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Location of meta-xylene in BaX zeolite and model for the filling of the supercages

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The structure of BaX zeolite containing sorbed deuterated meta-xylene has been studied for two different coverages at 11 K by powder neutron diffraction. From the two refinements, we suggest a molecular model for the filling of the supercages. For up to two molecules per supercage, strong interactions are observed between the aromatic ring and the Ba^{2+} cation ($d = 2.44(1)$ Å), and between the methyl groups and the framework oxygens. When coverage is increased above two molecules per supercage, a significant molecular rearrangement is observed. The aromatic molecules reorient at a larger distance from the Ba^{2+} cations than at low coverage ($d = 2.75(1)$ Å), the interactions between the methyl groups and the framework are weakened, and a second crystallographic site for the xylene is observed. This site has lower occupancy and apparently is the less favoured one since the aromatic ring is 2.90(3) Å from the Ba^{2+} cation. From these results, we demonstrate that the crystallographic arrangement of the sorbate is strongly dependent on intermolecular interactions. When coverage increases, different molecular orientations are adopted in order to maximize methyl–methyl distances and thereby minimize the intermolecular repulsion.

Keywords: neutron diffraction; adsorption; BaX zeolite; meta-xylene

1. Introduction

At present, the adsorption of aromatics in zeolites is of great industrial interest in separation and catalysis processes such as alkylation, transalkylation or isomerisation of meta-xylene into para-xylene. The separation of para-xylene from C_8 aromatics (para-, ortho-, meta-xylenes, and ethylbenzene) is performed industrially by adsorption processes such as "Parex" on zeolitic molecular sieves [1]. In the case of energetic selectivity, the separation properties of a zeolitic sorbent

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depends on its cationic form, the degree of the cation exchange, and the coverage with aromatics. Synthetic faujasite-type zeolites (X, Y) are commonly used and are converted into particularly selective sorbents by exchanging the sodium ions with barium cations, thereby improving their para/meta selectivity [2]. A large number of microscopic and macroscopic measurements, such as crystallographic [3–6] and infrared [7–9] studies, thermodynamic [10,11] and diffusion coefficient [12–15] measurements and molecular simulations [16–19], have been carried out on aromatics adsorbed in faujasite-type zeolites in order to understand their sorption and diffusion properties. However, very few structural studies of xylene adsorption are available in the literature, even less concerning the influence of coverage on sorbent–sorbate interactions. To investigate the sorption of meta-xylene in BaX zeolite on a molecular level and in an attempt to understand the influence of molecular geometry and coverage on the crystallographic arrangement of the sorbate, and consequently on the sorbent–sorbate interactions, a neutron diffraction study was undertaken. We report here the structural features of meta-xylene sorbed in BaX zeolite at two different coverages (approximately one and three molecules per supercage) and suggest a molecular model for the filling of the supercages, from low coverage to saturation.

2. Experimental

2.1. SAMPLE PREPARATION

The BaX zeolite was prepared starting with synthetic NaX faujasite supplied by Linde Co. (Union Carbide), with a Si/Al ratio of 1.25. Chemical analysis confirmed the composition to be $Na_{86}Si_{108}Al_{86}O_{384} \cdot nH_2O$ per unit cell. The BaX zeolite was obtained by ion exchange in successive batches with 0.01 M aqueous solution of $Ba(NO_3)_2$ at 50°C. The zeolite powders were then placed in glass cells connected to vacuum and adsorption branches to allow dehydration pretreatment and adsorption of xylene [20]. The sample was first dehydrated at 100°C under vacuum (10^{-5} Torr) for 4 h and then at 300°C for 48 h. Adsorption was then achieved by admitting deuterated meta-xylene vapor into the cell at a controlled pressure. Equilibrium between the zeolite sample and the vapor was maintained for 4 h. The amount of adsorbed xylene was estimated by weighing the sample before and after adsorption. Two samples, corresponding to approximately one and three molecules per supercage, were prepared. The cell was then transferred to a helium conditioned glove-box until the neutron experiments could be performed. Prior to the diffraction experiments, the zeolite powders were placed in an air-tight vanadium sample-holder ($\varnothing = 8$ mm). Similar samples, from different preparations, were used for the diffraction experiments. The chemical composition of the different samples and their cell parameters are specified in table 1.

