

STUDIES ON THE ACIDITY AND THE STABILITY OF Fe³⁺ IONS IN THE FRAMEWORK OF (Si,Fe)-MCM-22 ZEOLITE. SELECTIVE *PARA*-XYLENE PRODUCTION BY TOLUENE DISPROPORTIONATION

Ioana FECHETE,^{a,c,*} Eric GAUTRON,^b Emil DUMITRIU,^a Doina LUTIC,^d
Philippe CAULLET^c and Henri KESSLER^c

^a Lab. of Catalysis, “Gh. Asachi” Technical University of Iași, 71 D. Mangeron Av, 700050, Iași, Roumania

^b Lab. de Catalyse, Université de Poitiers, 40 Av. du R. Pineau, Poitiers, France

^c Laboratory of Materials with Controlled Porosity, UPRES-A 7016, 3 rue A. Werner, 68093 Mulhouse, France

^d Faculty of Chemistry “A.I. Cuza” University of Iasi, 11 Bd. Carol I, 700506, Iași, Roumania

Received September 25, 2006

(Si,Fe)-MCM-22 zeolite (IZA Code MWW) with Si/Fe ratio of 16 was synthesized at 423 K under dynamic synthesis conditions using hexamethylenimine as template. The as-synthesized and calcined samples of (Si,Fe)-MCM-22 zeolite were characterized by different techniques : X-ray diffraction, ⁵⁷Fe Mossbauer spectroscopy, X-ray emission and TEM coupled with EDX-analysis, SEM, N₂ adsorption-desorption and TPD of ammonia. The results show that the stability of Fe atom in T position is much higher in the as-synthesized sample than that of the calcined sample. As a consequence, the calcination causes the migration of Fe to extraframework positions. The toluene disproportionation reaction has been studied over (Si,Fe)-MCM-22 at 673 K. The fraction of *p*-xylene in xylene isomers formed was higher than its equilibrium value. This behaviour can be explained in terms of the samples acidity.

INTRODUCTION

Various zeolites have been used as catalysts in toluene disproportionation,¹⁻⁷ but the fraction in *p*-xylene isomers was close to the equilibrium value. MCM-22 zeolite,⁸ one of the member of the MWW family of zeolites, which combines the catalytic properties of zeolite with 10-MR and 12-MR, is very promising for this reaction.^{9,10} The Al-MCM-22,⁹ dealuminated Al-MCM-22¹⁰ and Al-MCM-22 modified with indium¹¹ were tested in toluene disproportionation reaction and it has been shown that the complex structure and the acidity of the sample play a significant role in the selective formation of *p*-xylene. Moreover, the high thermal stability, large sorption capacity, and high surface area render this material very interesting for catalysis.¹²

The replacement of Al³⁺ by Fe³⁺ in the framework of zeolite MCM-22 has been already reported. The first description of Fe-MCM-22

synthesis was made in 1997 by Wu *et al.*¹³ and it revealed a good selectivity for oxidative dehydrogenation and for selective catalytic reduction (SCR) of NO with NH₃ in the presence of O₂. Wu *et al.* have investigated the Bronsted acidity of the Fe-MCM-22 zeolite by using infrared spectroscopy and pyridine adsorption and showed that the acidity was much weaker than that of Al-MCM-22 zeolite. Another important example is Fe- and Fe,Al-MCM-22 zeolite synthesized by Testa *et al.*¹⁴ who, studying the acidity of the samples, obtained a similar result : the acid strength can be also decreased by isomorphous substitution of Al³⁺ by Fe³⁺.

In this work, we report the synthesis of (Si,Fe)-MCM-22 zeolite with Si/Fe ratio of 16, obtained under rotating conditions at 423 K and the physicochemical characterization of these samples. Also, we report the catalytic performances of the (Si,Fe)-MCM-22 zeolite in toluene disproportionation reaction.

