of the catalysts are given in table 1.

the process of calcination. The ESR spectrum of fresh Fe-ZSM-5 (IA) was similar to that of Fe-ZSM-5 (CA). The signals due to Fe^{3+} ions in tetrahedral coordination ($g = 4.3$, strong) and in the extraframework iron oxides ($g \approx 2.2$, weak) were also detected (figure 1(b)). The two spectra indicate that ion-exchange in aqueous solution resulted in many Fe^{3+} ions with tetrahedral coordination and only a small amount of iron oxides. By comparison, two new strong signals at $g = 6.5$ and 5.6 were observed on the spectra of fresh Fe-ZSM-5 (SS) and Fe-ZSM-5 (CV), besides the signals at $g = 4.3$, 2.2 and 2.0 (figure 1 (c) and (d)). The two new signals are attributed to Fe^{3+} ions in distorted tetrahedral coordinations [11,15]. In addition, on the spectrum of Fe-ZSM-5 (SS), the signal at $g \approx 2.2$ was very strong, indicating the formation of much extraframework α-Fe_2O_3 and/or Fe_3O_4 species. From the above results, it can be seen that different preparation methods resulted in different Fe^{3+} species in the fresh Fe-ZSM-5. After the four catalysts were tested in the SCR reaction for *ca.* 2 h, their ESR spectra were taken and are shown in figure 2. The ESR signals due to iron species in the used catalysts are very similar to those in the fresh samples. This indicates that the iron species are stable during the SCR reaction and did not change to other iron species.

The foregoing results indicate that the Fe-ZSM-5 catalysts were highly active for the SCR reaction, although they were prepared by using four different techniques. The

SCR activity was found to decrease in the rank order of Fe-ZSM-5 (IA) > Fe-ZSM-5 (CA), Fe-ZSM-5 (SS) > Fe-ZSM-5 (CV) (table 2). In our previous work [6,18], a possible reaction path for NO reduction was proposed for Fe-ZSM-5. After iron ions were exchanged to ZSM-5, a large amount of Brønsted acid sites were still present in the catalysts, besides Fe^{3+} ions. In the SCR reaction, some of the NO molecules are oxidized to NO_2 species by O_2 on the Fe^{3+} sites. NH_3 molecules are adsorbed on the Brønsted acid sites to form NH_4^+ ions. NO_2 first reacts with a pair of NH_4^+ ions to form a complex $[NH_4^+]_2NO_2$. Subsequently, the active complex reacts with another NO to produce N_2 and H_2O and thus complete the catalytic cycle. The role of the Fe^{3+} ions is to oxidize NO to NO_2. The difference in the SCR activities (table 2) might come from different properties of the four Fe-ZSM-5 catalysts. The above ESR spectra showed that the Fe^{3+} ions with distorted tetrahedral coordinations ($g = 6.5$ and 5.6) were formed in Fe-ZSM-5 (SS) and Fe-ZSM-5 (CV) (figure 1). The coordinately unsaturated ferric ions in Fe-ZSM-5 have been studied extensively by Kucherov *et al.* [11,17]. They were easily reducible, and even an interaction with inert xenon was able to displace them slightly [17]. Moreover, these ferric ions were reactive with H_2O and NO at low temperatures, and could also be irreversibly reduced to ferromagnetic species (probably Fe_3O_4) under only slightly reducing conditions at high temperatures [11]. Our above ESR spectra showed that these iron species were stable during the ammonia SCR reaction under an oxidizing condition (figures 1 and 2). Considering that the Fe^{3+} ions with distorted tetrahedral coordinations were not detected in Fe-ZSM-5 (IA) and Fe-ZSM-5 (CA), which showed higher/similar SCR activities as compared with Fe-ZSM-5 (SS) and Fe-ZSM-5 (CV), they may not be the necessary active sites for the SCR reaction. Moreover, a strong signal ($g \approx 2.2$) due to iron oxides (α-Fe_2O_3 and/or Fe_3O_4) was also observed in the Fe-ZSM-5 (SS) (figure 1(c)). They were probably generated from hydrolysis and oxidation of $FeCl_2 \cdot 4H_2O$ during the heating process. Our previous study showed that Fe_2O_3-doped H-ZSM-5 was much less active than Fe-exchanged ZSM-5 [5]. Hence, they are not likely the active sites for the SCR reaction. In all four Fe-ZSM-5 catalysts, a large amount of Fe^{3+} ions with tetrahedral coordination ($g = 4.3$) were detected (figure 1). The Fe^{3+} ions could be reduced to Fe^{2+} ions in flowing 5.34% H_2/N_2 at high temperatures, according to our previous TPR and ESR results [6]. When the reduced sample was treated by 5% O_2/He at $500\,^\circ$C, the Fe^{2+} ions were oxidized back to the Fe^{3+} ions. Hence, the Fe^{3+} ions with tetrahedral coordination are stable under the redox treatment [6]. In combination with the SCR results that these catalysts were highly active (table 2), Fe^{3+} ions with tetrahedral coordination appear to be the active sites for the SCR reaction. Since almost all of the Fe^{3+} cations in Fe-ZSM-5 (IA) and Fe-ZSM-5 (CA) were present as Fe^{3+} ions with tetrahedral coordination, they showed very high activities. However, because iron content will also affect the SCR activity [5], this factor makes it com-