Table 1
Composition of the samples

Composition of the zeolite per unit cell	Coverage per supercage	Cell parameter (Å)
$Ba_{34.5}Na_{15.5}Si_{108}Al_{84}O_{384}$	–	25.175(1)
$Ba_{40}Na_{5}Si_{108}Al_{84}O_{384}$	0.8 meta-xylene	25.185(1)
$Ba_{38.8}Na_{6.6}Si_{109}Al_{83}O_{384}$	2.8 meta-xylene	25.214(1)

2.2. NEUTRON DATA SAMPLING AND STRUCTURE REFINEMENT

The powder patterns were collected at 11 K on the DMC diffractometer [21] at the SAPHIR reactor at the Paul Scherrer Institute (Switzerland). Intensity data were collected in the 2θ range between 4° and 130° in steps of 0.1° 2θ. The wavelength was 1.698(1) Å. The data collection time was 48 h to obtain sufficiently good counting statistics. The diffraction patterns were analysed using the Rietveld refinement method [22]. The XRS-82 package of programs [23] and the complete set of data were used for the refinement of the structure. The framework geometry was first optimized by angle and distance least-squares refinement of the atomic coordinates. Xylene molecules adsorbed in the supercages were then located by calculating a series of difference Fourier maps. Structural parameters of the adsorbed molecules were refined using soft restraints on the bond lengths and angles in order to maintain the ideal planar molecular geometry.

3. Results

3.1. ADSORPTION OF META-XYLENE AT LOW COVERAGE

The crystal structure of BaX zeolite with meta-xylene was first determined for a low coverage of 0.8 molecule per supercage.The adsorption treatment does not lead to any change of symmetry. The space group used was Fd3m. First, the structural parameters of the framework were refined. The extra-framework Ba^{2+} cations were located and added to the model. At this stage, difference Fourier maps calculated perpendicular to the three-fold axis (the [111] direction) showed that the meta-xylene molecules were adsorbed close to the Ba^{2+} ions in site II of the supercage. The plane of the aromatic ring is perpendicular to the three-fold axis and centered around $x = y = z = 0.30$. The carbon and deuterium atoms of the aromatic ring were clearly observed. The deuterium atoms of the methyl groups were introduced in the refinement assuming an ideal tetrahedral geometry. The final structural parameters are reported in table 2, and the refined diffraction pattern is shown in fig. 1. The crystallographic position of the adsorbed meta-xylene molecule is described in fig. 2. In this position B, strong interactions are observed between the

Table 2
Atomic, thermal and population parameters for BaX + meta-xylene, at low coverage (0.8 molecule per supercage) [a]

Atom	Wyckoff position	x	y	z	B(iso)	N
SiAl	192i	−0.0566(3)	0.0356(3)	0.1257(3)	0.9(4)	1
O(1)	96h	−0.1104(2)	0	0.1104(2)	0.8(1)	1
O(2)	96g	−0.0042(2)	−0.0042(2)	0.1389(4)	0.8(1)	1
O(3)	96g	−0.0426(4)	0.0759(3)	0.0759(3)	0.8(1)	1
O(4)	96g	−0.0614(3)	0.0690(3)	0.1809(3)	0.8(1)	1
Ba0	16c	0	0	0	4(1)	0.29(5)
Ba1	32e	0.065(1)	0.065(1)	0.065(1)	4(1)	0.69(3)
Ba2	32e	0.2513(7)	0.2513(7)	0.2513(7)	4(1)	0.59(4)
C(1)	96g	0.3289(6)	0.3289(6)	0.2610(6)	14(3)	0.206(3)
C(2)	96g	0.2856(6)	0.2856(6)	0.3535(6)	14(3)	0.206(3)
D(1)	96g	0.346(1)	0.346(1)	0.226(1)	14(3)	0.068(1)
D(2)	96g	0.275(1)	0.275(1)	0.394(1)	14(3)	0.206(3)
C(3)	96g	0.3446(4)	0.3446(4)	0.2048(7)	14(3)	0.136(2)
D(31)	192i	0.3601(6)	0.3098(7)	0.184(1)	14(3)	0.136(2)
D(32)	48	0.375(1)	0.375(1)	0.206(1)	14(3)	0.272(4)