* Corresponding author: Ioana.Fechete@ecpm.u-strasbg.fr

RESULTS AND DISCUSSION

Synthesis and characterization

The chemical analysis of the as-synthesized sample (Figure 1) performed by EDX revealed that all the iron was incorporated in the zeolite phase. The Si/Fe ratio determined by Si and Fe EDX-analysis is similar to the Si/Fe ratio determined by chemical analysis (Si/Fe = 16). Moreover, it is shown that the amount of Fe is almost the same in

the gel (Si/Fe = 15) and in the solid (Si/Fe = 16). The color of the as-synthesized sample was completely white while the color of the calcined sample was brown, indicating the presence of the colored oxides of iron. It is also known, that the thermal and the hydrothermal stability of tetrahedral Fe in the framework of zeolites are significantly lower than that of Al.¹⁵ The thin platelets form spherical aggregates (Fig. 1) and the morphology does not depend on the treatment of the sample.

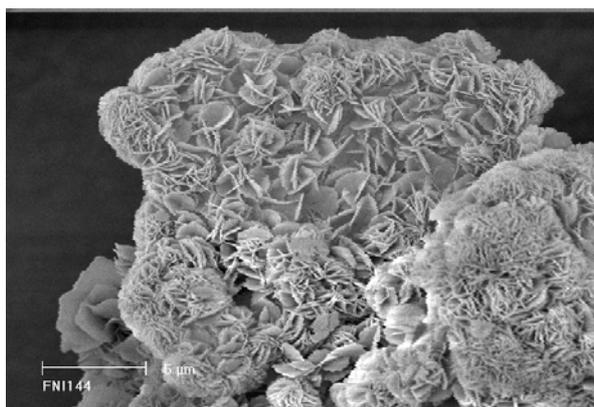


Fig. 1 – Scanning electron micrographs of the calcined sample of (Si,Fe)-MCM-22 zeolite (Si/Fe=16).

In Figs. 2 a and 2 b, the TEM image for the crystals of the as-synthesized Fe-MCM-22 (Si/Fe = 16) sample and the corresponding mapping for the homogeneous iron distribution within the crystals

are presented. The contour of the FeK α X-ray emission map matches the contour of the crystals on the micrographs.

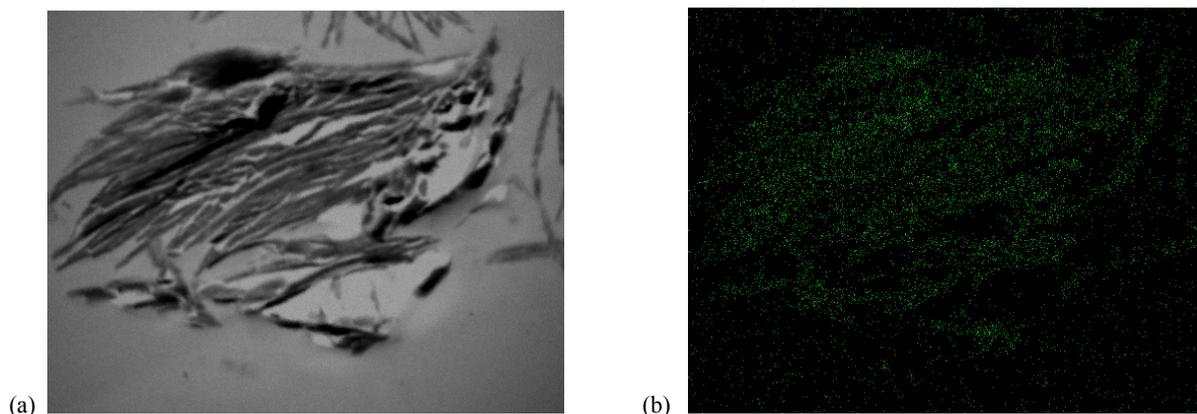


Fig. 2 – Transmission electron microscopy (TEM) (a) and FeK α X ray-emission mapping of the as-synthesized (Si,Fe)-MCM-22 zeolite (Si/Fe=16).

