

# Influence of the preparation method on the properties of Fe-ZSM-5 for the selective catalytic reduction of NO by *n*-decane

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## Abstract

The selective catalytic reduction of NO by *n*-decane was studied on Fe-ZSM5 catalysts prepared by chemical vapor deposition and solid-state ion exchange from FeCl<sub>3</sub>, ligand exchange from iron acetylacetonate in toluene, and impregnation or ion exchange with iron nitrate in water. These catalysts were characterized using a wide variety of techniques. Activity tests were carried out by temperature-programmed surface reaction (TPSR) or at steady state. The most active materials were those characterized by the presence of iron species reducible at approximately 640 K, and assigned to cationic iron oxo species such as [(OH)–Fe–O–Fe–(OH)]<sup>2+</sup>. The NO conversion during steady-state experiments was lower than in TPSR tests, due to the build-up of a carbonaceous deposit. Water and SO<sub>2</sub> reversibly poisoned the NO conversion.

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## 1. Introduction

The reduction to nitrogen of NO<sub>x</sub> emissions from mobile sources still remains challenging. Among the different possible NO<sub>x</sub> control techniques, the direct selective catalytic reduction (SCR) of NO<sub>x</sub> by hydrocarbons requires less technology and has attracted attention. In particular, zeolite-based catalysts have demonstrated interesting properties, which have been reviewed in recent reports [1–4]. Within this class of catalysts, there is renewed interest in Fe-loaded zeolites based on an initial report describing outstanding SCR catalytic activity [5], as well as on the lesser disposal problems of Fe-zeolite. It was further demonstrated that the protocol followed for catalyst

preparation constitutes a crucial point [6–12] and that conceptual design of the postulated active site is quite difficult to achieve. Further progress has to take into account the fact that the reductant most often used, isobutane, which provides the highest reaction rates with Fe-zeolite catalysts, is less practical for all commercial purposes. However, for deNO<sub>x</sub>ing on TMI zeolite, only a few works have focused on the use of the higher alkanes present in diesel exhaust and fuel [13–15]. On Cu-, Ag- and Co-ZSM-5, NO reduction with C<sub>n</sub>H<sub>2n+2</sub> (*n* = 1–6,8,10) showed a volcano-type correlation to the carbon number in the *n*-alkane [15]. The maximum was at *n* = 4 or 5, depending on the cation and the presence of water, and the use of *n*-decane led to a three- or four-fold decrease in activity. The aim of the present work was to evaluate the properties of Fe-ZSM-5 for the reduction of NO by *n*-decane. *n*-Decane was chosen as a compromise between the chain length representative of diesel fuel composition and practical use for laboratory experiments.

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Obviously, the preparation method and the degree of Fe exchange are vital parameters that determine the catalytic performance of Fe-ZSM-5. Thus, three general preparation methods for introducing Fe were investigated: sublimation of FeCl<sub>3</sub> in Ar [6], ligand exchange from Fe-acetylacetonate [Fe(acac)<sub>3</sub>] [16], and classical ion-exchange or impregnation with Fe(NO<sub>3</sub>)<sub>3</sub> in aqueous solution.

## 2. Experimental

### 2.1. Preparation of the catalysts

The various Fe-ZSM-5 catalysts were prepared by chemical vapor deposition (CVD), solid-state ion exchange (SSIE), ligand exchange (LE), impregnation (IMP) and ion exchange (IE). The sample coding was Fe(*x*)-ZSM5-CVD,SSIE,LE,IMP,IE, with *x* = Fe/Al (mol/mol).

#### 2.1.1. Materials

The starting zeolite was NH<sub>4</sub>-ZSM5 (Zeolyst CBV3024E, Si/Al = 15, *S*<sub>BET</sub> = 400 m<sup>2</sup> g<sup>-1</sup>). The Fe precursors were FeCl<sub>3</sub> (Aldrich, >97%), Fe(acac)<sub>3</sub> (Aldrich, >99.9%) and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Fluka, >99%).

