Preparation of dealuminated faujasites for adsorption of volatile organic compounds

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A series of dealuminatead faujasitic zeolites, obtained from the ammonium form of Y zeolite, was prepared by two different methodologies: a relatively common self-steaming method, where temperatures in the range 813 to 1093 K were used, and a less well studied solid-state dealumination method using ammonium hexafluorosilicate, which employed a lower temperature (453 K) than those used in the self-steaming method. It was possible to obtain samples by solid-state dealumination with both high levels of dealumination and good crystallinity. Textural and surface chemistry parameters, such as the micropore volume and the hydrophobic character of the surface, respectively, were correlated with the extent of dealumination. The adsorption isotherms of two selected volatile organic compounds (VOCs), one oxygenated (methyl ethyl ketone) and the other chlorinated (1,1,1-trichloroethane), were measured at 298 K by the gravimetric method. For one of the samples obtained by solid-state dealumination in particular, the adsorption isotherms of the studied VOCs presented adequate characteristics for the adsorption of these molecules, namely significant adsorption capacity and a moderately rectangular shape. This latter aspect can be of importance, for instance, in terms of regeneration of the adsorbent.

Introduction

The control of the emissions of volatile organic compounds (VOCs) poses challenges to both the scientific community and industry, whether they are large or small. In fact, as stated in EC Directive no. 1999/13, VOCs are defined as all organic compounds (except methane) with a vapour pressure equal to or higher than 0.01 kPa at 293 K. With some exceptions, these compounds are noxious to human health, either directly or indirectly, *e.g.* through the depletion of the ozone layer. The limiting values for the VOC emissions in each of the 15 EC countries were also recently the object of EC Directive 2001/81. Even if these regulations are met, more than 6.5×10^6 tons of volatile organic compounds will be released to the atmosphere up to the year 2010, and this only in the present 15 EC countries. The reduction of VOCs can be accomplished by thermal oxidation, although this is a process which consumes a large amount of energy and is not completely suitable for an important group of molecules, namely chlorinated VOCs.[1] In order to lower the temperatures used in the thermal oxidation of VOCs, the catalytic oxidation of these substances was envisaged and studied.[2,3] When dealing with the problems related to VOC abatement, one important question is that these pollutants are usually present in gas streams, but in low concentrations. Therefore, the possibility of using adsorbents in the control of VOCs is almost intuitive, not only as concentrators of the organic molecules in air streams and for improving the economic efficiency of thermal oxidation, but also due to the possibility of recollecting and reusing the organic compounds.[4] The use of adsorbents was also considered in order to improve the sampling of VOCs and, consequently, to achieve better accuracy in monitoring the organic compounds present in the atmosphere.[5]

Active carbons are considered good candidates for the adsorption of VOCs, mainly because they are cheap and have high adsorption capacities, but their regeneration, usually carried out by heating, can pose problems related to the flammability of these materials, a problem that is absent if inorganic adsorbents can be used. For this reason, zeolites are materials that could be considered as adsorbents for VOCs. Zeolites are inorganic crystalline solids, mostly aluminosilicates, that can present a variety of structures[6] and which are already used in various gas separation processes.[7] The fact that the more common zeolites, such as, for instance, faujasite-like zeolites,[6] easily adsorb water can be considered, to some extent, a drawback for the use of these solids in the adsorption of VOCs, due to possible competition effects. In the case of the aluminosilicates, this aspect is usually related to the presence of aluminium in the framework, which can be modified by dealumination processes. Therefore, modifications of zeolitic structures that could favour both the removal of structural aluminium and the regeneration of the adsorbent can be seen as a contribution to the potential use of zeolites as adsorbents for VOCs.

Although there are some studies in the literature that deal with the theme of the adsorption of VOCs in zeolites,[8–15] the number of studies that concern a series of dealuminated zeolites is very restricted. The aim of this work was to prepare a series of faujasitic zeolites dealuminated by a self-steaming method,[16] or by solid-state dealumination[17,18] with ammonium hexafluorosilicate, and, in the modified materials, to determine the adsorption isotherms, by the gravimetric method, of selected compounds, namely 1,1,1-trichloroethane (TCA) and methyl ethyl ketone (MEK), as examples of chlorinated and oxygenated VOCs, respectively.

