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Effect of Water Content on the Selective Coadsorption of Gaseous *p*-Xylene and *m*-Xylene on the BaY Zeolite

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ABSTRACT

The selective coadsorption of gaseous *p*-xylene and *m*-xylene is studied at 150°C on BaY with a water content which varies up to 3.5% in weight. The preadsorbed water seems to be located only in the α-cages, probably around the compensation cations in sites II. The water, which is the more strongly adsorbed component, is not replaced during the coadsorption of xylenes, and this leads to a weakening of the interactions between the aromatic ring and the compensation cation. As for the anhydrous zeolite, two selective adsorption processes are discerned according to the filling. At low filling, BaY adsorbs preferentially the more abundant isomer in the adsorptive mixture, and the presence of water has no significant effect on the selectivity except for mixtures rich in *p*-xylene with which the selectivity is up to three time as great as that with the anhydrous zeolite. At high filling, BaY is selective for *p*-xylene whatever the composition of the adsorptive mixture, and the higher the water content, the higher is the selectivity for *p*-xylene. Obviously the enhancement of the selectivity caused by water preadsorption is to the detriment of the adsorption capacity of α-cages, which is decreased up to 20%.

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Key Words. Coadsorption; Separation; Xylenes; Water; BaY; Selectivity

INTRODUCTION

The bulk separation of *p*-xylene from the C_8 aromatic cut is generally performed by liquid-phase adsorption using a simulated moving-bed technology (1–4). This process requires highly *p*-xylene selective adsorbents like X or Y zeolites exchanged with barium or potassium cations. In addition, water preadsorption is often required in order to enhance the selectivity. This has been evidenced by several papers (5, 6), but very little fundamental work has been reported.

Stoessel (7) and Guth et al. (8) studied the effect of the preadsorption of water, toluene, or methanol on the coadsorption of *p*-xylene and *m*-xylene on NaY and CuY zeolites at 60°C by frontal chromatography in the gas phase. Their results, performed at high filling of the zeolite with a water content ranging from 3 to 5% in weight, showed that the higher the water content, the lower the selectivity for *p*-xylene with NaY, whereas the reverse result was observed with CuY. Preadsorption of toluene gives a similar effect but preadsorption of methanol leads to a more noticeable modification of the selectivity. This effect could be the result, on the one hand, of steric constraints because water molecules adsorbed in the cavities add to the compensatory relocation of cations toward new sites and, on the other hand, to the formation of Brönsted acid sites because the dissociation of water solvating the cations leads to preferential adsorption of the more basic isomer, i.e., the *m*-xylene. Furlan et al. (9) studied the role of water content on the selectivity of adsorption of *p*-xylene, *o*-xylene, and ethylbenzene on KBaX zeolite. Using an elution chromatographic technique in the liquid phase for temperatures ranging from 50 to 150°C and for water contents between 2 and 6% in weight, they found that the water content has no effect on the selectivity of adsorption of *p*-xylene with respect to ethylbenzene. However, as the water content increases, the selectivity of *p*-xylene with respect to *o*-xylene increases, passes through a maximum at a water content of about 3.25%, and then decreases. These authors attribute the effect of water to an important modification of the interactions between the aromatic molecules and the zeolitic surface.

In our previous works we studied the adsorption of single or mixed *p*-xylene and *m*-xylene at 150°C in the gas phase on fully evacuated Y zeolites exchanged with Na or Ba cations (10–12). As regards adsorption, the results showed no significant difference in the capacities, heats, and diffusivities of adsorption of single components between the two isomers, except for high

filling where some slight differences were observed. Moreover, the Y zeolite exhibited a stronger affinity of adsorption for aromatic molecules with Ba than with Na as the exchangeable cation. The study of the adsorption of binary mixtures showed that the selectivity of *p*-xylene with respect to *m*-xylene depends on the exchangeable cation, the composition of the adsorptive mixture, and filling of the α-cages. Whatever the cation, two adsorption processes were discerned according to the filling. For filling lower than two molecules per α-cage, the selectivity depends only on the composition of the adsorptive mixture, the function of the adsorbent being only to store the mixture in a condensed state. Above two molecules per α-cage, the selectivity is governed by the zeolite and favors one isomer or the other one according to the cation. For example, NaY is selective for *m*-xylene while BaY is selective for *p*-xylene. The fact that selectivity appears only at high filling of α-cages was attributed to steric effects leading to an important rearrangement of the xylene molecules in the cavities, as was observed by neutron diffraction on NaX and BaX zeolites (13, 14). In view of such results, it seems obvious that the selectivity will be changed in the presence of guest molecules in the α-cages. This work is thus devoted to a study of the effect of the preadsorption of water on *p*-xylene/*m*-xylene adsorption selectivity in the gas phase of BaY at 150°C. The results will be compared with those previously obtained in the same experimental conditions for anhydrous BaY (11, 12).