#### 2.1.2. Fe(0.5)-ZSM5-CVD, Fe(0.83)-ZSM5-CVD

These two catalysts were prepared according to the protocol described by Chen and Sachtler [6]. Briefly, NH<sub>4</sub>-ZSM5 was changed to the H-ZSM5 form by calcination in air at 873 K. FeCl<sub>3</sub> as a separate bed was then sublimed at 593 K into the cavities of H-ZSM5, where it reacted chemically with protons according to the reaction: H<sup>+</sup> + FeCl<sub>3</sub> = [FeCl<sub>2</sub>]<sup>+</sup> + HCl<sup>+</sup>. The [FeCl<sub>2</sub>]<sup>+</sup>-loaded sample was washed with water and calcined in air at 823 K.

#### 2.1.3. Fe(1.02)-ZSM5-SSIE

Powdered solid H-ZSM5 + FeCl<sub>3</sub> was heated in Ar at 593 K. The resulting solid was washed with water and calcined in air at 823 K.

#### 2.1.4. Fe(0.96)-ZSM5-LE

A solution of Fe(acac)<sub>3</sub> in toluene was placed in contact with H-ZSM5 for 24 h at 298 K under stirring. The solvent was then evaporated and the solid was dried at 353 K and calcined at 823 K [16].

#### 2.1.5. Fe(0.87)-ZSM5-IMP

An aqueous solution of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O was placed in contact with NH<sub>4</sub>-ZSM5 at 398 K for 24 h. The water was then evaporated, and the solid was first dried at 353 K and then calcined at 823 K.

#### 2.1.6. Fe(0.35)-ZSM5-IE

An aqueous solution of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O was placed in contact with NH<sub>4</sub>-ZSM5 at 398 K for 24 h. After filtration, the solid was dried at 353 K and then calcined at 823 K.

### 2.2. Characterization

Chemical analyses were performed at the Service Central d'Analyse du CNRS (Vernaison, France) by ICP (Table 1). All the materials were characterized by N<sub>2</sub> physisorption at 77 K on a Micromeritics ASAP 2100 instrument, X-ray diffraction (XRD), <sup>27</sup>Al NMR magic-angle spinning (MAS), Mössbauer spectroscopy and temperature programmed reduction (TPR). TPR by H<sub>2</sub> was carried out using a Micromeritics AutoChem 2910 instrument with thermal conductivity detection (TCD). The H<sub>2</sub> consumption was determined after trapping H<sub>2</sub>O at approximately 200 K. The TPR was carried out with H<sub>2</sub>/Ar (3:97 v/v) after 200 mg of sample was calcined at 823 K in air for 2 h, then cooled to room temperature (RT) in air. After outflowing the sample with air, the TPR was then started up to 1300 K (flow 13 cm<sup>3</sup> min<sup>-1</sup>; ramp 10 K min<sup>-1</sup>).

### 2.3. Catalytic tests

The SCR of NO by *n*-decane was studied in a flow reactor operating at atmospheric pressure. Catalyst aliquots (~100 mg) were activated in situ at 823 K in air (O<sub>2</sub>/N<sub>2</sub> ratio 20:80) for 2 h and then cooled to room temperature. The reaction gas, a mixture of NO/*n*-decane/O<sub>2</sub>/He (0.1:0.03:9.0:90.87), was fed to the catalyst. The gas hourly space velocity (GHSV) was 35,000 or 10,000 h<sup>-1</sup>. Catalytic tests were carried out using temperature-programmed surface reaction (TPSR) from 473 to 823 K at 10 K min<sup>-1</sup>, 1, or at steady state. The effluent composition was continuously monitored by on-line sampling linked to a quadruple mass spectrometer (Pfeiffer Omnistar) equipped with Channeltron and Faraday detectors (0–200 amu) and by IR spectroscopy using a Brüker Vectra 22 equipped with a

Table 1  
Chemical composition of the various samples and hydrogen consumption during the H<sub>2</sub>-TPR experiments

