Synthesis of SAPO-41 and SAPO-44 and their performance as acidic catalysts in the conversion of methanol to hydrocarbons

Jiesheng Chen and John M. Thomas

Davy Faraday Research Laboratory, The Royal Institution of Great Britain, 21 Albemarle Street, London, W1X 4BS, U.K.

Received 3 September 1991; accepted 1 October 1991

Crystalline samples of medium-pore SAPO-41 and small-pore SAPO-44 have been prepared by respective use of diethylamine and cyclohexylamine as templates. They were characterized using X-ray powder diffraction, DTA-TGA and diffuse reflectance infra-red Fourier transform (DRIFT) spectroscopy. SAPO-44 has larger void volume and stronger framework acidity than SAPO-41. Whereas the products of methanol conversion on SAPO-41 are dominated by dimethylether, the main products on SAPO-44 are ethene and propene. Nevertheless, SAPO-44 is less active than SAPO-34 (which possesses a similar framework structure to SAPO-44) and suffers deactivation in about an hour at 450°C.

Keywords: Silicon-aluminophosphates; molecular sieves; solid catalysts; methanol convertion; olefins

1. Introduction

By using various amines or quaternary ammonium ions as templates, large numbers of open framework aluminophosphates (ALPOs) have been synthesized [1] hydrothermally. After calcination at elevated temperatures, these crystalline materials become microporous and possess adsorptive and catalytic properties similar to those of zeolites. Furthermore, the framework P and/or Al atoms of some ALPOs can be substituted by silicon to a certain degree and the subsequent silico-aluminophosphates (SAPOs) often have superior catalytic properties to those of the analogous ALPOs [2]. With some templates, the incorporation of silicon can lead to the formation of new types of SAPO structures without parallel in the ALPO family. Among these new silico-aluminophosphates is SAPO-41 which, as yet, has not had its structure solved. On the basis of its adsorptive properties, SAPO-41 possesses a framework of medium-sized pores; SAPO-44, on the other hand, has a framework structure similar to SAPO-34, an analogue of chabazite with three-dimensionally connected small pores (ca. 4.5 Å).

The SAPOs are classic examples of so-called uniform heterogeneous catalysts in the sense defined elsewhere [3,4]: the active sites are distributed in a more or less spatially uniform manner throughout their bulk and accessible to reactants small enough to diffuse through their microporous structures. The conversion of methanol to hydrocarbons, studied extensively by many [5–8], is believed to be acid-catalyzed. Depending on the activity and structure of the catalysts, a wide variety of species may occur in the product. Much effort has been focused in arriving at highly-selective catalysts, and a very effective one is the medium-pore zeolite ZSM-5. Very recently there have been reports that the silicoaluminophosphate SAPO-34 [7–9] and its Ni(II)-substituted analogue Ni-SAPO-34 [10,11] were remarkable catalysts for the conversion of methanol to light alkenes.

The present work reports the preparation of the medium-pore SAPO-41 and the small-pore SAPO-44, and their catalytic properties for the conversion of methanol.

2. Experimental

Crystalline samples of both SAPO-41 and SAPO-44 were synthesized hydrothermally following the procedures described elsewhere [2]. The templates used were diethylamine(Et_2NH) and cyclohexylamine($CHXNH_2$), respectively. SAPO-41 crystallized from a homogeneous reaction mixture of Cabosil silica powder, pseudoboehmite, phosphoric acid (85%), diethylamine and water at 190°C for 48 hours, the composition of a typical reaction mixture being $0.4SiO_2:Al_2O_3:P_2O_5:Et_2NH:55H_2O$. The crystallization conditions and the reactants except for the template for the synthesis of SAPO-44 were the same as those used for SAPO-41: a typical composition being $0.6SiO_2:Al_2O_3:P_2O_5:1.8CHXNH_2:60H_2O$. Prior to testing the catalytic performance, the as-synthesized SAPO-41 and SAPO-44 were detemplated by calcination at 550°C for 3–5 hours.

