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Iron–pentasil molecular sieves: Characterisation and catalytic behaviour in syngas conversion^a

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Abstract

Two series of iron–pentasil molecular sieve catalysts were synthesized. One series consisted of H-ZSM-5 type zeolites with different silicon/aluminium ratios impregnated with ferric nitrate, and the other included ferrisilicates with different silicon/iron ratios. The catalytic tests on syngas conversion were effected at 0.7–2.1 MPa at between 240–300°C in a flow system with a fixed bed reactor. The characterization of the solids shows that in the impregnated series, the iron was transformed into α -iron and carbide phases by means of treatment with hydrogen, carbon monoxide and by the effect of the syngas under the reaction conditions. On the other hand, in the ferrisilicate series, the iron retains the ionic form [iron (III)–iron (II)], regardless of the treatment, thereby indicating its incorporation into the structure of the solid. The catalytic behaviour of both series also differs. The solids produced by impregnation were seen to produce mostly hydrocarbons in the petrol range with the expected selectivity properties, whereas the ferrisilicates were selective towards the formation of i-C₄.

Keywords: ferrisilicates; iron carbides; Mössbauer characterisation; pentasil molecular sieves; syngas conversion

INTRODUCTION

The last few years have seen the appearance of growing interest in syngas conversion as an alternative energy source and means of exploiting the vast

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existing reserves of coal and natural gas [1,2]. Of the Group VIII active elements in this reaction, iron stands out, being the most electropositive and therefore tending to bind more tightly with the other elements such as oxygen and carbon [3]. One of the problems in obtaining hydrocarbons using the Fischer-Tropsch technology is the fact that this reaction follows an Anderson-Schultz-Flory (ASF) type distribution, therefore producing a wide range of products.

A great deal of effort has been devoted recently to the search for alternatives in order to make the reaction more selective. High silica content molecular sieves are interesting because of their low coke formation and form selectivity characteristics [4]. These advantages applied together with an active metal allow the minimization of the formation of hydrocarbons with carbon atoms above the petrol range [5].

Iron may be deposited on zeolite by impregnation or may be introduced during the molecular sieve synthesis into the tetrahedral sites on the structure. The amount of iron added depends on the synthesis conditions [6,7].

According to Meagher et al. [8], the iron in a molecular sieve may be simultaneously present in the following forms: iron(III) in the aluminosilicate framework sites, iron(III) ions acting as counter ions, and as iron oxides precipitated on the zeolite crystals.

In the present work, two series of iron pentasil molecular sieves were prepared where the iron was impregnated or introduced during the synthesis. Characterisation was carried out in order to assess the location and chemical state of the iron and the solids were tested for the hydrogenation of carbon monoxide.

EXPERIMENTAL

Two series of catalysts were synthesized. The first comprised iron impregnated on H-ZSM-5 type zeolites with different silicon/aluminium ratios (19, 41, 56, 73, 114). The solids of this series were prepared following, with little modifications, the method given by the literature [9].

The reaction mix was heated for 24 or 48 h at 170°C. The composition of the initial reaction mix was varied according to the silicon/aluminium ratio desired.

Upon obtaining the solid, it was dried at 120°C for one hour and interchanged with ammonium chloride at 45°C for one hour. The solids were filtered and washed with distilled water until a negative chloride result was obtained. They were then dried and calcined at 500°C in an air flow for three hours to remove ammonia, producing the protonated acid form and then impregnated with a ferric nitrate solution ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) using the incipient wetness technique, which gave a metal percentage of 18% in all cases.

The second catalyst series consisted of ferrisilicates with silicon/iron ratios

of 100 and 3200, prepared with the same iron precursor, using the method of Inui et al. [10]. Prior to any catalytic experiment, the solids were treated with the following procedures at atmospheric pressure:

(a) air calcination (30 ml/min, 450°C, 3 h) followed by reduction with hydrogen (30 ml/min, 450°C, 16 h), "CR" sample.

(b) calcination-reduction in similar conditions to those of (a) followed by carburation with carbon monoxide (12 ml/min, 150-280°C, 14 h), "CRC" sample.