The XRD patterns of as-synthesized (Fig. 3) and calcined (Fig. 4) Fe-MCM-22 samples agreed well with the published data.^{13,14} The high intensity of the peaks in the as-synthesized and calcined samples indicates a high degree of crystallinity. Incorporation of tetrahedral iron atoms into the

zeolite lattice results in an increase of the unit-cell parameters, as a consequence of the higher ionic radius of Fe³⁺ compared to Al³⁺.^{15,16} The cell volume of the calcined Fe-MCM-22 sample was 4450,1 Å³ and 4385,8 Å³ for its analogue Al-MCM-22 zeolite, respectively.¹⁷

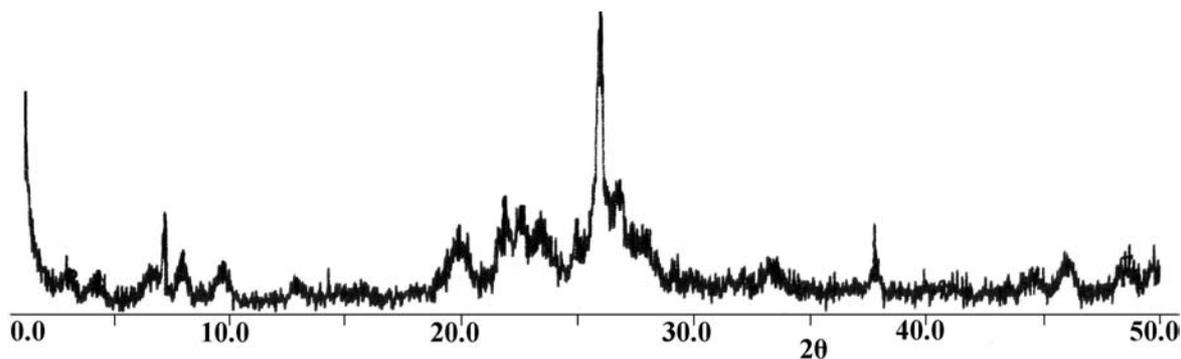


Fig. 3 – XRD of the as-synthesized sample of (Si,Fe)-MCM-22 zeolite (Si/Fe = 16).

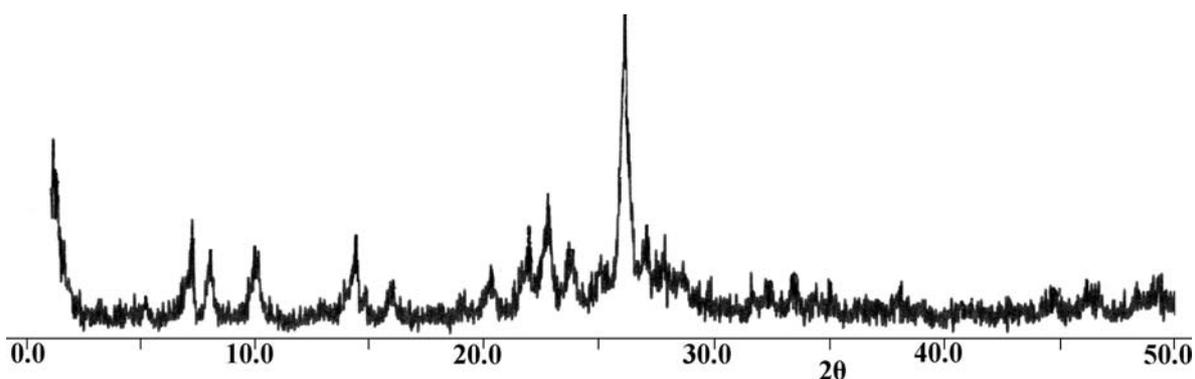


Fig. 4 – XRD of the calcined sample of (Si,Fe)-MCM-22 zeolite (Si/Fe = 16).