[a] Space group Fd3m; origin at 3m, $a = 25.185(1)$ Å.

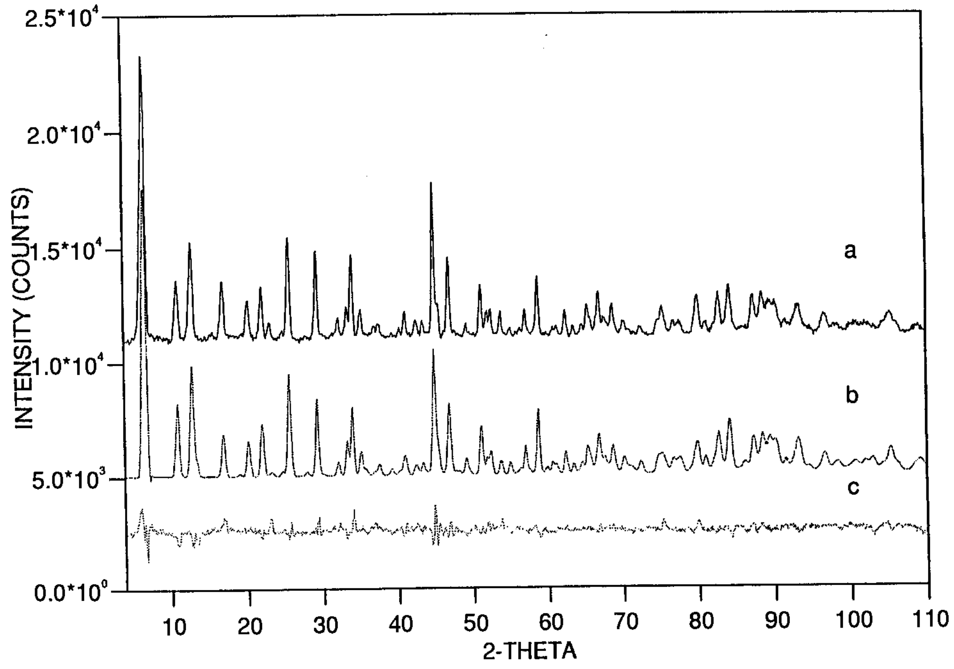

Fig. 1. Neutron powder diffraction pattern of BaX zeolite with deuterated meta-xylene at 11 K, at low coverage ($\Theta \approx 1$ molec./s). (a) Experimental data; (b) calculated profile; (c) difference between experimental and calculated profiles.

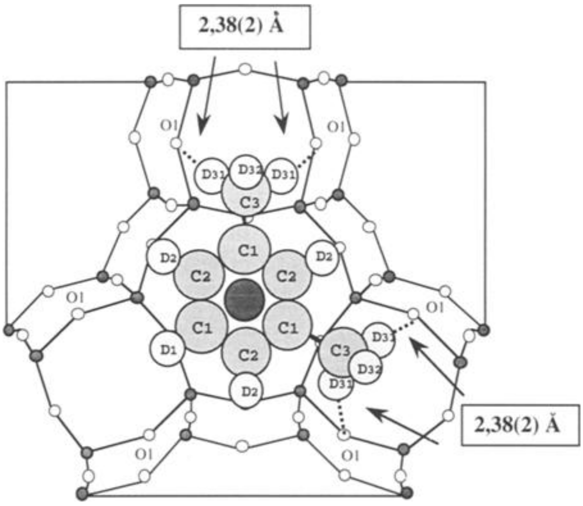

Fig. 2. BaX + meta-xylene at low coverage ($\Theta \approx 1$ molec./s). The molecule is adsorbed in position B within the supercage, forming a π-complex with the Ba^{2+} cation. The shortest distances between the molecule and the framework are indicated.