The solids were characterized using atomic absorption spectroscopy (AAS), BET surface area, X-ray diffraction (XRD), electron paramagnetic resonance (EPR), IR and Mössbauer spectroscopy.

The X-ray power diffraction data were obtained using a Philips X-ray diffractometer (Ni filtered Cu K α , 2 θ range 5-40°). For comparison, known samples of the aluminosilicate ZSM-5 were used. Chemical analyses of the samples were performed by atomic absorption spectroscopy, correlated with energy-dispersive X-ray-scanning electron microscopy (EDX-SEM) analysis.

Mössbauer spectra were measured using a conventional constant acceleration spectrometer, using a source of ⁵⁷Co in a palladium matrix. Spectra were recorded in zero field at room temperature. All isomer shifts were quoted relative to an absorber of metallic iron. Fits were performed using a standard least squares fitting routine. IR and EPR studies were conducted in a similar way as reported elsewhere [11,12]

The syngas conversion reaction was studied in a flow system with a stainless steel reactor (20 cm, 0.7 cm I.D.), using 1 g of catalyst, under 0.7-2.1 MPa, 240-300°C, different spacial velocities and a hydrogen/carbon monoxide ratio of 2. The composition of the reaction mix and the products was determined by means of gas chromatography-mass spectrometry.

Carbon monoxide, nitrogen, carbon dioxide and methane were analyzed with a thermal conductivity cell Varian 3700 chromatograph using a Carbosive SII column (60/80 mesh, 1.5 m, 2 mm I.D.).

RESULTS AND DISCUSSION

The values obtained on the surface areas (286-312 m²/g) together with the diffractograms and micrographs, show the production of highly crystalline solids ($\geq 90\%$), as compared with commercial pentasil zeolite, with typical hexagonal morphology. No significant structural changes were recorded following impregnation of these solids.

Fig. 1 shows the Mössbauer spectra of the solid Fe(18)/H-ZSM-5(41) subjected to reduction-carburation treatments and also after reaction.

The spectrum of the untreated impregnated solid (I), manifests a doublet characteristic of iron(III). In addition, a slight asymmetry is observed, indi-