X-ray powder diffraction patterns were recorded using a Siemens D500 diffractometer(CuKα radiation). Differential thermal(DT) and thermogravimetric(TG) analyses were performed on a Stanton Redcroft STA 1500 thermal analyser, and the diffuse reflectance infra-red Fourier transform spectra (DRIFTS) were recorded on a Perkin-Elmer 1725X FTIR spectrometer fitted with a Spectratech diffuse reflectance attachment. The sample cell was bathed in a stream of dry air. The catalytic activity of SAPO-41 and SAPO-44 for methanol conversion was tested in a tubular quartz reactor under the following conditions: catalyst amount, 0.2 g; activation temperature, 450°C; activation time, 1 hour; total pressure, 1 atm; methanol partial pressure, 0.2 atm; flowing gas, nitrogen; GHSV, 3000 h^{-1}. The reaction products were analysed on a Perkin-Elmer gas chromatograph with a flame ionisation detector. A Chrompack column was used to separate the products.

3. Results and discussion

Previously, SAPO-41 was reported [2] to be prepared by using dipropylamine (Pr_2NH) or tetrabutylammonium hydroxide(TBAOH) as the template. In our synthesis for SAPO-41, the template was diethylamine, the molecular size of which is considerably smaller than that of Pr_2NH and TBAOH. This is further evidence that the framework pore size of an ALPO or SAPO is not strictly proportional to the size of its template. For SAPO-44, the $CHXNH_2$ content and subsequently the basicity of the reaction mixture plays an important role in the preparation. When the Si : Al : P ratio was fixed at 0.3 : 1 : 1, if $CHXNH_2/Al < 0.85$, SAPO-5 appeared in the product; and if a ratio of $CHXNH_2/Al > 1.0$ is used, an unidentified phase, the structure of which collapses after calcination for the removal of the template, crystallizes out (a similar phenomenon was previously observed in the synthesis of SAPO-34 [12]). We also investigated situations in which there was more silica in the reaction systems, namely the SiO_2/Al_2O_3 ratios in the reaction mixtures were larger than 0.4 and 0.6 for SAPO-41 and SAPO-44, respectively. Under these circumstances, however, we failed to obtain highly-crystalline monophasic materials.

The X-ray powder diffraction data of the as-synthesized SAPO-41 and SAPO-44 are essentially identical to those presented in the literature [2]: there was no evidence for the presence of any other phase. From the diffraction patterns (fig. 1), one can see that both SAPO-41 and SAPO-44 change their framework structures slightly after removal of the templates since quite a few of diffraction peaks for both compounds appear at different positions and/or in different intensities before and after calcination at elevated temperature.

From the DTA-TGA curves (fig. 2) for the as-synthesized SAPO-41 and SAPO-44, and those of the corresponding detemplated and rehydrated samples, it is seen that both the as-synthesized compounds lose their occluded water and templates separately, the latter being removed at higher temperatures. In addition, the detemplating temperature of SAPO-44 (~ 550°C) is much higher than that of SAPO-41 (~ 300°C), a fact which is in line with the smaller framework channel windows and bigger occluded template molecules of SAPO-44 compared with those of SAPO-41. Rehydrated SAPO-41 loses water at around 130°C with a total weight loss of 12.7% whereas the DTA curve of the rehydrated SAPO-44 exhibits a broad peak at about 180°C, higher than that of SAPO-41. Moreover, the total weight loss for the samples of the rehydrated SAPO-44 is 28.1%, more than double that for the corresponding SAPO-41. This suggests that SAPO-44 has a void volume much larger than that of SAPO-41