The characterization by Mossbauer spectroscopy at room temperature (Fig. 5a) revealed that almost all the iron cations occupy framework positions (tetrahedral Fe³⁺) in the as-synthesized Fe-MCM-22 sample. The isomer shift of the framework Fe³⁺ is equal to 0.18 mm s⁻¹. In the calcined Fe-MCM-

22 sample (Fig. 5b), it was observed the presence of the tetrahedral and octahedral iron cations. Octahedrally coordinated iron is detected with higher isomer shift -0.32 mm s⁻¹ and quadrupolar splitting -0.91 mm s⁻¹. These values are in good agreement with those reported in the literature.^{14,18-20}

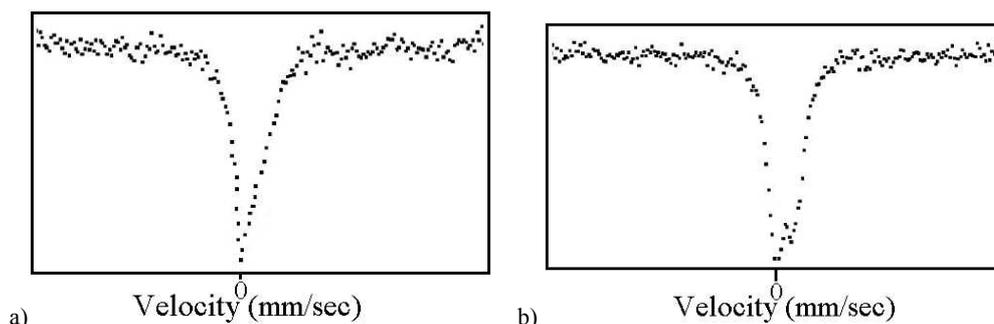


Fig. 5 – Room temperature Mossbauer spectra of as-synthesized (a) and calcined (b) samples of (Si,Fe)-MCM-22 zeolite (Si/Fe=16).

From N₂ adsorption experiments (Fig. 6), resulted that, the calcined Fe-MCM-22 sample had a specific surface area of 530 m² g⁻¹, comparable with that reported by Wu et al.

The TPD curve for the calcined sample of (Si,Fe)-MCM-22 zeolite is given in Figure 7 and the corresponding acidity values in mmol NH₃/g are reported in Table 1. Two desorption peaks

clearly appeared, at 423 K and 623 K respectively. The first peak is attributed to physisorbed NH₃ and partially chemisorbed on weak acid sites, while the second peak corresponds to the decomposition of NH₄⁺ ions and is generally attributed to Bronsted sites, which data are associated with the weak and medium acid strength.

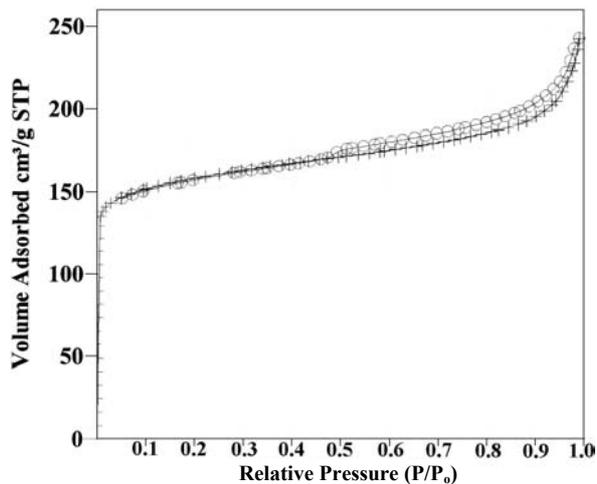


Fig. 6 – N₂ adsorption-desorption isotherm of the calcined sample of (Si,Fe)-MCM-22 zeolite (Si/Fe=16).