Experimental

Materials

NaY from Aldrich (lot. 03910KG) was used as the starting material. To prepare the ammonium form (NH4Y), three exchanges were made at ambient temperature with an NH4Cl solution (2 M), using 5 mL of the solution per gram of NaY. The exchanged solid was exhaustively washed until the water proved to be Cl⁻-free (AgNO3 test) and, finally, dried at 353 K.

The samples labelled SS(813, 1093) and SS(813, 1033, 1093)

DOI: 10.1039/b205367e

were obtained by self-steaming treatments. For this, the hydrated NH$_4$Y sample was placed in a covered crucible and introduced into a muffle furnace at 473 K. The temperature was then increased to the indicated values and maintained for 3 h. The samples SS(813, 1093) and SS(813, 1033, 1093) result from successive calcinations, for periods of 3 h, at 813 and 1093 or 813, 1033 and 1093 K, respectively. After each subsequent heat treatment, the samples were again ion-exchanged, following the procedure described above, washed, dried at 353 K and, finally, hydrated.

The samples labeled SiF6/0.5, SiF6/1 and SiF6/4, were obtained by solid-state dealumination through a reaction between the NH$_4$Y, prepared as above, and ammonium hexafluorosilicate (Aldrich, 99.999%), using a procedure based on that reported in the literature,[17] with the molar ratio between the ammonium hexafluorosilicate and the aluminium in the framework of the parent NaY zeolite set at 0.7. In order to obtain homogeneous mixtures, the zeolite and the ammonium hexafluorosilicate were mixed in an agate mortar. The mixtures were heat treated at a temperature of 453 K for 0.5, 1 or 4 h, as indicated in the sample designation. Therefore, the temperatures involved in the solid-state dealumination are much lower than those used in the self-steaming method. Although ammonium hexafluorosilicate is, at this stage, an expensive reagent, a process that occurs at a temperature that is nearly 600 K lower than the temperatures used in the self-steaming can also have potential advantages in terms of energy consumption and the technology involved. The heat treatments were carried out in a vertical tubular oven in a quartz reactor under a nitrogen flow of 5 cm^3 s^{-1}. At the end of the heat treatments, the samples were washed until the washing water proved to be aluminium-free (NaOH test), dried at 353 K and finally hydrated.

Methods

The X-ray diffractograms were obtained using a Phillips PX 1820 instrument, (Cu-K$_\alpha$ radiation) for degrees of 2θ between 5 and 40. The unit cell parameter (a_0) was obtained from the (440), (620), (533), (444), (551) and (642) reflections of the X-ray diffractogram. The crystallinity was gauged by calculating the ratio between the sum of the intensities of the (331), (333), (440), (533), (642), (822), (555) and (664) peaks. Thermogravimetric experiments were carried out under a flow of nitrogen with a ramp of 2.5 K min^{-1} in a Setaram TG/DSC 111 instrument, which had a sensitivity of 10 μg. Prior to each measurement, the sample was kept in a sealed wet environment for a minimum of three days.

The nitrogen adsorption isotherms at 77 K were determined in a manual volumetric installation made in Pyrex and equipped with a Datametrics model 600 transducer (Wilmington, MA, USA). Prior to the measurements, the samples were outgassed for 2 h at 573 K, after a ramp of 10 K min^{-1}, under a dynamic vacuum of better than 10^{-2} Pa. As noted in previous works, no changes in the adsorption isotherms were observed when longer outgassing times were used.[19–21] The adsorption isotherms of methyl ethyl ketone (BDH, 99.5%) and 1,1,1-trichloroethane (Flucka, 99%) were determined by the gravimetric method using microbalances from C.I. Electronics (Salisbury, UK), which allowed a precision of 10 μg. The pressure readings were made with capacitance transducers from Shaevitz (Slough, UK). A combination of rotary/oil diffusion pumps and heating, in a similar manner as described for the case of the nitrogen adsorption isotherms, accomplished the outgassing of the adsorbents. The temperature of adsorption was maintained at 298 $\pm$ 0.1 K with a VWR Scientific water bath (Buffalo Grove, IL, USA). Prior to adsorption, the vapours were purified in situ by freeze–vacuum–thaw cycles. The amounts adsorbed (including for the nitrogen adsorption) are reported in terms of liquid volume by gram of adsorbent material, that is, in cm^3 g^{-1}. These values were obtained by converting the direct experimental uptake through the respective molar volumes at the adsorption temperature.