Sample	Chemical composition (wt.%)			Volume in micropores (cm <sup>3</sup> g <sup>-1</sup> )	H <sub>2</sub> /Fe consumption (mol/mol)		
	Si	Al	Fe		<750 K	750–1000 K	>1000 K
Fe(0.5)-ZSM5-CVD	40.3	2.08	2.1	0.13	0.53	0.15	–
Fe(0.83)-ZSM5-CVD	37.4	2.2	3.8	0.11	0.50	0.13	0.27
Fe(1.02)-ZSM5-SSIE	37.5	2.1	4.4	0.11	0.10	0.70	–
Fe(0.96)-ZSM5-LE	36.4	2.1	4.2	0.11	0.34	0.03	0.23
Fe(0.87)-ZSM5-IMP	37.3	2.1	3.9	0.11	0.35	0.26	–
Fe(0.35)-ZSM5-IE	39.4	2.2	1.6	–	0.37	0.06	–

gas cell. The concentrations of reactants and products were derived from intensities using standardization procedures before and after each experiment.

### 3. Results and discussion

The results of the N<sub>2</sub> adsorption experiments revealed that there was no great modification of the textural properties of H-ZSM5 after Fe loadings. The same holds for the coordination of Al, which remained almost tetrahedral, as shown by the peak at 55 ppm in <sup>27</sup>Al NMR MAS. The XRD powder patterns of Fe-containing zeolites showed that the zeolite crystallinity was also retained after Fe loading. Low-intensity diffraction lines characteristic of hematite were only detected for Fe(1.02)-ZSM5-SSIE. A mean particle size for α-Fe<sub>2</sub>O<sub>3</sub> of 6.5 nm was determined by small-angle X-ray scattering on this sample.

The presence of α-Fe<sub>2</sub>O<sub>3</sub> clusters was confirmed by Mössbauer spectroscopy, with the occurrence of a sextet signal in Fe(1.02)-ZSM-SSIE with hyperfine field HF = 51.3 close to 52.1 T usually observed for the α-Fe<sub>2</sub>O<sub>3</sub> phase (Table 2). Two sextets were also observed for Fe(0.87)-ZSM5-IMP, providing evidence of the presence of several aggregated oxide or oxo/hydroxo phases, not detectable by XRD. All the samples exhibited a well-resolved doublet due to the mutual interaction of neighboring Fe<sup>3+</sup> atoms [17].

These spectra show that the catalysts prepared by CVD and LE are composed of Fe species of a rather homogeneous nature (Fig. 1).

A study of the reducibility of iron species of calcined materials was carried out by H<sub>2</sub>-TPR. The TPR plots for the various samples are presented in Fig. 2, as well as for a reference 8% α-Fe<sub>2</sub>O<sub>3</sub> + H-ZSM5. From various TPR studies of Fe-ZSM5 [9,10,18–20], there is general agreement that the peak for hydrogen consumption centered around 640 K can be attributed to the reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> in Fe species by charge compensation of the framework. In-depth studies by extended X-ray absorption fine structure (EXAFS), <sup>27</sup>Al NMR MAS and Mössbauer

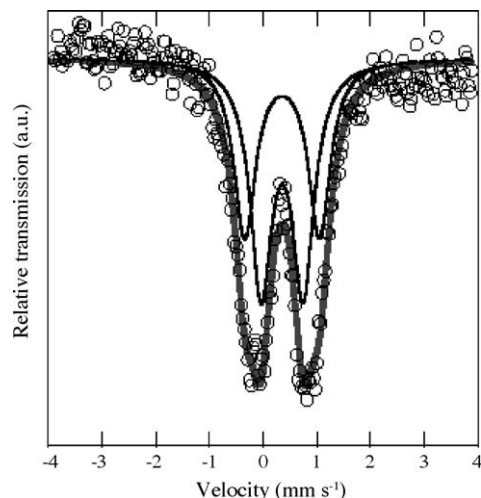


Fig. 1. Mössbauer spectrum of Fe(0.83)-ZSM5-CVD.