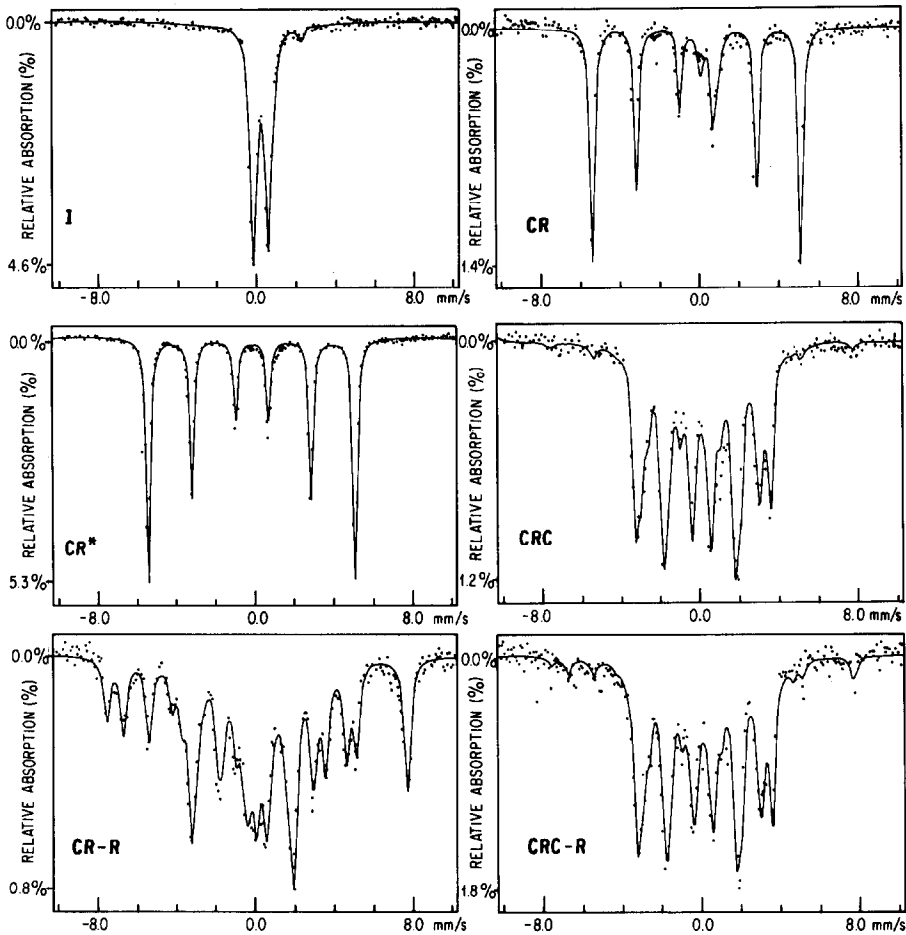


Fig. 1. Mössbauer spectra at room temperature of Fe(18)/H-ZSM-5(41) and (*) Fe(18)/H-ZSM-5(56) solids.

cating the presence of iron (II) in small quantities (7%), which isomeric shift value $IS = 0.25$ mm/s suggests an extra-framework octahedral symmetry.

The spectrum of the calcined and reduced solid Fe(18)/H-ZSM-5(41) (Fig. 1 CR) shows mostly a reduction to α -iron ($H_{hf} = 330$ kG). However, the centre doublet indicates that part of the iron is not completely reduced to metallic iron but 14% remains as Fe^{II} , which would mean a certain degree of iron-support interaction. The carburization of the α -iron sample (Fig. 1 CRC) leads to the transformation into Hägg ($H_{hf} = 216, 186, 111$ kG) and Fe_2C ($H_{hf} = 173$ kG) carbides. The values of the hyperfine fields observed correlated with those recorded by Maksimov et al. [13] and Niemantsverdriet et al. [14].

If a solid is subjected to a syngas reaction for 24 h following calcination-

reduction, it undergoes an in-situ transformation producing a relatively complex spectrum (Fig. 1 CR-R) in which the formation of Hägg (35%) and Fe_2C (12%) carbides is observed coexisting with magnetite (26%), $\alpha\text{-Fe}$ (15%) and Fe^{2+} (12%). When the same solid is precarburated in the presence of carbon monoxide before the syngas reaction, the iron is transformed mostly into Hägg (74%) and Fe_2C (13%) carbides (Fig. 1 CRC). When this solid is subjected to the syngas reaction (Fig. 1 CRC-R) its composition is not significantly modified: 82% of the iron remains in the form of carbides with magnetite being formed to a small extent. The spectrum composition is given in Table 1.

Fig. 1 also shows the Mössbauer spectrum of the $\text{Fe}(18)/\text{H-ZSM-5}(56)$ solid, calcined and reduced (CR^*). In this case a total reduction of iron(III) to metallic iron was observed showing that there is no iron-support interaction, possibly due to the lower density of acid sites of the zeolite, since its silicon/aluminium ratio is lower.

Fig. 2 shows, in the ferrisilicate series, the EPR spectrum of the as-synthesized form of ferrisilicate with a silicon/iron ratio of 100. A doublet at $g=4.3$ and $g=3.8$ assigned to the iron(III) ion in tetrahedral coordination can be seen in addition to a wide signal in the proximity of $g=2.00 \pm 0.02$ possibly due to magnetite occluded within the solid [15]. When this solid is subjected to reduction treatment (spectrum b) the signal at low fields intensifies and the intensity of the wide signal decreases. Having reduced the iron, the signals at low fields would be expected to fall or disappear as in the case of the impregnated solids, but, on the contrary, this signal was seen to increase. This result indicates that the iron(III) ion is within the structure of the solid.