Results and discussion

X-Ray powder diffraction

In Table 1, the unit cell parameter (a_0) and the degree of crystallinity, obtained from XRD as mentioned in the Experimental, as well as the dealumination ratio, estimated from the unit cell parameter using the Breck–Flanigen equation,[22] are given. In general, the degree of aluminium removal estimated in this way parallels the severity of the dealumination treatment within each series. It should be emphasised at this point that the two dealumination methods used, that is, on the one hand the self-steaming and, on the other, the solid-state dealumination, imply different mechanisms for the removal of the aluminium from the framework in each case. In the first case, aluminium leaves the framework, is deposited in the form of aluminium oxide species in the intra- or intercrystalline spaces and the vacancies are filled by lattice silicon and oxygen.[23] In the solid-state reaction method, which is far less studied than the self-steaming method, the mechanism is less understood, but a lower degree of structural defects than in the case of the self-steaming method is expected, since there is an external source of silicon. Moreover, according to some authors,[17] partial realumination of the zeolitic structure can occur in some situations when solid-state dealumination is used. This last observation can explain the case of the sample labeled SiF6/4, which, according the values in Table 1, is the exception to the trend where an increase in the severity of the dealumination treatment corresponds to a decrease in the micropore and total pore volumes (Table 1).

Nitrogen adsorption at 77 K

Nitrogen adsorption isotherms at 77 K for the dealuminated samples and the parent NaY zeolite are shown in Fig. 1. For simplicity, only the adsorption points are given, although

Table 1 Results of the characterisation of the studies samples by XRD and nitrogen adsorption at 77 K

Sample	$a_0{}^a$/Å	Dealumination^b (%)	Crystallinity (%)		Pore volume/cm^3 g^{-1}	
			XRD^c	N$_2$ adsorption^d	Micro^e	Micro + meso
NaY	24.640	—	100	100	0.34	0.36
SS(540, 820)	24.421	47	39	62	0.21	0.29
SS(540, 760, 829)	24.274	87	20	44	0.15	0.24
SiF6/0.5	24.514	28	59	74	0.25	0.33
SiF6/1	24.450	53	44	47	0.16	0.24
SiF6/4	24.461	58	69	76	0.26	0.32

^{a}Obtained using the program developed by Appleman and Evans.[29] Uncertainty (average): ± 0.008 Å. ^{b}Estimated with the Breck–Flanigen equation[20] using the ammonium form ($a_0 = 24.666$ Å) as reference. ^{c}From X-ray diffraction studies, according to ref. 30. ^{d}From nitrogen adsorption studies. ^{e}Calculated using the Dubinin–Radushkevich equation.[23]
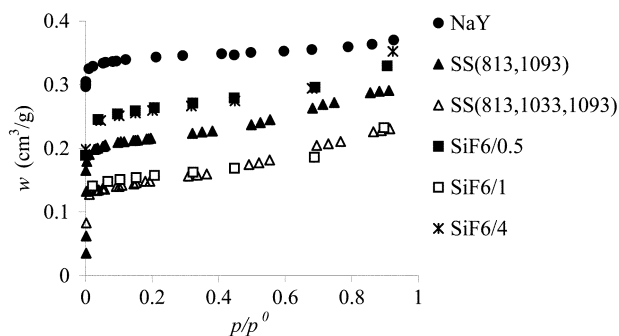
Fig. 1 Nitrogen adsorption isotherms, at 77 K, in the parent NaY zeolite, in the samples dealuminated by self-steaming (SS) at the temperatures indicated in brackets and by solid-state reaction (SiF6) for the reaction times indicated in the sample designation.