spectroscopy concluded that these species are very likely binuclear oxocations with an oxygen bridge of the simplified formula [(OH)–Fe–O–Fe–(OH)]<sup>2+</sup> responsible for various electrostatic interactions with the framework [11,21–23]. In particular, H<sub>2</sub>-TPR and CO-TPR have shown a similar H<sub>2</sub>/Fe and CO/Fe consumption value of approximately 0.5 [18]. The subsequent reduction of Fe<sup>2+</sup>(OH)<sup>−</sup> to Fe<sup>0</sup> occurs in one step above 900–1100 K. A higher content of Fe<sup>2+</sup>(OH)<sup>−</sup> may favor this reduction process at a lower temperature, as shown with samples Fe(0.83)-ZSM5-CVD and Fe(0.96)-ZSM5-LE. The several hydrogen consumption peaks between 700 and 1000 K are associated with the reduction of clustered Fe<sub>2</sub>O<sub>3</sub> phases (Fe<sub>2</sub>O<sub>3</sub> → Fe<sub>3</sub>O<sub>4</sub> → FeO → Fe<sup>0</sup>), as shown by the TPR profile for the reference α-Fe<sub>2</sub>O<sub>3</sub> + H-ZSM5 material (Fig. 2, trace a). The exact temperature at which this stepwise reduction process takes place depends on the nature of the α- or γ-Fe<sub>2</sub>O<sub>3</sub> phase [11] and on the cluster size. It is clearly evident that the samples prepared by SSIE and IMP contain the largest proportion of clustered oxide phase. In contrast, the IE- and LE-synthesized samples do contain this type of Fe phase at more than trace amounts. Moreover, it can be assumed that CVD and LE preparations

Table 2

Mössbauer parameters from the spectra of some samples (δ: isomer shift, Δ: quadrupole splitting, HF: hyperfine field, Γ: linewidth, C: contribution)

Sample	δ (mm s <sup>−1</sup> )	Δ (mm s <sup>−1</sup> )	HF (T)	Γ (mm s <sup>−1</sup> )	C (%)	Attribution
Fe(1.02)-ZSM5-SSIE	0.37(4)	−0.21(1)	51.3(3)	0.32(1)	75	α-Fe <sub>2</sub> O <sub>3</sub>
	0.37(2)	0.80(3)	–	0.63(5)	25	Fe <sup>III</sup>
Fe(0.87)-ZSM5-IMP	0.37(1)	−0.23(2)	50.8(4)	0.37(2)	46	α-Fe <sub>2</sub> O <sub>3</sub>
	0.36(1)	0.80(2)	–	0.63(3)	22.5	Fe <sup>III</sup>
	0.35(1)	−0.23(2)	44.7(3)	0.36(2)	14.8	δ-FeOOH
	0.37(1)	−0.06(1)	39.4(2)	0.36(2)	13.5	δ-FeOOH
Fe(0.96)-ZSM5-LE	0.41(2)	4.99(4)	–	0.54(2)	3.2	Fe <sup>III</sup>
	0.35(1)	0.81(2)	–	0.59(2)	100	Fe <sup>III</sup>
Fe(0.5)-ZSM5-CVD	0.350(11)	1.37(64)	–	0.45	26(4)	β-FeOOH
	0.350(11)	0.72(25)	–	0.45	62(4)	β-FeOOH
	1.460(60)	1.312	–	0.45	12(2)	Fe <sup>II</sup>
Fe(0.83)-ZSM5-CVD	0.355	1.38(27)	–	0.49(2)	44(3)	β-FeOOH
	0.355	0.77(22)	–	0.49(2)	56(3)	β-FeOOH