EXPERIMENTAL SECTION

BaY was obtained in pure crystalline powder form from NaY by cation exchange. The degree of exchange was 99.5% and the silicon to aluminum ratio was 2.43. The chemical formula of the anhydrous zeolite is $Ba_{28}(AlO_2)_{56}(SiO_2)_{136}$. The geometric volume of α-cages calculated from structural data is $V_\alpha = 0.238\ cm^3 \cdot g^{-1}$ and of β-cages is $V_\beta = 0.047\ cm^3 \cdot g^{-1}$ (10).

The adsorption of gaseous xylenes was studied by manometry and GPC. The specific experimental device (Fig. 1) was described in detail in a previous paper (11). The operating procedure was as follows:

- A sample of 500 mg was activated in situ in the adsorption cell V_A at 400°C under 10^{-3} hPa for 12 hours.
- The temperature was brought to 200°C. Water was adsorbed after successive introductions of vapor into the adsorption cell via pipe V_{p1} while controlling the pressure with sensor P_3.
- The adsorption cell was isolated and its temperature was lowered to 150°C in order to adsorb the residual water in the cell in such a way that the vapor pressure never exceeded 0.1 hPa.

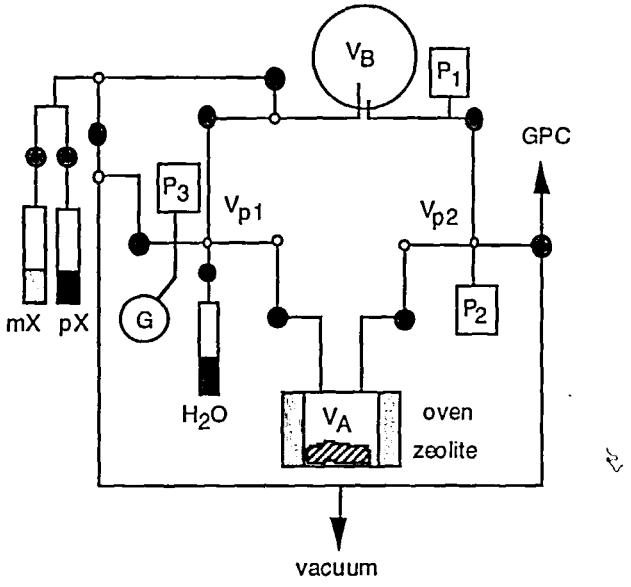

FIG. 1 Experimental setup.

- The adsorption of Xylenes was then performed by introducing the gas stored in bulb V_B into the cell by means of pipe V_{p2} and controlling the pressure with the capacitance manometer P_2.
- The amount adsorbed and the selectivity $\alpha_{pX/mX}$ were determined from the pressure reported by the sensor P_2 and the mole fractions of gas measured by GPC before and after each adsorption step.

The gas mixture is homogenized by thermal convection due to the large difference in temperature between the adsorption cell (150°C) and the pipe (25°C). A CG analysis of one adsorptive mixture as a function of time was performed. After 3 hours the pressure and the composition of the gas phase were constant, meaning that equilibrium had been reached and the gas phase was uniform.

The adsorption equilibria of single xylene and *p*-xylene–*m*-xylene mixtures were carried out at 150°C for pressure ranging from 0.01 to 4 hPa. The initial compositions of the adsorptive mixtures and the water content of the BaY are given in Tables 1 and 2. The single xylenes and the five mixtures were adsorbed on Sample BaY_1, and only Mixture 2 was adsorbed on Samples $BaY_{0.5}$ and BaY_2. Considering the strong adsorption affinity of the faujasite zeolites for water compared to those for xylenes (15), the water partial pres-

TABLE 1
Composition of Initial Adsorptive Mixtures, Gas Phase, and Adsorbate at Equilibrium

		Mole fraction					
		p = 0.5 hPa		p = 1.5 hPa		p = 3 hPa	
Mixture	y^0_{pX}	y_{pX}	x_{pX}	y_{pX}	x_{pX}	y_{pX}	x_{pX}
1	0.14	0.30	0.09	0.10	0.09	0.06	0.10
2	0.25	0.40	0.25	0.23	0.24	0.12	0.26
3	0.50	0.47	0.50	0.45	0.50	0.37	0.52
4	0.75	0.50	0.75	0.54	0.78	0.63	0.81
5	0.90	0.61	0.92	0.72	0.93	0.79	0.96

sure was assumed to remain constant during the experiment. The adsorption data were analyzed by assuming the zeolite and the preadsorbed water constitute a hydrous adsorbent, the physicochemical properties of which are unchanged during the adsorption of aromatic isomers. The adsorbate/adsorbent system was then defined as (pX and/or mX)/$BaY_{0.5}$, BaY_1, or BaY_2. Thus the results were analyzed in the same way as those deduced from the study with the anhydrous zeolite whose adsorbate/adsorbent system was (pX and/or mX)/BaY.