hysteresis was observed in the case of the dealuminated samples. As expected for the NaY zeolite, the isotherm is of type I according to the IUPAC classification,[24] a curve which is typical of a highly microporous material. It is evident from Fig. 1 that the dealumination processes have the effect of decreasing the amounts adsorbed in the region of the lower relative pressures, that is, in the region of the microporosity, but increasing the slope of the curve at higher relative pressure, a fact that can be related to the development of mesoporosity partially due to the accumulation of Al as Al_2O_3 in the external surfaces of the crystallites. Fig. 2 shows pore size distributions, estimated from the nitrogen adsorption isotherms by the Pierce method,[25] for the samples obtained by self-steaming (a) and by solid-state dealumination (b). In the case of the former, although a shoulder appears for r_p around 3 nm, the curves decrease almost monotonously. For the samples obtained by solid-state dealumination, different peaks can be seen in the pore size distribution, particularly for r_p between 2 and 5 nm. It seems that the solid-state dealumination promotes the development of sets of mesoporoes, with similar dimensions within each set, rather than the continuous range of pore sizes that is observed in the case of the samples obtained by self-steaming. The textural characteristics of the samples are quantified in Table 1, where the micropore volumes, estimated using the
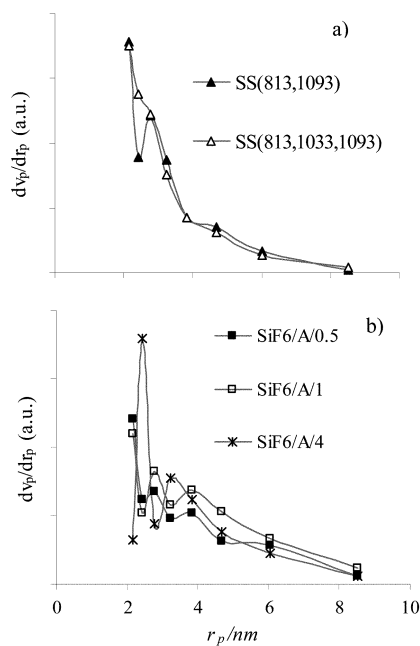

Fig. 2 Pore size distributions, estimated from the nitrogen adsorption, in the samples dealuminated by (a) self-steaming and (b) solid-state reaction. (Symbols as in Fig. 1.)
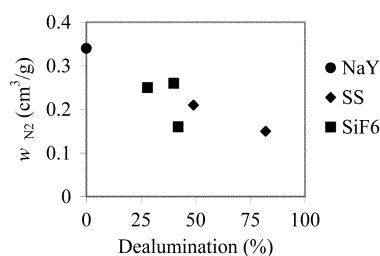
Fig. 3 Relation between the micropore volumes of the studied samples and the dealumination level. SS stands for samples dealuminated by self-steaming and SiF6 for the samples dealuminated by solid-sate reaction.

Dubinin–Radushkevich equation,[25] and the total pore volumes are recorded. In Table 1, the degree of crystallinity of the samples (in %), estimated from the ratio of the micropore volumes for the NaY zeolite and for the dealuminated samples, are also given. The evaluation of the crystallinity of dealuminated zeolites, by adsorption, XRD and other methodologies, has been discussed in the literature.[26] In principle, if the crystallinity values obtained from the nitrogen adsorption and XRD experiments are close, this would mean that the microporosity is not blocked either by oxide species removed from the structure or by defects.[26] In Fig. 3 the micropore volumes are related to the dealumination level, and appear to be inversely related, to a good approximation.