molecule and the sorbent. The center of the aromatic ring is 2.44(1) Å from the Ba^{2+} cation. Both methyl groups are directed towards the 4-ring windows, having equivalent environments. Two deuterium atoms of each methyl group point in the direction of O(1) atoms, at a distance of 2.38(2) Å. The D . . . O distance given by the sum of the van der Waals radii of oxygen and deuterium atoms should be about 2.6 Å. Consequently, these particularly short distances are indicative of a strong interaction between the methyl groups and the framework. The negatively charged framework may have a polarizing effect on the methyl group C–D bonds, leading to electrostatic interactions. The molecular geometry of meta-xylene allows optimal interaction between both methyl groups and the framework oxygens in the 4-ring windows. At low coverage, the shortness of the Ba^{2+}–meta-xylene distance (2.44 Å), compared to the Ba^{2+}–para-xylene distance (2.70 Å) [22], suggests that the meta-xylene molecular geometry enhances the π-complex formation. These results clearly demonstrate that the adsorbed molecules are stabilized not only by a π-type interaction between the aromatic ring and the cation, but also by attractive interactions between methyl groups and framework oxygens.

3.2. ADSORPTION OF META-XYLENE AT SATURATION

The crystal structure of BaX zeolite with meta-xylene (2.8 molecules per supercage) was determined in a similar way. It is noteworthy that the site S_{II} is now fully occupied with Ba^{2+} ions. As the zeolite is saturated with meta-xylene, there appears to be a concomitant migration of Ba^{2+} ions to the supercage. Difference Fourier maps calculated perpendicular to the [111] axis close to the Ba^{2+} ion in site

S_{II} showed two crystallographic orientations, A and B′, of the adsorbed molecules (fig. 3). The refined atomic positions are shown in fig. 4 and the final structural parameters are given in table 3. The refined profile is shown in fig. 5. It is apparent that the position B′ is different from the position B observed at low coverage. The aromatic ring has similar orientations in both cases, but the methyl groups in position B′ are pointed towards the 12-ring windows, whereas those in position B are pointed towards the 4-ring windows. Position B′ is rotated by 30° with respect to position A. The population parameter refinement leads to the following occupan-

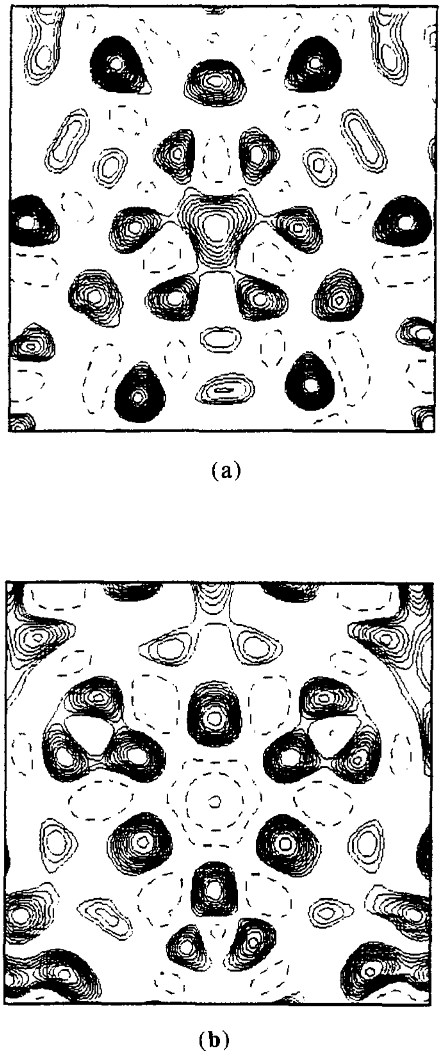

Fig. 3. Difference Fourier maps perpendicular to the [111] axis for BaX saturated with meta-xylene. (a) meta-xylene adsorbed in position A (center at $x = y = z = 0.30$); (b) meta-xylene adsorbed in position B′ (center at $x = y = z = 0.31$).