RESULTS AND DISCUSSION

Adsorption of Single Xylenes

The adsorption isotherms of single xylenes on BaY and BaY_1 are shown in Fig. 2. The anhydrous BaY exhibits an unusual behavior. Indeed, the adsorption isotherms of *p*-xylene and *m*-xylene are the same although the zeolite is selective for *p*-xylene. This result is discussed in more detail in Ref. 11. It suggests that the selective adsorption process of xylenes on BaY is governed

TABLE 2
Water Content of BaY (V_{H_2O} is the volume of water adsorbed at 150°C and n_{H_2O} is the number of water molecules per Ba^{2+} cation in one unit cell)

Sample	m_{H_2O} ($g \cdot g^{-1}$)	V_{H_2O} ($cm^3 \cdot g^{-1}$)	n_{H_2O} (molecules/Ba^{2+})
$BaY_{0.5}$	0.016	0.018	0.5
BaY_1	0.033	0.037	1
BaY_2	0.066	0.074	2

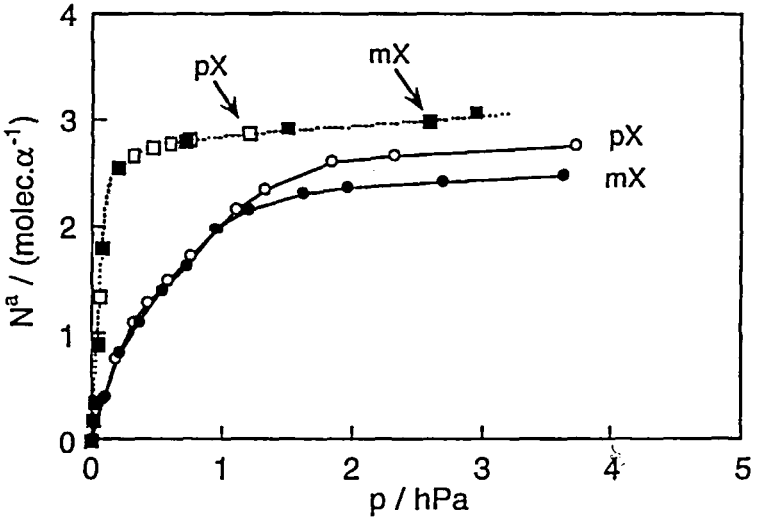

FIG. 2 Adsorption isotherms of single xylenes on BaY_I at 150°C (dashed line: anhydrous BaY).

by entropic effects. The adsorption isotherms of single xylenes on BaY_I lie below those determined on BaY. For pressure up to 1 hPa, the adsorption isotherms of *p*-xylene and *m*-xylene overlap, and at very low pressure ($p <$ 0.2 hPa) the adsorption follows Henry's law. The values of Henry constants are lower for BaY_I than for BaY (Table 3). This means that the adsorbate/adsorbent interactions are weakened by the presence of water in the cavities. Indeed, water molecules, solvating the cations located on Sites II in the α-cages, probably cause screening effects in the interactions between the aromatic ring and the compensation cation. For pressure higher than 1 hPa, the

TABLE 3
Henry Constants for the Adsorption of *p*-Xylene and *m*-Xylene on Anhydrous and Hydrous BaY at 150°C

	K_H (molecules·α^{-1}·hPa^{-1})	
Sample	*p*-Xylene	*m*-Xylene
BaY	82	82
BaY_I	4	4