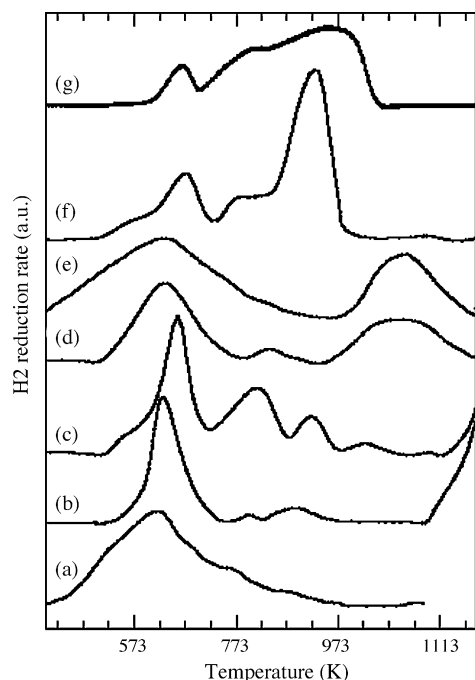


Fig. 2.  $H_2$ -TPR profiles of calcined Fe-ZSM-5 catalysts: (a) Fe(0.5)-ZSM5-CVD, (b) Fe(0.35)-ZSM5-IE, (c) Fe(0.87)-ZSM5-IMP, (d) Fe(0.96)-ZSM5-LE, (e) Fe(0.83)-ZSM5-CVD, (f) Fe(1.02)-ZSM5-SSIE, (g) 8%Fe<sub>2</sub>O<sub>3</sub> + H-ZSM-5. Conditions:  $H_2/Ar$  (3/97 v/v), ramp: 10 K min<sup>-1</sup>.

lead to samples with the highest wt.% content of cationic iron oxo species.

The results of the catalytic reduction of NO by *n*-decane on Fe-ZSM5 are presented in Fig. 3 and Table 3. Fig. 3 shows the NO and *n*-decane conversions, as well as the CO and CO<sub>2</sub> yields, on (0.5)Fe-ZSM5-CVD (TPSR protocol) as an example. The shapes of the plots are similar for all of the samples. As in most of the previous studies of NO<sub>x</sub> reduction by hydrocarbons on Fe-ZSM5, NO conversion peaked at 650–670 K when full *n*-decane oxidation was reached. Below 623 K, significant CO content was present in the

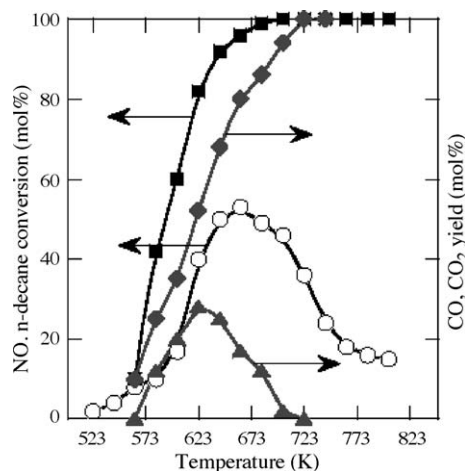


Fig. 3. NO (○) and *n*-decane (■) conversions, CO (▲) and CO<sub>2</sub> (◆) yields, on Fe(0.5)-ZSM5-CVD; catalytic experiments in TPSR mode. NO/*n*-decane/O<sub>2</sub>/He (0.1/0.03/9.0/90.87), GHSV = 35,000 h<sup>-1</sup>, ramp: 10 K min<sup>-1</sup>.

Table 3

Some catalytic properties of the samples in the reduction of NO by *n*-decane in TPSR mode: NO/*n*-decane/O<sub>2</sub>/He (0.1/0.03/9.0/90.87), GHSV = 35,000 h<sup>-1</sup>, ramp: 10 K min<sup>-1</sup>

Sample	Maximum NO conversion		$T_{50}^a$ (K)	Yield at 673 K (mol%)	
	Conversion (mol%)	$T_{max}$ (K)		CO	CO <sub>2</sub>
Fe(0.5)-ZSM5-CVD	53	663	585	15	85
Fe(0.83)-ZSM5-CVD	54	665	580	60	40
Fe(1.02)-ZSM5-SSIE	56	673	578	60	40
Fe(0.96)-ZSM5-LE	53	670	578	60	40
Fe(0.87)-ZSM5-IMP	47	700	598	60	40
Fe(0.35)-ZSM5-IE	35	716	653	60	40