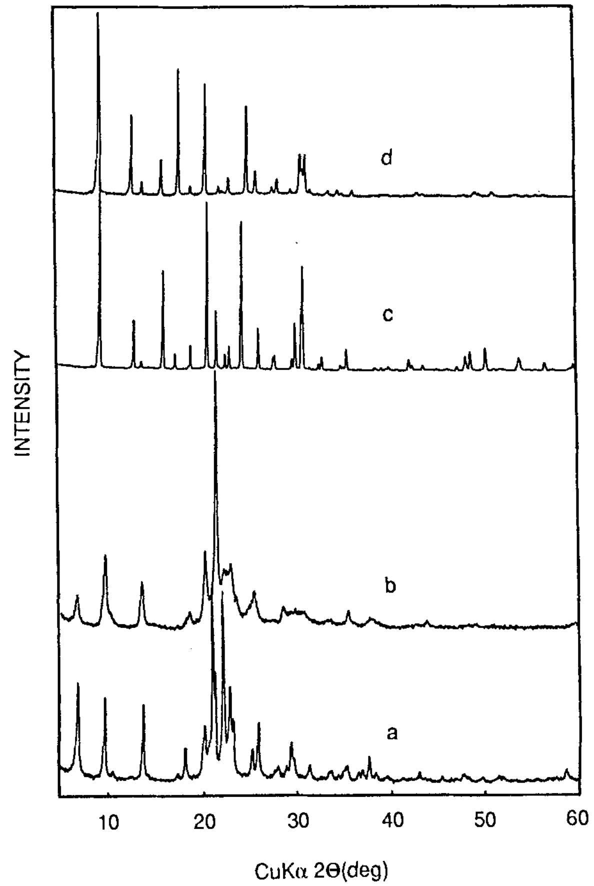

Fig. 1. X-ray powder diffraction patterns of (a) as-synthesized SAPO-41, (b) calcined-rehydrated SAPO-41, (c) as-synthesized SAPO-44 and (d) calcined-rehydrated SAPO-44.

even though the latter possesses medium-sized framework channels whereas the former has only small-sized ones. This evidence supports the view that the framework of SAPO-41 contains only one-dimensional channels comparable with the well-known examples of SAPO-5 and SAPO-11 [13].

Fig. 3 shows the DRIFT spectra of rehydrated SAPO-41 and SAPO-44 at room tempertaure and at 500°C, respectively. At room temperature, the spectra of the two compounds are quite similar, indicating that the adsorbed water molecules are not much influenced by the SAPO frameworks. However, after the adsorbed water is removed at 500°C, the spectra for the two SAPOs differ greatly especially within the frequency range of O-H stretching vibrations. SAPO-41 gives three relatively weak absorptions at 3733, 3665 and 3601 cm^{-1} (The O-H acidity, which is inversely proportional to the O-H stretching frequency, should follow the order 3601 $\mathrm{cm}^{-1} >$ 3665 $\mathrm{cm}^{-1} >$ 3733 cm^{-1}). On the whole, SAPO-41 has not many acid sites since none of the three absorptions appears to be strong. By contrast, SAPO-44 exhibits a very strong O-H stretch-