In a tetrahedral weak ligand field the d-electrons of the iron(III) species will show a high spin configuration $S=5/2$, while in a tetrahedral strong ligand

TABLE 1

Designation and spectral composition of the iron phases on $\text{Fe}(18)/\text{H-ZSM-5}(41)$ after different treatments

Hyperfine fields (kG): $\chi\text{-Fe}_5\text{C}_2=216, 186, 111$; $\text{Fe}_2\text{C}=173$; $\text{Fe}_3\text{O}_4=479, 451$

Fase	Procedure		
	CR-R	CRC	CRD-R
$\chi\text{-Fe}_5\text{C}_2$	35\ 38	74\ 87	69\ 82
Fe_2C	3/	13/	13/
Fe_3O_4	26	1	6
$\alpha\text{-Fe}$	15	3	3
Fe^{2+}	12	1	1
Fe^{3+}	90	8	8

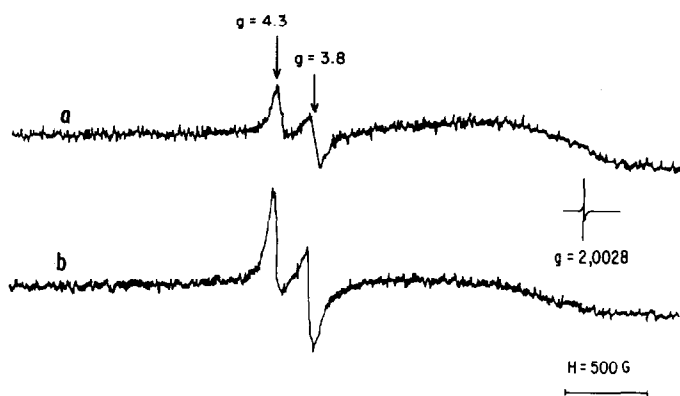


Fig. 2. EPR spectra of iron silicate Si/Fe=100. (a) Fresh and (b) after reduction.

field a low spin configuration $S=1/2$ could be attained [16]. In both cases a single EPR line in the proximity of $g=4.3$ should be expected. The doublet observed in our experiments could be interpreted either as (a) the location of iron (III) species in two different crystallographic environments or (b) in the low spin configuration for a silicon/iron=100, ratio it is statistically possible to have two iron(III) species close enough that a pair $Fe_{1/2}-Fe_{1/2}$ is formed with a total spin $S=1$ [17]. Other authors [5,18] have also observed a doublet in the vicinity of $g=4.3$. In order to clarify this open question, more work is presently under way using different iron (III) concentrations.

The Mössbauer spectra of these solids after syngas reaction (Fig. 3) show an asymmetrical centre doublet, characteristic of the coexistence of iron (III)-iron (II) species (60 and 40%, respectively). The absence of other iron species corroborates the observations made by EPR on the existence of iron in these solids within the ferrisilicate structure.

Supplementary evidence of the incorporation of iron into the zeolite structure was found via IR characterization. Fig. 4 shows the IR spectra of the following solids: (a) Fe(18)/H-ZSM-5 (73), (b) ferrisilicate (Si/Fe=3200), (c) silicalite and (d) Fe(3.8)/silicalite.

In the aluminium silicate zeolites, the symmetric (ν_s) and asymmetric (ν_{as}) stretching vibrations of the $-\{Si-O-Si(Al)\}_n-$ group appear between 600 and 1200 cm^{-1} . The similarity in mass between the silicon and aluminium does not give rise to distinct contributions from the $-\{Si-O-Si\}_n$ and $-\{Si-O-Al\}_n-$ vibrations. However, in the ferrisilicate, the silicon and iron are sufficiently different in atomic weight to change the reduced mass of the harmonic oscillator when iron is substituted for silicon. This difference is sufficient to produce separate bands [7].