<sup>a</sup> Temperature of 50% conversion of *n*-decane.

effluent and the oxidation of *n*-decane to CO<sub>2</sub> became clearly selective above 700 K. A similar volcano-type profile for the CO yield was reported for the reduction of NO by isobutane [6] and by propane [24] on Fe-ZSM5. In both cases, the CO yield peaked at 50–60% around 600–620 K. It was generally agreed that the volcano-type conversion of NO as a function of temperature was due to the prevailing occurrence of direct alkane oxidation by oxygen at high temperature, without the involvement of NO. In addition, there was no interpretation of the apparent correlation between the volcano-shaped dependence of NO conversion and CO yield, other than a factual observation.

Table 3 summarizes the catalytic data found for various samples at the temperature of maximum NO conversion ( $T_{max}$ ) and of half *n*-decane conversion ( $T_{50}$ ), as well as the CO<sub>2</sub> and CO yield at 673 K. These data call for several comments:

- (1) The temperature  $T_{max}$  at which NO conversion peaked is very similar (52–56% NO conversion at approximately 670 K) for the samples prepared by CVD, SSIE and LE. The samples prepared from impregnation or ion exchange in the aqueous phase are less active (35–45% NO conversion at 700–715 K). This is in agreement with a previous report on NO reduction by propene [25] on a Fe-ZSM5-IE, which showed  $T_{max}$  of approximately 700 K.
- (2) The changes in  $T_{50}$  correlate with those in  $T_{max}$  for NO conversion. Namely, for the less active samples prepared in the aqueous phase,  $T_{50}$  ranges between 600 and 660 K, while the value is  $570 \pm 5$  K for the other samples. This reflects the fact that for elaboration of an efficient HC-deNO<sub>x</sub> catalyst, the ability to activate the alkane at low temperature is crucial.
- (3) There are significant differences in the yields of CO and CO<sub>2</sub> during the oxidation of *n*-decane at 673 K. All samples but one exhibited similar CO yields of 40–50%, in agreement with most of values reported in the literature for HC-deNO<sub>x</sub> with lower alkanes [6,24]. Interestingly, the (0.5)Fe-ZSM5-CVD sample exhibited a much lower CO yield, which is an attractive point.

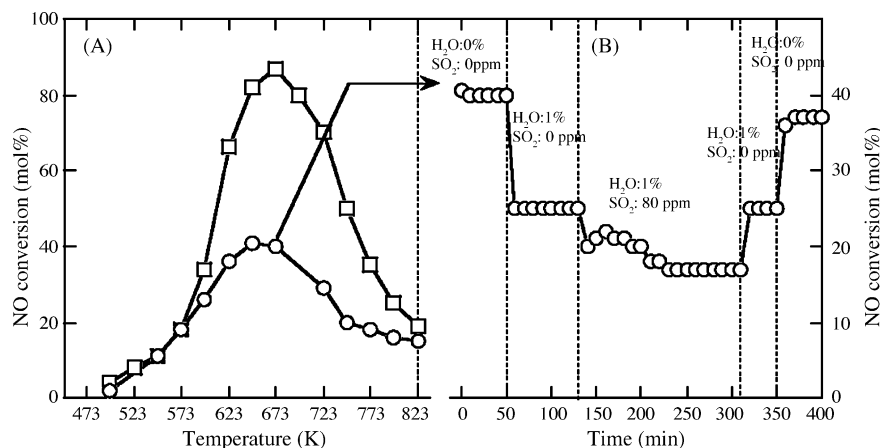


Fig. 4. (A) NO conversions on Fe(0.5)-ZSM5-CVD, (□) TPSR mode, (○) steady state experiments. (B) NO conversions on Fe(0.5)-ZSM5-CVD as a function of time in the presence of 1% of H<sub>2</sub>O and 80 ppm of SO<sub>2</sub>. NO/*n*-decane/O<sub>2</sub>/He (0.1/0.03/8.0/91.87), GHSV = 10,000 h<sup>-1</sup>, ramp: 10 K min<sup>-1</sup> (TPSR mode).