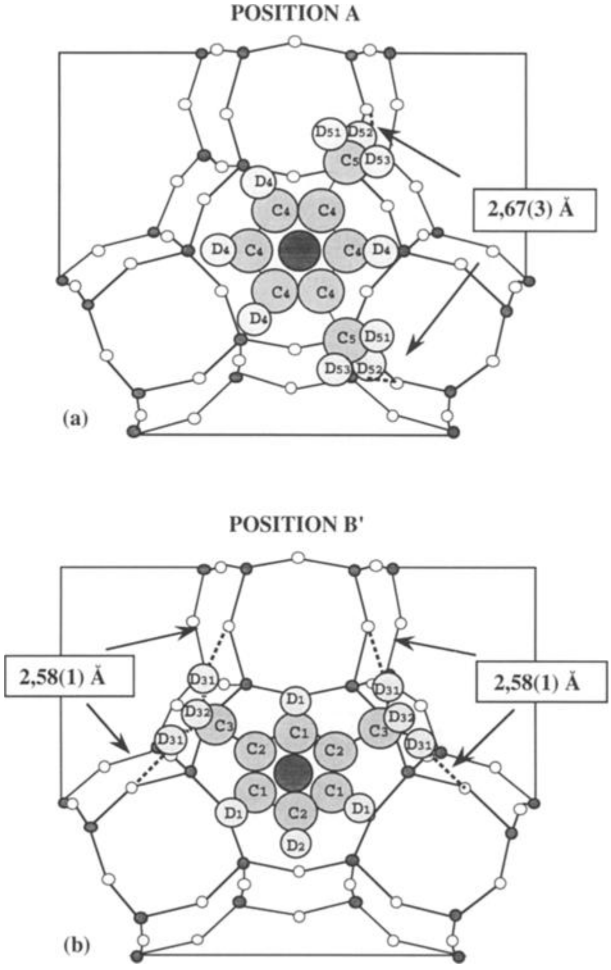

Fig. 4. BaX+meta-xylene at saturation ($\Theta \approx 3$ molec./s). The molecules are adsorbed in position A (a) and in position B′ (b). The shortest distances between the molecules and the framework are indicated.

cies: approximately two meta-xylene molecules per supercage are adsorbed in position B′, whereas only one meta-xylene molecule per supercage is adsorbed in position A. In view of their relative occupancies and their respective structural characteristics, position B′ seems to be more favourable than position A. Therefore, adsorption in position A could be characteristic of a state of saturation. A summary of the distance from the center of the aromatic ring to the cation and the $C\text{–}D_{\text{methyl}} \ldots O_{\text{framework}}$ contact lengths as a function of coverage is presented in table 4. The Ba^{2+}–ring distance observed in position B′ (2.75(1) Å) is much shorter than in position A (2.90(3) Å). Moreover, four short $D_{\text{methyl}}\text{–}O_{\text{framework}}$ contacts of 2.58(1) Å are observed when meta-xylene is in position B′, whereas only two contacts of 2.67(3) Å are observed when in position A.