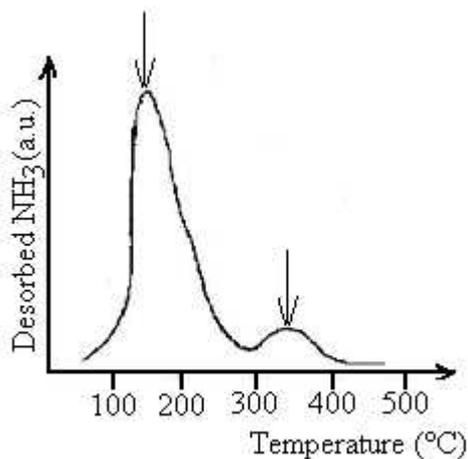
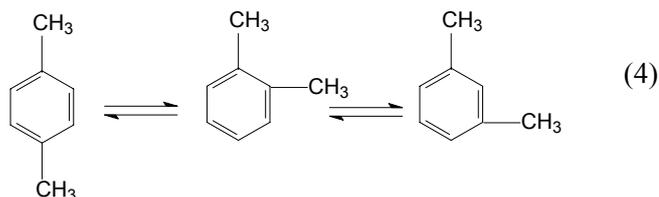
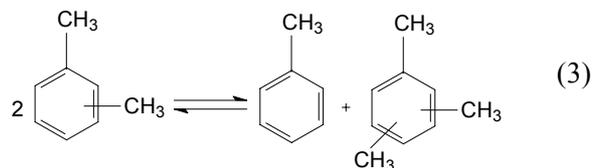
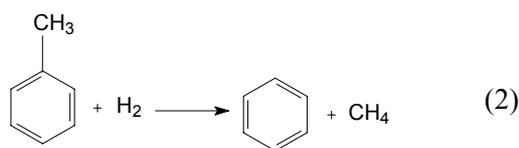
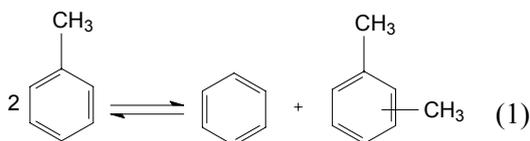


Fig. 7 – NH₃ – TPD profile of the calcined sample of (Si,Fe)-MCM-22 zeolite (Si/Fe=16).

Disproportionation of toluene

We have studied the toluene disproportionation over H(Si,Fe)-MCM-22 zeolite (Si/Fe=16) at 673 et 723 K to obtained xylenes and benzene (eq.1). Generally, this reaction occurs by an intermediate of the diphenylmethane type which can be formed in

the large cavities of the solid.^{2,21} The disproportionation reaction may be accompanied by a dealkylation of toluene to benzene (eq. 2), and also by the disproportionation (eq. 3) and isomerisation of xylenes (eq. 4).



The catalytic activity is characterized by the values of the conversion percentages :

Toluene conversion into disproportionation:

$$C_{dis} = 2 \sum X_i \quad (5)$$

where X_i are the concentrations of the three xylene isomers.

Toluene conversion into dealkylation:

$$C_{des} = B - \sum X_i \quad (6)$$

where B is the concentration of the benzene.

Total conversion of toluene:

$$C_{tot} = C_{dis} + C_{des} \quad (7)$$

These expressions were established taking into account the material balance for components

involved in eqs. (1) – (4) and the concentrations of aromatic hydrocarbons which were evaluated from GC analysis. Each experimental point was the average value of the five pulses.

The catalytic activity and the acidity of H(Si,Fe)-MCM-22 zeolite (Si/Fe=16) (Table 1) have been compared with those of H(Si,Al)-MCM-22 zeolite (Si/Al=15).¹⁷ From the results, the H(Si,Fe)-MCM-22 zeolite showed a lower toluene conversion than that of H(Si,Al)-MCM-22 zeolite under identical conditions, as a result of the decrease in Bronsted acid sites concentration due to the isomorphous substitution. This can be explained by the fact that the isomorphous substitution of iron into the framework of zeolites would induce changes in acidity, the acid strength is lower with respect to the parent zeolite.²²

Table 1

Acidity and the catalytic activity of the H(Si,Fe)-MCM-22 and H(Si,Al)-MCM-22 zeolite in toluene disproportionation

Sample	Si/Fe = 16		Si/Al = 15*
Total acidity measured by TPD (mmol g ⁻¹)	2.1		3.7
Temperature (K)	673	723	673
Toluene conversion in :			
-disproportionation (%)	2.36	2.85	18.44
-dealkylation (%)	1.52	1.71	0.58
Toluene total conversion (%)	3.88	4.56	19.02
B/X	2.4	2.7	1.06
p-xylene (%)	67	78	29