Although there are no marked differences between the spectra, in the ferrisilicate spectrum (Fig. 5b), a new band appears at 1050 cm^{-1} as a shoulder of

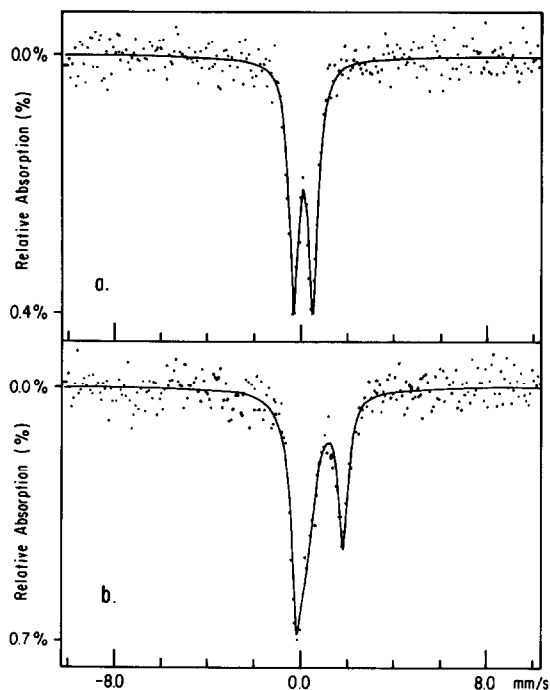


Fig. 3. Mössbauer spectra of iron silicate Si/Fe = 100. (a) Fresh and (b) after syngas exposure.

the 1100 cm^{-1} band which has been attributed to the asymmetric vibration of the $-\{\text{Si-O-Fe}\}_n$ -oscillator consistent with the difference in reduced mass.

The results of the n-hexane cracking reaction with the H-ZSM-5 zeolite with a variable silicon/aluminium ratio (Fig. 5) indicate that the acidity of these solids diminishes drastically as the silicon/aluminium ratio increases. A drop in initial activity is observed which has been attributed to covering the acid sites in the channel intersections of the zeolite with alkyl aromatics [19]. The activity in the Fe/H-ZSM-5 series follows the previous pattern with less activity than in the respective non-impregnated solids, which could mean that iron deposits on the acid sites of the zeolite.

As regards the catalytic behaviour of these solids in the syngas conversion reaction, the product distribution is seen to depend to a great extent on the pretreatment used. (Table 2).

The non carburated solids show an increase in activity with time-on-stream, reaching steady-state reaction conditions after 24 h. The carburated solids in the Fe/H-ZSM-5 series before subjecting them to the syngas conversion reaction makes far more stable catalysts. Thus, the initial activity of the pre-carburated solids was similar to that of noncarburated catalysts at the end of a 24 h period. Several authors [20,21] have also observed a direct correlation

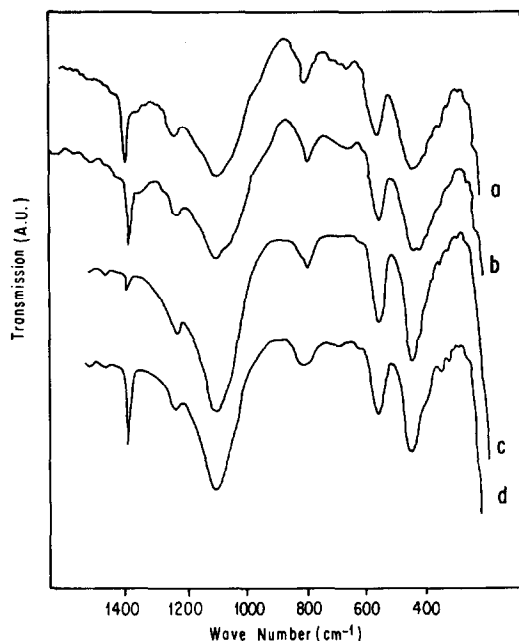


Fig. 4. Framework vibration region in the infrared spectra: (a) Fe(18)/H-ZSM-5(73); (b) iron silicate (Si/Fe=3200); (c) silicate; (d) Fe(3.8) silicalite.

between initial activity increase with carbide formation on iron reduced catalysts.

Greater selectivities towards the formation of compounds in the petrol range was also achieved (Table 2: Fe/H-ZSM-5 (19), CRC against CR). This increase in the C_{5+} selectivity and decrease in methane formation could be correlated to the iron phases present on the solids. As can be seen from Table 1 the non pre-carburated solids show higher magnetite and lower Hägg carbide contents. Soled et al. [22], comparing magnetite and Hägg carbide, also found on bulk iron catalysts that the oxide surface limits the extent of chain growth; the C_{5+} fraction is higher with the carbide.