Table 3
Atomic, thermal and population parameters for BaX + meta-xylene, at saturation (2.8 molecules per supercage) [a]

Atom	Wyckoff position	x	y	z	B(iso)	N
SiAl	192i	−0.0569(3)	0.0344(3)	0.1248(3)	1.1(2)	1
O(1)	96h	−0.1121(3)	0	0.1121(3)	0.4(1)	1
O(2)	96g	−0.0068(3)	−0.0068(3)	0.1393(5)	0.4(1)	1
O(3)	96g	−0.0416(5)	0.0723(4)	0.0723(4)	0.4(1)	1
O(4)	96g	−0.0639(5)	0.0692(4)	0.1807(4)	0.4(1)	1
Ba0	16c	0	0	0	3(1)	0.73(4)
Ba1	32e	0.072(1)	0.072(1)	0.072(1)	1(1)	0.28(2)
Ba2	32e	0.2413(5)	0.2413(5)	0.2413(5)	2(1)	1
C(1)	96g	0.3270(5)	0.3270(5)	0.2590(5)	15(1)	0.66(1)
C(2)	96g	0.2816(5)	0.2816(5)	0.3496(5)	15(1)	0.66(1)
D(1)	96g	0.3422(7)	0.3422(7)	0.2218(6)	15(1)	0.66(1)
D(2)	96g	0.265(1)	0.265(1)	0.385(1)	15(1)	0.22(1)
C(3)	96g	0.2525(4)	0.2525(4)	0.3955(4)	15(1)	0.44(1)
D(31)	192i	0.2095(4)	0.2601(4)	0.3926(6)	15(1)	0.44(1)
D(32)	96g	0.2672(5)	0.2672(5)	0.4335(5)	15(1)	0.44(1)
C(4)	192i	0.270(1)	0.348(1)	0.309(1)	15(1)	0.27(1)
C(5)	192i	0.224(1)	0.388(1)	0.306(1)	15(1)	0.09(1)
D(4)	192i	0.238(1)	0.377(1)	0.308(1)	15(1)	0.18(1)
D(51)	192i	0.212(1)	0.394(1)	0.264(1)	15(1)	0.09(1)
D(52)	192i	0.189(2)	0.373(2)	0.329(3)	15(1)	0.09(1)
D(53)	192i	0.236(2)	0.426(1)	0.323(2)	15(1)	0.09(1)

[a] Space group Fd3m; origin at 3m, $a = 25.214(1)$ Å.

4. Discussion

With increasing coverage, the location of meta-xylene molecules is strongly influenced by steric hindrance and intermolecular interactions. An analysis of sorbate–sorbate interactions is helpful in elucidating the different crystallographic positions adopted. Starting with the results of both refinements and considering intermolecular interactions, we propose a molecular model for the filling of the supercages, from low coverage to saturation.

– At low coverage, position B is the more energetically favoured position as strong sorbent–sorbate interactions are observed. At the coverage of one molecule per supercage, no intermolecular hindrance prevents the meta-xylene molecule from having free rotation in its adsorption site. Consequently, the molecule may have three crystallographically equivalent orientations around the three-fold axis.

– The study of steric hindrance does not show any restriction for the location of a second meta-xylene molecule in position B. Yet, the relative orientation of the two sorbed molecules is restricted and free rotation is prohibited because of intermolecular repulsion. Fig. 6 shows two meta-xylene molecules sorbed in position B