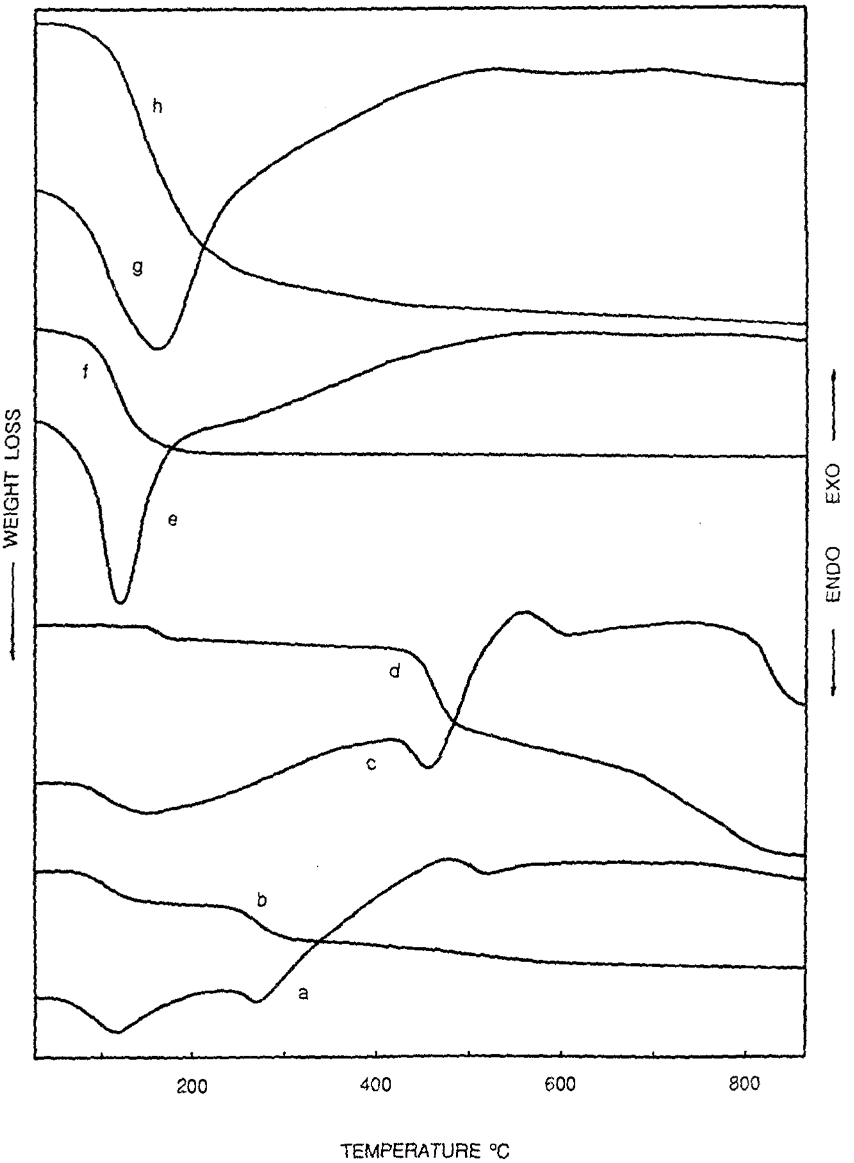

Fig. 2. DTA (a, c, e, g) and TGA (b, d, f, h) curves of as-synthesized SAPO-41, 44 and calcined-rehydrated SAPO-41, 44 in air atmosphere.

ing absorption around 3600 cm^{-1}, the same frequency as that of the strongest acid O-H group in SAPO-41. We therefore expect, and do indeed find that SAPO-44 is a better catalyst than SAPO-41 for the methanol conversion reactions discussed here. In previous work, O-H stretching IR absorptions similar to SAPO-44 were observed for SAPO-34 and Ni-SAPO-34 [11], both of which proved to be excellent catalysts for the methanol conversion to light alkenes.

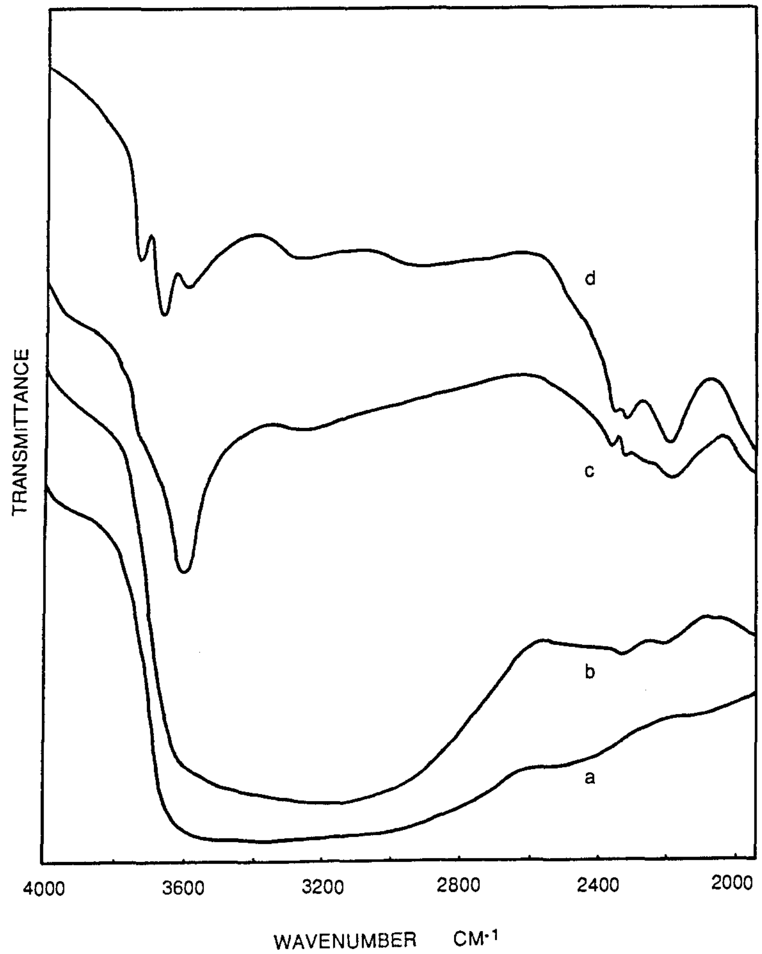

Fig. 3. Diffuse reflectance infra-red Fourier transform spectra of (a) calcined-rehydrated SAPO-44 at 25°C, (b) calcined-rehydrated SAPO-41 at 25°C, (c) recalcined SAPO-44 at 500°C and (d) recalcined SAPO-41 at 500°C.