These catalytic data were obtained by carrying out reactions in the TPSR mode. With the aim of testing the stability of the catalysts in wet and dry conditions, and in the presence of SO<sub>2</sub>, we chose Fe(0.5)-ZSM5-CVD, which was one of the most active samples and showed the lowest selectivity for CO, for further experiments. The sample was tested by ramping from 473 to 823 K in steps of 50 K, after which the reaction temperature was kept constant for 2 h (GHSV = 10,000 h<sup>-1</sup>).

Fig. 4A shows the conversion of NO on Fe(0.5)-ZSM5-CVD during tests performed in TPSR mode and at steady state. The activity was much lower at steady state in comparison with TPSR experiments. This difference comes from the build-up of a carbonaceous deposit during the reaction; the sample turned dark brown during the course of the reaction. It seems that carbon deposition was nearly complete at the end of the TPSR test at 823 K, since the NO conversion rate then became similar to that observed at steady state. To explain this behavior, some studies on the deactivation process are in progress [26].

The influence of 1% of H<sub>2</sub>O and/or 80 ppm SO<sub>2</sub> on the SCR activity of (0.5)Fe-ZSM5-CVD at 753 K is shown in Fig. 4B. First, the addition of H<sub>2</sub>O alone decreased the NO conversion two-fold. This behavior is not in line with previous reports, which claimed that H<sub>2</sub>O has no effect on the SCR activity, or even a slightly positive influence [5,6]. These latter studies were carried out with lower alkanes, indicating that the effect of H<sub>2</sub>O might be different with higher alkanes.

When SO<sub>2</sub> and H<sub>2</sub>O were both present in the feed, there was an additional decrease in activity. It is worth noting that this poisoning effect of H<sub>2</sub>O and SO<sub>2</sub> was not permanent, since the initial NO conversion rate was recovered when the feed was switched to an SO<sub>2</sub>-free dry feed. The reversible inhibiting effect of SO<sub>2</sub> may be interpreted as being due to strong adsorption on [(OH)-Fe-O-Fe-(OH)]<sup>2+</sup> active sites to yield [(OH)-Fe-(SO<sub>x</sub>)-Fe-(OH)]<sup>2+</sup>, in competition with the adsorption of NO to yield [(OH)-Fe-(NO<sub>x</sub>)-Fe-(OH)]<sup>2+</sup>.

This step was indeed considered as rate-determining in SCR by isobutane [27] and by NH<sub>3</sub> [28].

#### 4. Conclusions

The activity of SCR by *n*-decane was lower at steady state in comparison with TPSR tests, due to the build-up of a carbonaceous deposit. Differently from lower alkanes, water poisoned the SCR activity. An additional poisoning effect was observed when SO<sub>2</sub> was present in the feed; this inhibition by H<sub>2</sub>O and SO<sub>2</sub> was reversible, and the SO<sub>2</sub> effect might originate from competitive adsorption between SO<sub>2</sub> and NO on the [(OH)-Fe-O-Fe-(OH)]<sup>2+</sup> active sites.

The catalysts prepared by chemical vapor deposition from FeCl<sub>3</sub>, and by ligand exchange from iron acetylacetonate were the most efficient materials. They contained a higher proportion of the postulated [(OH)-Fe-O-Fe-(OH)]<sup>2+</sup> active sites, characterized by a reduction peak at approximately 640 K in H<sub>2</sub>-TPR.