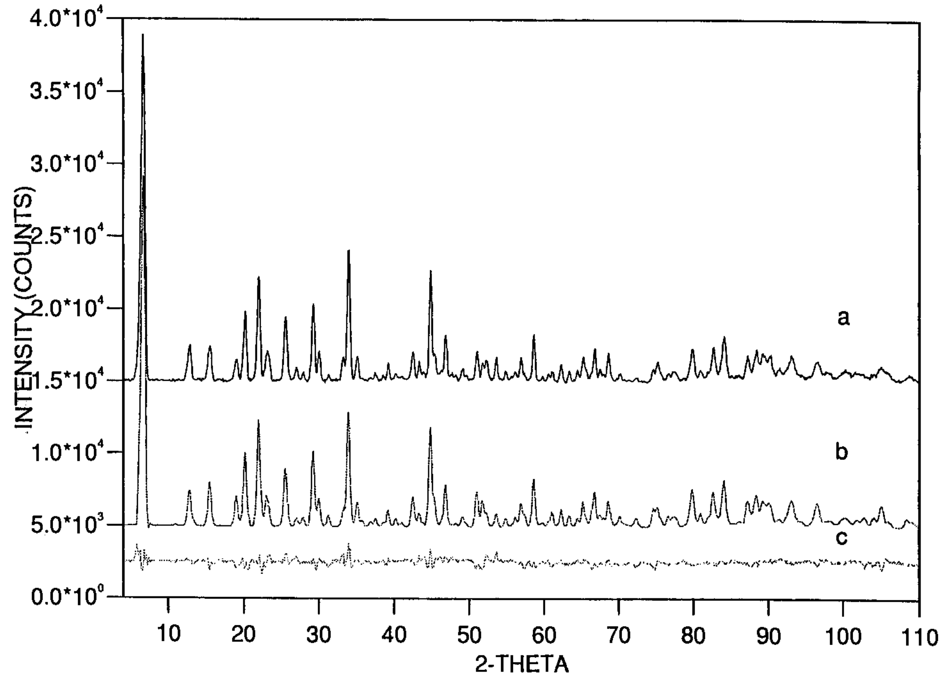

Fig. 5. Neutron powder diffraction pattern of BaX zeolite saturated with deuterated meta-xylene at 11 K (2.8 molecules per supercage). (a) Experimental data; (b) calculated profile; (c) difference between experimental and calculated profiles.

in a prohibited orientation with a contact between a methyl group and the aromatic ring of the neighbouring molecule shorter than 2 Å. Both molecules have to reorient in order to minimize repulsive interactions (fig. 7).

– In the situation shown in fig. 7, a third meta-xylene molecule, whatever its crystallographic orientation, cannot come close to a barium cation without producing strong repulsive interactions with the methyl groups of both molecules sorbed in position B. Consequently, the loading of the zeolite to saturation with three molecules per supercage leads to a significant molecular rearrangement. Both molecules sorbed in position B reorient to the less favourable position B′ and this rearrangement allows a third meta-xylene molecule in position A to approach a barium

Table 4
Relevant bond lengths for adsorbed meta-xylene molecules, as a function of their crystallographic position in the supercage

Meta-xylene positions	$d(\mathrm{Ba}^{2+}\text{–ring})$ (Å)	$d(\mathrm{D}_{\mathrm{methyl}} \cdots \mathrm{O}_{\mathrm{framework}})$ (Å)
position B	2.44(1)	2.38(2)
position B′	2.75(1)	2.58(1)
position A	2.90(3)	2.67(3)

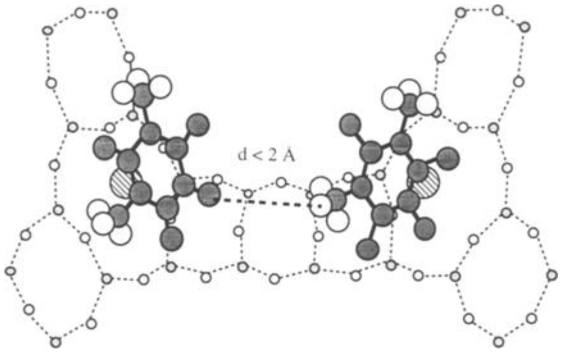

Fig. 6. Two meta-xylene molecules adsorbed close to Ba^{2+} cations in position B′, in a prohibited orientation.

cation. As it is shown by the structural refinement, the crystallographic arrangement of the sorbate molecules at saturation allows interactions between each aromatic ring and a Ba^{2+} cation. Nevertheless, the increase of coverage leads to a clear decrease in sorbate–sorbent interactions.

These results establish that sorbent–sorbate interactions are strongly dependent on the geometry of the sorbate molecules and on steric hindrance occurring as coverage increases. Further investigations are carried out on the influence of cations and other isomers such as para-xylene. In case of competitive adsorption of xylene isomers, one may suggest that each isomer may have a specific location in the supercages. This will probably influence the selectivity, either in separation or in catalytic processes. Better understanding of adsorption at a molecular level could be of great interest in the study of reactivity, especially in the field of interactions between molecules and catalytic sites.