plicated to compare the SCR activities of the four Fe-ZSM-5 catalysts.

4. Conclusions

Based on the above results, it can be concluded that all of the Fe-ZSM-5 catalysts were highly active for SCR of NO with ammonia, although they were prepared using different methods. Under the same conditions with a very high space velocity (GHSV $= 1.1 \times 10^6$ h^{-1}), SCR activities decreased in the sequence of Fe-ZSM-5 (IA) > Fe-ZSM-5 (CA), Fe-ZSM-5 (SS) > Fe-ZSM-5 (CV). ESR results indicated that iron oxides, Fe^{3+} ions with tetrahedral and distorted tetrahedral coordinations were present in the catalysts, but only Fe^{3+} ions with tetrahedral coordination were the active sites for the SCR reaction.

Acknowledgement

References

[1] H. Bosch and F. Janssen, Catal. Today 2 (1988) 369.
[2] P. Forzatti and L. Lietti, Heterogen. Chem. Rev. 3 (1996) 33.
[3] G. Busca, L. Lietti, G. Ramis and F. Berti, Appl. Catal. B 18 (1998) 1.
[4] R.Q. Long and R.T. Yang, J. Am. Chem. Soc. 121 (1999) 5595.
[5] R.Q. Long and R.T. Yang, J. Catal. 188 (1999) 332.
[6] R.Q. Long and R.T. Yang, J. Catal. 194 (2000) 80.
[7] R.Q. Long, R.T. Yang and K.D. Zammit, US Patent pending, US Patent file no. 60/136 626.
[8] X. Feng and W.K. Hall, Catal. Lett. 41 (1996) 45.
[9] W.K. Hall, X. Feng, J. Dumesic and R. Watwe, Catal. Lett. 52 (1998)13.
[10] H.Y. Chen and W.M.H. Sachtler, Catal. Today 42 (1998) 73.
[11] A.V. Kucherov, C.N. Montreuil, T.N. Kucherova and M. Shelef, Catal. Lett. 56 (1998)173.
[12] R. Joyner and M. Stockenhuber, J. Phys. Chem. B 103 (1999) 5963.
[13] L.J. Lobree, I.-C. Hwang, J.A. Reimer and A.T. Bell, J. Catal. 186 (1999) 242.
[14] P. Marturano, L. Drozdova, A. Kogelbauer and R. Prins, J. Catal. 192 (2000) 236.
[15] A.V. Kucherov and A.A. Slinkin, Zeolites 8 (1988) 110.
[16] D. Goldfarb, M. Bernardo, K.G. Strohmaier, D.E.W. Vaughan and H. Thomann, J. Am. Chem. Soc. 116 (1994) 6344.
[17] A.V. Kucherov and A.A. Slinkin, J. Phys. Chem. 93 (1989) 864.
[18] R.Q. Long and R.T. Yang, J. Catal. 198 (2001) 20.