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#### References

- [1] Y. Traa, B. Burger, J. Weitkamp *Microporous Mesoporous Mat.* 30 (1999) 3.
- [2] V.I. Parvulescu, P. Grange, B. Delmon, *Catal. Today* 46 (1998) 233.
- [3] A. Fritz, V. Pitchon, *Appl. Catal. B* 13 (1997) 1.
- [4] G. Delahay, D. Berthomieu, A.B. Goursot, in: M.A. Keane (Ed.), *Coq Interfacial Application of Environmental Engineering*, Marcel Dekker, New York, 2002, p. 1.
- [5] X. Feng, W.K. Hall, *J. Catal.* 166 (1997) 368.



- [6] H.-Y. Chen, W.M.H. Sachtler, *Catal. Lett.* 50 (1998) 125.
- [7] P. Marturano, A. Kogelbauer, R. Prins, *Stud. Surf. Sci. Catal.* 125 (1999) 619.
- [8] M. Kögel, R. Mönnig, W. Schwieger, A. Tissler, T. Turek, *J. Catal.* 182 (1999) 470.
- [9] R.W. Joyner, M. Stochenhuber, *J. Phys. Chem. B* 103 (1999) 5963.
- [10] J.J. Lobree, I.-C. Hwang, J.A. Reimer, A.T. Bell, *J. Catal.* 186 (1999) 242.
- [11] F. Heinrich, C. Schmidt, E. Löffler, W. Grünert, *Catal. Commun.* 2 (2001) 317.
- [12] I.M. Saaid, A.R. Mohamed, S. Bhatia, *React. Kinet. Catal. Lett.* 75 (2002) 359.
- [13] F. Witzel, G.A. Sill, W.K. Hall, *J. Catal.* 149 (1994) 229.
- [14] G. Delahay, B. Coq, L. Broussous, *Appl. Catal. B* 12 (1997) 49.
- [15] A. Schichi, Y. Kawamura, A. Satsuma, T. Hattori, *Stud. Surf. Sci. Catal.* 135 (2001) 4876.
- [16] G. Delahay, A. Guzmán-Vargas, D. Valade, B. Coq, *Stud. Surf. Sci. Catal.* 154 (2004) 2501.
- [17] A.A. Battiston, J.H. Bitter, F.M.H. de Groot, A.R. Overweg, O. Stephan, J.A. van Bokhoven, P.J. Koyman, C. van der Spek, G. Vankó, D.C. Koningsberger, *J. Catal.* 213 (2003) 251.
- [18] E.-M. El-Malki, R.A. van Santen, W.M.H. Sachtler, *J. Phys. Chem. B* 103 (1999) 4611.
- [19] Z. Sobalík, A.A. Belhekar, Z. Tvaruzková, B. Wichterlová, *Appl. Catal. A* 188 (1999) 175.
- [20] A. Guzmán-Vargas, G. Delahay, B. Coq, *Appl. Catal. B* 42 (2003) 369.
- [21] T.M. Voskoboinikov, H.-Y. Chen, W.M.H. Sachtler, *Appl. Catal. B* 19 (1998) 279.
- [22] P. Marturano, L. Drozdová, A. Kogelbauer, R. Prins, *J. Catal.* 192 (2000) 236.
- [23] A.A. Battiston, J.H. Bitter, W.M. Heijboer, F.M.H. de Groot, D.C. Koningsberger, *J. Catal.* 215 (2003) 279.
- [24] M. Kögel, V.H. Sandoval, W. Schwieger, A. Tissler, T. Turek, *Catal. Lett.* 51 (1998) 23.
- [25] R.W. Joyner, M. Stochenhuber, *Catal. Lett.* 45 (1997) 15.
- [26] G. Delahay, A. Guzmán-Vargas, B. Coq, *Appl. Catal. B*, submitted for publication.
- [27] H.-Y. Chen, E.-M. El-Malki, X. Wang, R.A. van Santen, W.M.H. Sachtler, *J. Mol. Catal. A* 162 (2000) 159.
- [28] R.Q. Long, R.T. Yang, *J. Catal.* 207 (2002) 224.