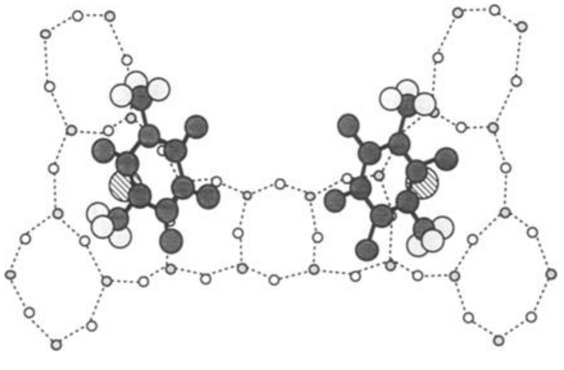

Fig. 7. Two meta-xylene molecules adsorbed close to Ba^{2+} cations in position B′, in an allowed orientation.

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References

[1] R.W. Neuzil, US Patents 3 558 730, 3 558 732 (1971).
[2] R.W. Neuzil, US Patent 3 626 020 (1971).
[3] A.N. Fitch, H. Jobic and A.J. Renouprez, J. Phys. Chem. 90 (1986) 1311.
[4] R. Goyal, A.N. Fitch and H. Jobic, J. Chem. Soc. Chem. Commun. (1990) 1152.
[5] M. Czjzek, T. Vogt and H. Fuess, Zeolites 11 (1991) 832.
[6] M. Czjzek, H. Fuess and T. Vogt, J. Phys. Chem. 95 (1991) 5255.
[7] B. Lian Su, J.M. Manoli, C. Potvin and D. Barthomeuf, J. Chem. Soc. Faraday Trans. 89 (1993) 857.
[8] D. Barthomeuf and A. de Mallmann, Ing. Eng. Chem. Res. 29 (1990) 7, 1437.
[9] A. de Mallmann and D. Barthomeuf, J. Chem. Soc. Chem. Commun. (1986) 476.
[10] D.M. Ruthven and M. Goddard, Zeolites 6 (1986) 275.
[11] J.P. Bellat, M.H. Simonot-Grange and S. Jullian, Compt. Rend. Acad. Sci. 316 (II) (1993) 1363.
[12] J. Kärger and H. Pfeifer, Zeolites 9 (1989) 267;
J. Kärger and D.M. Ruthven, Zeolites 7 (1987) 90.
[13] M. Eic, M.V. Goddard and D.M. Ruthven, Zeolites 8 (1988) 258.
[14] A. Germanus, J. Kärger, H. Pfeifer, N.N. Samulevic and S.P. Zdanov, Zeolites 5 (1985) 91.
[15] H. Jobic, M. Bée, J. Kärger, H. Pfeifer and J. Caro, J. Chem. Soc. Chem. Commun. (1990) 341.
[16] J. Sauer and D. Deininger, Zeolites 86 (1982) 1327.
[17] P. Demontis, S. Yashonath and M.L. Klein, J. Phys. Chem. 93 (1989) 5016.
[18] L. Uytterhoven, D. Dompas and W.J. Mortier, J. Chem. Soc. Faraday Trans. 88 (1992) 2753.
[19] A.K. Nowak, A.K. Cheetham, S.D. Pickett and S. Ramdas, Mol. Simul. (1987) 167.
[20] C. Mellot, PhD Thesis, Université Pierre et Marie Curie, Paris, France (1993).
[21] J. Schefer, P. Fischer, H. Heer, A. Isacson, M. Koch and R. Thut, Nucl. Instr. Meth. A 288 (1990) 477.
[22] H.M. Rietveld, J. Appl. Crystallogr. 2 (1969) 65.
[23] C. Baerlocher, *The X-ray Rietveld System*, Institut für Kristallographie und Petrographie, ETH, Zurich (1982).