For comparison, the catalytic performance of SAPO-34 was tested under the same conditions as for those of SAPO-41 and SAPO-44 in the present work. The results are listed in table 1. The main product on SAPO-41 is dimethylether: evidently hydrocarbons appear only at higher temperature. This is congruent with the IR result which indicates that SAPO-41 has weak acidity. Compared with SAPO-41, the catalytic activity of SAPO-44 is markedly superior. On average the methanol conversion rate on SAPO-44 is ca. 20% higher than on SAPO-41; and at 350°C or upwards, the main products are C_2 to C_4 alkenes. However, the data in table 1 also reveal that the catalytic behaviour of SAPO-44 is inferior to SAPO-34 even though there is no significant difference between the DRIFT O-H absorptions. Above 350°C, SAPO-34 can convert almost all the generated dimethylether into hydrocarbons and is not significantly

Table 1
Effect of temperature on the catalytic properties of SAPO-41, SAPO-44 and SAPO-34 for methanol conversion reaction (see text)

	SAPO-41					SAPO-44					SAPO-34			
Temperature (°C)	300	350	400	450	500	300	350	400	450	500	300	350	400	450
Methanol conversion (%)	48.9	69.9	78.6	67.5	68.7	83.7	85.4	83.4	89.4	85.9	73.9	84.3	92.4	94.2
Product distribution (%) (exclusive of water)														
$(CH_3)_2O$	99.0	99.9	95.2	73.4	76.9	98.7	12.6	12.2	19.4	33.7	62.0	0.4	0.8	0.8
CO_2	–	–	–	–	0.7	0.5	0.6	–	0.5	–	–	–	–	–
CH_4	0.9	–	–	0.8	3.6	–	1.2	0.7	0.9	1.2	1.8	0.9	0.6	0.7
C_2H_4	–	–	0.3	1.6	2.7	–	23.9	26.3	30.0	30.0	10.5	26.6	30.2	35.0
C_2H_6	–	–	–	–	0.4	–	–	1.1	1.4	1.0	–	0.4	0.6	0.6
C_3H_6	–	–	3.4	6.3	9.2	0.7	46.3	46.1	36.5	24.4	25.5	72.0	55.4	50.1
C_3H_8	–	–	–	–	–	–	–	–	–	–	–	0.3	1.2	2.7
C_4H_8	–	–	–	–	–	–	15.0	12.2	10.0	8.7	–	8.7	5.3	3.9
C_4H_{10}	–	–	1.0	3.5	3.4	–	–	–	–	–	–	10.9	5.7	4.4

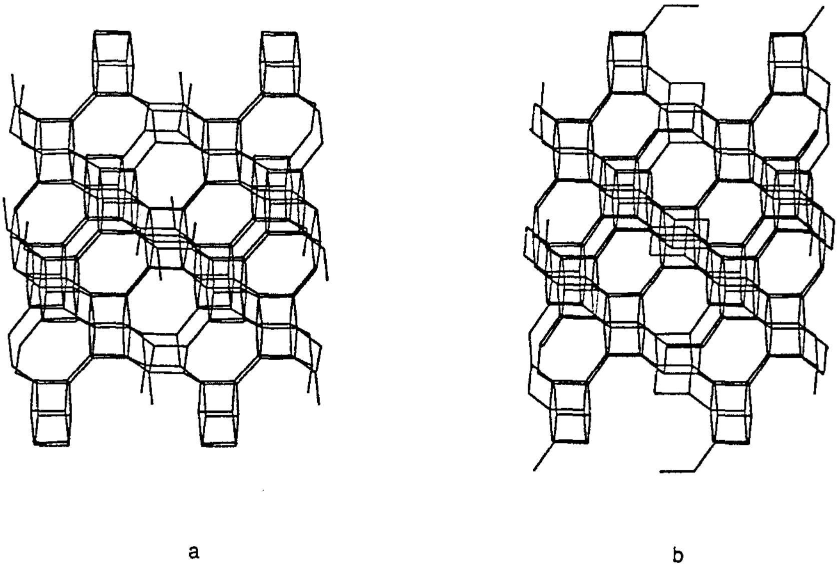

Fig. 4. Framework structures of (a) SAPO-44 and (b) SAPO-34 viewed along [1 1 0].