As in the case of n-hexane reaction, the activity of the Fe/H-ZSM-5 catalyst series is shown to be affected by the silicon/aluminium ratio. The best results of the impregnated series are obtained with the Fe/H-ZSM-5 zeolite with a silicon/aluminium ratio of 73, with a low acid sites density. The effect of the acidity of the support on product distribution has been recognized. On zeolites it has been found that an increase either on the acidity strength or on the density of acidic sites causes the product selectivity to shift toward lower molecular weight hydrocarbons, especially methane [23]. Metal-support interactions as well as a direct involvement of acidic sites on the support were invoked to explain this behaviour.

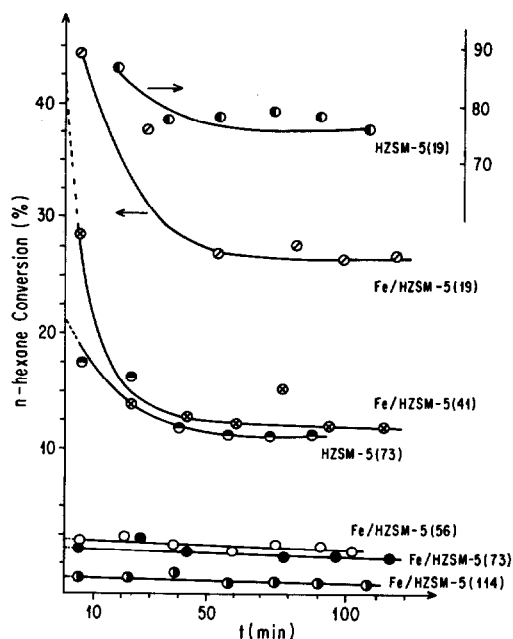


Fig. 5. n-Hexane conversion with time-on-stream. Space velocity $100 \text{ cm}^3 \text{ g}^{-1} \text{ min}^{-1}$, $P=33.5 \text{ kPa}$.

TABLE 2

Hydrocarbon distribution

$\text{H}_2/\text{CO}=2$; reaction time=24 h; $p^{a,b,c}=0.7 \text{ MPa}$; $p^d=1.1 \text{ MPa}$; $T^{a,b,c}=240^\circ\text{C}$; $T^d=345^\circ\text{C}$; $X_{\text{CO}}^{a,b,c}=54\%$; $X_{\text{CO}}^d=25\%$

Catalyst W (%)	Fe/H-ZSM-5 (19)		Fe/H-ZSM-5 (73)	Fe-silicate ^d Si/Fe=3200
	Cr ^a	CRC ^b	CRC ^c	
C ₁	50	35	14	13
C ₂	21	21	14	8
C ₃	12	10	9	11
C ₄	9	14	10	-
i-C ₄	-	-	-	3
C ₅₊	8	20	53	3
C ₂ -C ₄	42	40	33	84

Barrault et al. [24] showed that the acidity of the support of an iron/cobalt catalyst affects the product distribution: with decreasing acidity the proportion of C₅₊ hydrocarbons and alkenes increases, that is to say that the effect of decreasing acidity is similar to that of alkali promotion [25].

In addition, a decrease in the density of acid sites (lower silicon/aluminium ratio) diminishes the probability of secondary cracking reactions on the support, that give rise to lower molecular weight hydrocarbons.

Whereas the solids prepared by impregnation require pre-carburation in order to achieve a stable conversion, this stability is attained after four hours in the case of ferrisilicates whose iron content retains an ionic nature.

It was observed that those solids prepared by impregnation produce mostly hydrocarbons in the petrol range (53%) and present selectivity properties as expected for bulk iron, whereas the ferrisilicates are selective towards the formation of $i\text{-C}_4$ (65%) showing properties of ionic iron.

CONCLUSIONS

The two synthesized series show marked differences in both the iron phases produced during activation and the catalytic behaviour in the presence of the syngas reaction.