* (Si,Al)-MCM-22 zeolite [17]

The value of B/X ratio is different to unity over H(Si,Fe)-MCM-22 zeolite at the two temperatures studied and very close to unity for H(Si,Al)-MCM-22 zeolite (Table 1). It is clear that the disproportionation of toluene takes place predominantly over the H(Si,Al)-MCM-22 zeolite, and the importance of the secondary reactions, like the dealkylation of toluene and the disproportionation of xylenes, is not negligible over isomorphously substituted H(Si,Fe)-MCM-22 zeolite. Moreover, the stability of the iron in the framework is low by rapport to the aluminium, and the small amounts of extra-framework iron in the zeolites formed at high temperatures help the evolution of secondary reaction as dealkylation of toluene.

With regard to the conversion of toluene into p-xylene, the highest values are obtained on the sample of H(Si,Fe)-MCM-22 zeolite for the two studied temperatures (Table 1). The results are compared to that of H(Si,Al)-MCM-22 zeolite. The

fraction of p-xylene (primary product toluene disproportionation) in excess of the equilibrium value for the H(Si,Fe)-MCM-zeolite can be explained on the basis of the isomorphous substitution of iron, which leads generally to the weaker acid strength. In this case, the acid sites within the 10 MR window of the 12 MR MWW cages of MCM-22 zeolite are the weak strength and the secondary isomerization of p-xylene to o- and m-xylene can be retarded. Moreover, only p-xylene diffuses much faster out of supercages through 10 MR windows because of its smaller diameter. At 723 K, probably the high para-selectivity can be due to the coke formation in the pores. These results are in good agreement with those reported.^{9,10}

Finally, we can conclude that is a really competition between the disproportionation of toluene (primary reaction) and the dealkylation of toluene (secondary reaction) over H(Si,Fe)-MCM-22 zeolite at the 673 and 723 K. The toluene

conversion decreased over H(Si,Fe)-MCM-22 zeolite compared to the H(Si,Al)-MCM-22 zeolite while the fraction of p-xylene increased. The fraction of p-xylene increases with decreasing of the acidity by isomorphous substitution.

EXPERIMENTAL PART

Catalysts synthesis

The ferrisilicate zeolite (Si,Fe)-MCM-22 was prepared under hydrothermal conditions following the method reported by P.Wu *et al.*,¹³ using hexamethyleneimine (HMI, Aldrich 99%), NaOH (Prolabo, 98%), Fe(NO₃)₃·9H₂O (Fluka), SiO₂ (Aerosil 200, Degussa) and H₂O as starting materials. The molar composition of the synthesis mixture was the following: 1.0 SiO₂: 0.033 Fe₂O₃: 0.12 Na₂O: 0.5 HMI: 45 H₂O. The gel was transferred into a Teflon autoclave and crystallized at 423 K. After 12 days, the sample was isolated by filtration, washed with deionized water and dried at 353 K overnight. The solid material was calcined in air at 823 K for 5 h. The calcined sample was ion-exchanged with 1M NH₄NO₃ aqueous solution (liquid to solid ratio of 20 ml g⁻¹) under continuous stirring at 353 K for 8 h. This procedure was repeated twice. After filtering and drying, the resulting NH₄⁺ forms of Fe-MCM-22 were calcined at 803 K for 4 h in air to form acid (H-Fe-MCM-22).

Catalysts characterization

The elemental analysis of the solids was performed by the Service Central d'Analyse of CNRS-Solaize. The purity and the crystallinity of the product was determined by X-ray diffraction (Philips diffractometer PW 1800-Cu K α). The transmission electron microscopy (TEM) with X-ray energy-dispersive spectroscopic analysis (EDX) were performed on Philips CM120 apparatus. The morphology of the samples was determined by scanning electron microscopy using a Philips XL 30 scanning electron microscope (SEM). Measurements of nitrogen adsorption at 77 K was carried out using a Micromeritics ASAP 2010 system. The Mossbauer measurements were made using a ⁵⁷Co source at room temperature. The acid amount was measured using temperature programmed desorption (TPD) of ammonia.