Hydrophobicity studies

The dealumination process, in principle, modifies the nature of the surface and these modifications can have implications for the adsorption of VOCs, particularly in cases where, besides the volatile organic compound, humidity is also present. The assessment of the degree of hydrophilicity of a given material is not a straightforward subject, but different proposals for acheiving this can be found in the literature. In this way, Anderson and Klinowski[27] proposed a definition of hydrophilicity based on the ratio of the amounts of water lost on heating up to 423 K and up to 673 K. Giaya *et al.*[12] proposed a different definition, obtained by subtracting from the total pore volume, estimated from low temperature nitrogen adsorption, the water loss above 423 K and dividing it by the total pore volume. These definitions lead to values between 0 (more hydrophilic) and 1 (more hydrophobic), and will be referred in this work as h_1 and h_2, respectively. The values of h_1 and h_2 were computed from thermograms obtained for the different samples previously saturated with water vapour, and are plotted in Fig. 4 against the dealumination degree. As can be seen, although the values for the NaY zeolite are lower than for the other solids, for the dealuminated samples the increased dealumination level does not seem to imply a clear trend in the loss of hydrophilicity, at least as evaluated by h_1 or h_2. In fact, if only the h_1 values are considered, the
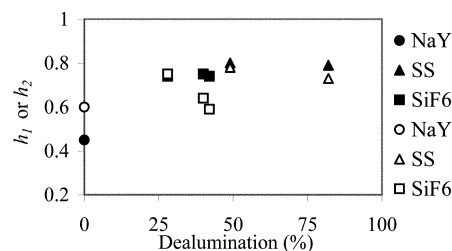

Fig. 4 Relation between the degree of hydrophilicity, given by h_1 (solid symbols) or h_2 (open symbols), and the dealumination level of the studied materials. SS stands for samples dealuminated by self-steaming and SiF6 for the samples dealuminated by solid-sate reaction.
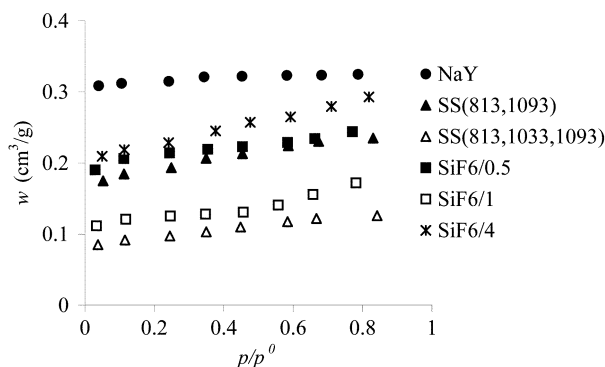
Fig. 5 Adsorption isotherms of methyl ethyl ketone, at 298 K, in the NaY zeolite and in samples dealuminated by self-steaming (SS) at different temperatures and by solid-state reaction (SiF6) for different reaction times.
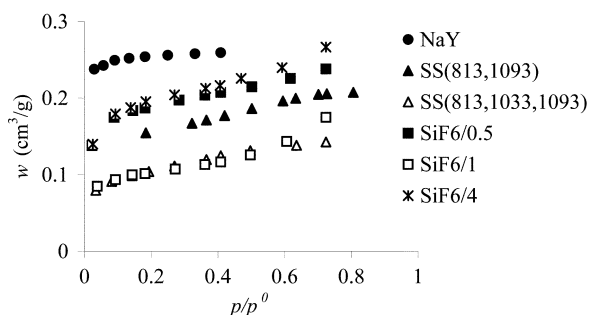

Fig. 6 Adsorption isotherms of 1,1,1-trichloroethane, at 298 K, in the NaY zeolite and in samples dealuminated by self-steaming (SS) at different temperatures and by solid-state reaction (SiF6) for different reaction times.

hydrophilicity of the studied dealuminated samples remains almost constant.

Adsorption of methyl ethyl ketone and 1,1,1-trichloroethane

The adsorption isotherms of methyl ethyl ketone and 1,1,1-trichloroethane in the studied samples are shown in Fig. 5 and 6, respectively. As occurred in the case of the low temperature nitrogen adsorption (Fig. 1), the highly rectangular character of the isotherms observed for the parent NaY zeolite is not so marked for the dealuminated samples, and the adsorbed amounts are lower.

The isotherms of both VOCs in the sample SiF6/4, which has the highest degree of crystallinity of the dealuminated samples, present a remarkable feature. In fact, the isotherm has the least rectangular character and, although the amounts of the studied VOCs adsorbed in this sample in the low pressure region are lower than for the NaY zeolite, at high relative pressures, the amounts adsorbed approach those obtained in this zeolite. These facts and, particularly, the less rectangular character of the isotherms of the studied VOCs, are good indications for the potential of this solid for the adsorption of volatile organic compounds, since the process of regeneration of the adsorbent could, in this way, be favoured.