deactivated at least within 4 hours on reaction at 450°C. In contrast, at 450°C SAPO-44 is deactivated dramatically with reaction time and after one hour only dimethylether appears in the product. Evidently, two similar framework structures have quite different catalytic properties when their templated precursors are different. It is known that the crystalline precursor of SAPO-34 is trigonal (space group R3) [14] and that of SAPO-44 is triclinic (space group $P\bar{1}$) [15] (The framework of the latter can be considered as a slightly distorted analogue of the former (fig. 4).) This slight distortion permits the two solids to display somewhat different framework compositions, which subsequently give rise to different catalytic behaviour. Chemical analysis reveals that the P/Al and Si/Al ratios for SAPO-34 are 0.76 and 0.26 whereas those for SAPO-44 are 0.67 and 0.30, respectively: more phosphorus is substituted by silicon in SAPO-44 than in SAPO-34. The higher concentration of the negative framework charges and subsequently the Bronsted acid sites explains [16] the fast deactivation of SAPO-44. On the other hand, a framework with more Bronsted acid sites can possess weaker acidity than a framework with less Bronsted acid sites as observed for ZSM-5 with various Si/Al ratios [17]. This is why SAPO-44 is less active than SAPO-34.

4. Conclusion

The medium pore SAPO-41 can be synthesized by using templates with various sizes. Its framework has a relatively small void volume and weak acidity.

Unlike the medium-pore ZSM-5, SAPO-41 is not a favourite catalyst for methanol conversion reaction. Monophasic small-pore SAPO-44 can crystallize in a system involving cyclohexylamine as a template provided that the reaction composition is strictly controlled. The detemplated SAPO-44, having large void volume and strong framework acidity on the basis of the IR spectrum, is much superior in catalysis to SAPO-41 but inferior to SAPO-34, which possesses a similar three-dimensional framework structure to SAPO-44.

Acknowledgements

We would like to thank the Unilever Plc, the Royal Society and the SERC for valuable support, and D. Waller and S. Natarajan for technical help.

References

[1] S.T. Wilson, B.M. Lok, C.A. Messina, T.R. Cannan and E.M. Flanigen, J. Amer. Chem. Soc. 104 (1982) 1146.
[2] B.M. Lok, C.A. Messina, R.I. Patton, R.T. Gajek, T.R. Cannan and E.M. Flanigen, US. Patent, 4, 440, 871 (1985).
[3] J.M. Thomas, Angew. Chem., Int. Ed. Engl. 27 (1988) 1673.
[4] J.M. Thomas, Philos. Trans. R. Soc. London A 333 (1990) 173.
[5] C.D. Chang, Cat. Rev. Sci. 112 (1980) 11.
[6] S. Natarajan and J.M. Thomas, Catal. Today (1991), in press.
[7] J. Liang, H. Li, S. Zhao, W. Guo, R. Wang and M. Ying, Appl. Catal. 64 (1990) 31.
[8] Y. Xu, C.P. Grey, J.M. Thomas, A.K. Cheetham, Catal. Lett. 4 (1990) 251.
[9] T. Inui, H. Matsuda, H. Okaniwa and A. Miyamoto, Appl. Catal. 58 (1990) 155.
[10] T. Inui, S. Phatanasri and H. Matsuda, J. Chem. Soc., Chem. Commun. (1990) 205.
[11] J.M. Thomas, Y. Xu, C.R.A. Catlow and J.W. Couves, Chem. Mater. 3 (1991) 669.
[12] Y. Xu, P.J. Maddox and J.W. Couves, J. Chem. Soc., Faraday Trans. 86 (1990) 425.
[13] J.V. Smith, Chem. Rev. 88 (1988) 149.
[14] M. Ito, Y. Shimoyama and Y. Saito, Acta Cryst. C41 (1985) 1698.
[15] J.M. Bennett and B.K. Marcus, in: *Innovation in Zeolite Materials Science*, eds P.J. Grobet et al. (Elsevier Science Publishers B.V., Amsterdam, 1988) 269.
[16] G. Ohlmann, H.G. Jerschkewitz, G. Lischke, R. Eckelt, B. Parlitz, E. Schreier, B. Zibrowius and E. Loffler, in: *Studies in Surface Science and Catalysis 65: Catalysis and Adsorption by Zeolites*, eds. G. Ohlmann et al. (Elsevier Science Publishers B.V., Amsterdam, 1991) 1.
[17] D. Barthomeuf, in: *Studies in Surface Science and Catalysis 65: Catalysis and Absorption by Zeolites*, eds G. Ohlmann et al. (Elsevier Science Publishers B.V., Amsterdam, 1991) 157.