Catalytic tests

Dismutation reaction of toluene was carried out on a pulse type microreactor coupled in line with GC. The microreactor consisted of a stainless steel tube (o.d. 6 mm, i.d. 3.5 mm, and length 90 mm) containing 40 mg of catalyst (without binder) with particle size 0.25-0.5 mm packed between two quartz wool plugs. This allowed to obtain a ca. 3.5 mm x 5 mm cylindrical fixed bed of catalyst, which was found to be

optimal for avoiding diffusion-controlled phenomena. Before reaction, the catalyst was activated or regenerated in air stream at 773 K for 2.5 h, followed by cooling to the reaction temperature in a nitrogen flow. Samples of 0,1 μ l of reagent (toluene) were injected at constant temperature. Nitrogen was used as a carrier gas (30 ml min⁻¹ flow rate). The reaction products were analyzed on line GC, using a 4,5 m column packed with 16 % SE-30 + 3 % Benton 34 on Chromosorb W-AWDCMS and FI detector.

REFERENCES

1. W.O. Haag, D.H. Olson and P.G. Rodewald, *U.S. Patent* 4358395, **1982**.
2. W.W. Kaeding, C. Chu, L.B. Young and S.A. Butter, *J. Catal.*, **1981**, 69, 392.
3. D.H. Olson and W.O. Haag, *ACS Symp. Ser.*, **1984**, 248, 275.
4. N.R. Meshram, S.G. Hegde, S.B. Kulkarni and P. Ratnasamy, *Appl. Catal. A*, **1983**, 8, 359.
5. M.A. Uguina, J.L. Sotelo, D.P. Serrano and J.L. Valverde, *Ind. Eng. Chem. Res.*, **1994**, 33, 26.
6. I. Wang, T. Ch. Tsai and Sh. T. Huang, *Ind. Eng. Chem. Res.*, **1990**, 29, 2005.
7. J. Das, Y.S. Bhat and A.B. Halgeri, *Catal. Lett.*, **1994**, 23, 161.
8. M.E. Leonowicz, J.A. Lawton, S.L. Lawton and M.K. Rubin, *Science*, **1994**, 264, 1910.
9. G.G. Juttu and R.F. Lobo, *Micropor. Mesopor. Mater.*, **2000**, 40, 9.
10. P. Wu, T. Komatsu and T. Yashima, *Micropor. Mesopor. Mater.*, **1998**, 22, 343.
11. V. Mavrodinova and M. Popova, *Catal. Commun.*, **2005**, 6, 247.
12. A.M. Prakash, Tomasz Wasowicz and Larry Kevan, *J. Phys. Chem. B*, **1997**, 101, 1985.
13. P.Wu, H. Lin, T. Komatsu and T. Yashima, *Chem. Commun.*, **1997**, 663.
14. F. Testa, F. Crea, G.D. Diodati, L. Pasqua, L., R. Aiello, G. Terwagne, P. Lentz and J.B. Nagy, *Microp. Mesop. Mater.*, **1999**, 30, 187.
15. R. Kumar, A. Thangaraj, R.N. Bhat and P. Ratnasamy, *Zeolites*, **1990**, 10, 85.
16. R. Szostak and T.L. Thomas, *J. Catal.*, **1986**, 100, 555.
17. I. Fechete, P. Caultet, C. Guimon and E. Dumitriu, *Scientific Bulletin of Iassy University*, **2003**, XLIX, 53.
18. A. Meagher, V. Nair and R. Szostak, *Zeolites*, **1988**, 8, 3.
19. K. Lazar, G. Borbely and H. Beyer, *Zeolites*, **1991**, 11, 214.
20. A. Hagen, F. Roessner, I. Weingart and B. Spliethoff, *Zeolites*, **1995**, 15, 270.
21. Y.S. Xiong, P.G. Rodewald and C.D. Chang, *J. Am. Chem. Soc.*, **1995**, 117, 9427.
22. C.T.-W. Chu and C.D. Chang, *J. Phys. Chem.*, **1985**, 89, 1569.