The adsorbed amounts of MEK and TCA at a relative pressure of 0.1, that is, at a relative pressure where adsorption in the micropores is generally accomplished, are plotted in Fig. 7 against the dealumination level. The relevant observation from this figure is that the correlation between the adsorbed amounts and the dealumination level is much the same as that shown in Fig. 3, which concerns the adsorption of nitrogen. In this way, it seems that the surface chemistry does not play a major role in the adsorption of the studied VOCs, even if both molecules have high dipole moments (1.8 and
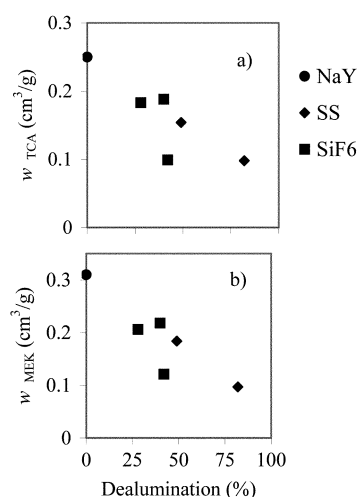

Fig. 7 Adsorbed amounts of TCA (a) and MEK (b), at a relative pressure of 0.1, plotted against the dealumination level. SS stands for samples dealuminated by self-steaming and SiF6 for the samples dealuminated by solid-sate reaction.
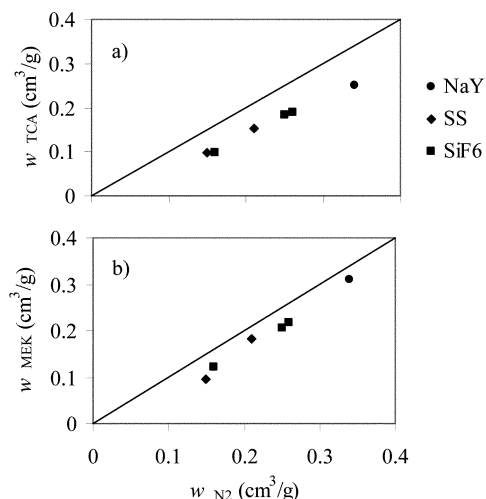

Fig. 8 Adsorbed amounts of TCA (a) and MEK (b), at a relative pressure of 0.1, plotted against the total micropore volumes estimated from low temperature nitrogen adsorption. (Symbols as in Fig. 7.)

3.3 debye for TCA and MEK, respectively[28]) and, therefore, could in principle interact with different types of surfaces. This obviously does not mean that those interactions do not exist, but that the more determinant are, most probably, the dispersive forces in micropore spaces. In fact, as shown in Fig. 8, the amounts of MEK and TCA adsorbed at a relative pressure of 0.1, although always lower than the total microporous volume of the respective samples obtained from the low temperature adsorption of nitrogen, correlate well with this magnitude, reinforcing the idea that the textural properties of the samples most probably play the major role in the adsorption of the studied molecules.

Conclusions

The use of dealumination processes is a promising route to zeolitic structures with adequate properties for the adsorption of volatile organic compounds. Although both, the surface chemistry and the textural properties are changed by dealumination, the latter seem to play a major role when the adsorption of VOCs at ambient temperature is concerned. By using a method of dealumination that involves the solid-state reaction between the zeolitic structure and ammonium hexafluorosilicate at a moderate temperature (453 K), it was

possible to obtain solids with different dealumination levels, including a sample with a considerable dealumination level (40%) which retained about 76% of the crystallinity of the precursor. In addition, the moderate rectangular character of the isotherms of the studied VOCs in this sample and the high limiting value of the total amounts adsorbed are indicative of the potential of these materials as far as the adsorption of volatile organic compounds is concerned.