In the impregnated series, the extra-framework iron (III) evolves to carbide phases, whereas in the ferrisilicates, it remains as intra-framework iron (III)-iron (II). The different phases present cause the variations in the hydrocarbon distribution.

The carburation of solids prior to subjecting them to the syngas conversion reaction makes far more stable catalysts with greater selectivity towards the formation of compounds in the petrol range.

Those solids prepared by impregnation produce mostly hydrocarbons in the petrol range, whereas the ferrosilicates are selective towards the formation of $i\text{-C}_4$.

REFERENCES

- 1 M.L. Cubeiro, M.R. Goldwasser, V. Báez, F. Navas and M.J. Pérez Zurita, *Rev. Soc. Venez. Catal.*, 3(1) (1989) 38.
- 2 R. Snel, *Catal. Rev. Sci. Eng.*, 29(4) (1987) 361.
- 3 L. Guzzi, *Catal. Rev. Sci. Eng.*, 23(3) (1981) 329.
- 4 W. Holderich, M. Hesse and F. Naumann, *Angew. Chem. Int. Ed. Engl.*, 27 (1988) 226.
- 5 R.B. Borade, *Zeolites*, 7 (1987) 398.
- 6 R.M. Barrer, *Hydrothermal Chemistry of Zeolites*, Academic Press, New York, 1982, p. 251.
- 7 R. Szostak, V. Nair and T.L. Thomas, *J. Chem. Soc. Faraday Trans. 1*, 83 (1987) 487.
- 8 A. Meagher, V. Nair and R. Szostak, *Zeolites*, 8 (1988) 3.
- 9 C. Lechthaler and P. Weisz, *Chem. Tech.*, 6 (1976) 86.
- 10 I. Inui, H. Matsuda, O. Yamase, H. Nagata, K. Fukuda, T. Ukawa and A. Miyamoto, *J. Catal.*, 98 (1986) 491.
- 11 M.R. Goldwasser, J.F. Dutel and C. Naccache, *Zeolites*, 9 (1989) 54.
- 12 E. Pietri de García, M.R. Goldwasser, C.F. Parra and O. Leal, *Appl. Catal.*, 50 (1989) 55.

- 13 Y. Maksimov, I.P. Suzdalev, R.A. Arents and S.M. Lokatev, *Kinet. Katal.*, 15(5) (1974) 1293.
- 14 J.W. Niemantsverdriet, A.M. Van der Kraan, W.L. van Dijk and H.S. van der Baan, *J. Phys. Chem.*, 84 (1980) 3363.
- 15 A. Kotasthane, V.P. Shiralkar and S.G. Hegde, *Zeolites*, 6 (1986) 253.
- 16 H.M. Assenheim, in H.M. Assenheim (Editor), *Introduction to Electron Spin Resonance*, Hilger and Watts Ltd., London, 1966, p. 25.
- 17 G.E. Pake and T.L. Estle, in D. Pines (Editor), *The Physical Principles of Electron Paramagnetic Resonance (Frontiers in Physics, Lecture Note Series)*, 2nd ed., Benjamin, Reading, M.A., 1973, p. 172.
- 18 L.M. Kustov, V.B. Kazanisky and P. Ratnasamy, *Zeolites*, 7 (1987) 80.
- 19 P. Magnoux, P. Cartrud, S. Mignard and M. Guisnet, *J. Catal.*, 106 (1987) 242.
- 20 J.A. Amelse, J.B. Butt and L.J. Schwartz, *J. Phys. Chem.*, 82 (1978) 558.
- 21 G.B. Raupp and W.N. Delgass, *J. Catal.*, 58 (1979) 348.
- 22 S. Soled, E. Iglesia and R.A. Fiato, *Catal. Lett.*, 7 (1990) 271.
- 23 R. Oukaci, J.C.S. Wu and J.G. Goodwin, *J. Catal.*, 110 (1988) 47.
- 24 J. Barrault, J.C. Menezo and R. Maurel, *Bull. Soc. Chim.*, I (1980) 281.
- 25 M. Baerns, *Proceedings of the 9th Iberoamerican Symposium on Catalysis*, Lisbon, Portugal, Vol. 1, 1984, p. 222.