Acknowledgement

References

1 X. Dang, R. Daniels and R. W. Baker, *AIChE J.*, 2001, **47**, 1094.
2 E. M. Cordi, P. J. O'Neill and J. L. Falconer, *Appl. Catal., B*, 1997, **14**, 23.
3 J. J. Spivey, *Ind. Eng. Chem. Res.*, 1987, **26**, 2165.
4 M. J. Ruhl, *Chem. Eng. Prog.*, 1993, **July**, 37.
5 J. Gawlowski, T. Gierczak, A. Jezo and J. Niedzielski, *The Analyst*, 1999, **124**, 1553.
6 D. W. Breck, *Zeolite Molecular Sieves: Structure, Chemistry and Use*, Wiley, New York, 1974 pp. 29–133.
7 R. T. Yang, *Gas Separation by Adsorption Processes*, Butterworths Series in Chemical Engineering, Butterworths, Boston, 1987.
8 M. V. Chandak, Y. S. Lin, W. Ji and R. J. Higgins, *J. Membr. Sci.*, 1997, **133**, 231.
9 C. F. Mellot, A. K. Cheetham, S. Harms, Scott Savitz, R. J. Gorte and A. L. Myers, *Langmuir*, 1998, **14**, 6728.
10 B. Clausse, B. Garrot, C. Cornier, C. Paulin, M.-H. Simonot-Grange and F. Boutros, *Microporous Mesoporous Mater.*, 1998, **25**, 169.
11 C. K. W. Meininghaus and Roel Prins, *Microporous Mesoporous Mater.*, 2000, **35–36**, 349.
12 A. Giaya, R. W. Thompson and R. Denkewicz Jr., *Microporous Mesoporous Mater.*, 2000, **40**, 205.
13 T. P. O'Connor and J. Mueller, *Microporous Mesoporous Mater.*, 2001, **46**, 341.
14 J. Pires, A. Carvalho and M. B. Carvalho, *Microporous Mesoporous Mater.*, 2001, **43**, 277.
15 R. Schumaker, S. Ernest and J. Weitkamp, in *Proceedings of the 9th International Zeolite Conference*, ed. R. von Ballmoos, Butterworth-Heineman, London, 1993, p. 89.
16 J. Scherzer, in *Catalytic Materials, Relationships Between Structure and Reactivity*, ed. T. E. White, R. A. Dalla Betta, E. G. Derouane and R. T. K. Baker, ACS Symp. Ser. vol. 248, American Chemical Society, Washington, DC, 1984, p. 157.
17 H. K. Beyer, G. B.-Pálné and J. Wu, in *Zeolites and Related Microporous Materials: State of the Art 1994*, ed. J. Weitkamp, H. G. Karge, H. Pfeifer and W. Hölderich, Studies on Surface Science and Catalysis vol. 84, Elsevier, Amsterdam, 1994, p. 933.
18 G. W. Skeels and D. W. Breck, in *Proceedings of the 6th International Zeolite Conference*, ed. D. H. Olson and A. Bisio, Butterworths, Surrey, 1984, p. 87.
19 M. B. Carvalho, J. Pires and A. P. Carvalho, *Microporous Mater.*, 1996, **6**, 65.
20 J. Pires, M. B. Carvalho and A. P. Carvalho, *Zeolites*, 1997, **19**, 107.
21 P. Pereira, J. Pires and M. B. Carvalho, *Langmuir*, 1998, **14**, 4584.
22 D. W. Breck and E. M. Flanigen, *Mol. Sieves, Pap. Conf. 1967*, 1968, 47.
23 C. V. McDaniel and P. K. Maher, *Mol. Sieves, Pap. Conf. 1967*, 1968, 186.
24 K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquérol and T. Siemieniewska, *Pure Appl. Chem.*, 1985, **57**, 603.
25 S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, London, 1982.
26 A. P. Carvalho, M. B. Carvalho and J. Pires, *Zeolites*, 1997, **19**, 382.
27 M. W. Anderson and J. Klinowski, *J. Chem. Soc., Faraday Trans.*, 1986, **82**, 1449.
28 R. C. Reid, J. M. Prausnitz and B. E. Poling, *The Properties of Gases and Liquids*, McGraw-Hill, New York, 1988, pp. 656–732.
29 D. E. Appleman and H. T. Evans, *Indexing and Least-Squares Refinement of Powder Diffraction Data*, Report No. USG-6D-73-003, Washington DC, 1973.
30 *Annu. Book ASTM Stand.*, D 3942-91, 15.03, 1991, 612.