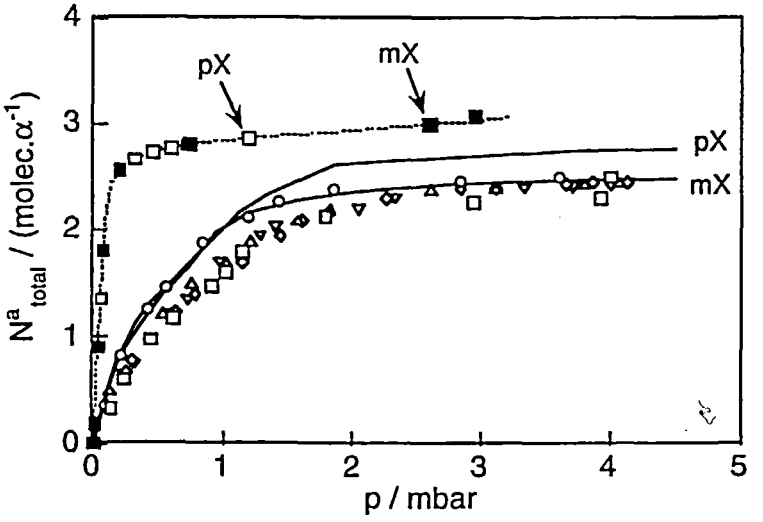

FIG. 3 Adsorption isotherms of xylenes mixtures on BaY_1 at 150°C (solid lines: single xylenes on BaY_1; dashed line: anhydrous BaY; ▽, Mixture 2; ◇, Mixture 3; □, Mixture 5).

amount of xylene adsorbed on BaY_1 is higher with *p*-xylene than with *m*-xylene. Thus, the amounts of *p*-xylene and *m*-xylene adsorbed under 4 hPa are 2.75 and 2.45 molec·α^{-1}, respectively, on BaY_1 whereas they are the same on BaY (3 molec·α^{-1}). The presence of water in the cavities decreases the adsorption capacity of BaY to about 8 and 18% for *p*-xylene and *m*-xylene, respectively.

Adsorption of Binary Mixtures

The coadsorption isotherms $N^a = f(p)_T$ for BaY_1 are shown in comparison with those for BaY in Fig. 3, and the partial adsorption isotherms $N_i^a = f(p)_T$ are given in Fig. 4. The coadsorption isotherms are superimposed on the single *m*-xylene adsorption isotherm in the whole range of investigated pressure, with the experimental accuracy taken into account. Whatever the composition of the adsorptive mixture, the amounts of mixture adsorbed under 4 hPa is 2.45 molec·α^{-1}. It may be noticed that for Mixture 3, with the pressure higher than 2.5 hPa, the amount of *m*-xylene adsorbed decreases slightly while that of *p*-xylene increases continuously. This result means that at high filling of α-cages, some molecules of *m*-xylene are replaced by *p*-xylene. The effect of the water content on the adsorption capacity was investigated with Mixture 2 and the samples $BaY_{0.5}$, BaY_1, and BaY_2 (Table 2). Figure

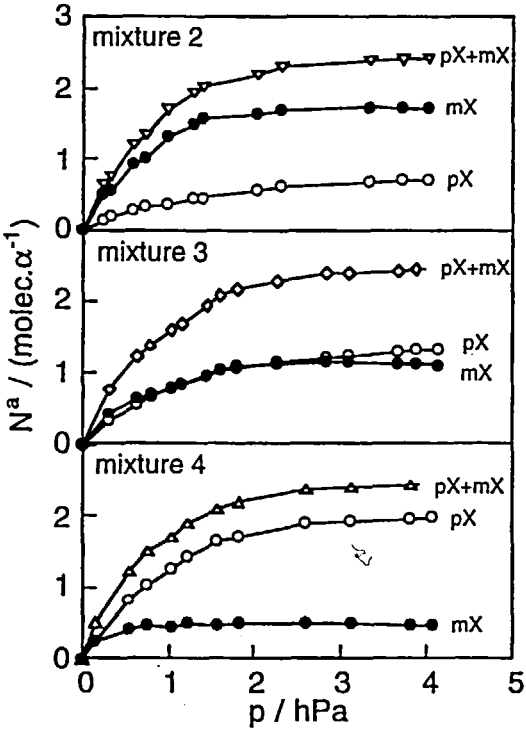

FIG. 4 Coadsorption and partial adsorption isotherms on BaY_1 at 150°C.

5 shows the volumes of water and xylenes adsorbed as a function of the water content expressed in molecules per Ba^{2+} cation in one unit cell. The adsorbate volume was determined by taking the density of the adsorbate given in Table 4, and it was calculated by assuming that above the boiling point the adsorbate is like a pressurized gas, as suggested by Nikolaev and Dubinin (16). When the water content increases, the volume of xylenes adsorbed decreases and the total volume of adsorbate (xylenes + water) never exceeds the geometric volume of α-cages, and it decreases too. As the xylene isomers can be adsorbed only in the α-cages, this result shows 1) that water is also adsorbed in the α-cages and probably solvates the compensation cation located in Sites II, and 2) that water is not replaced by xylenes during their adsorption.

As observed for anhydrous BaY, the selective coadsorption process of *p*-xylene and *m*-xylene on partially hydrated BaY_1 depends on the filling of α-cages and the composition of the adsorbate. Two ranges of filling are also

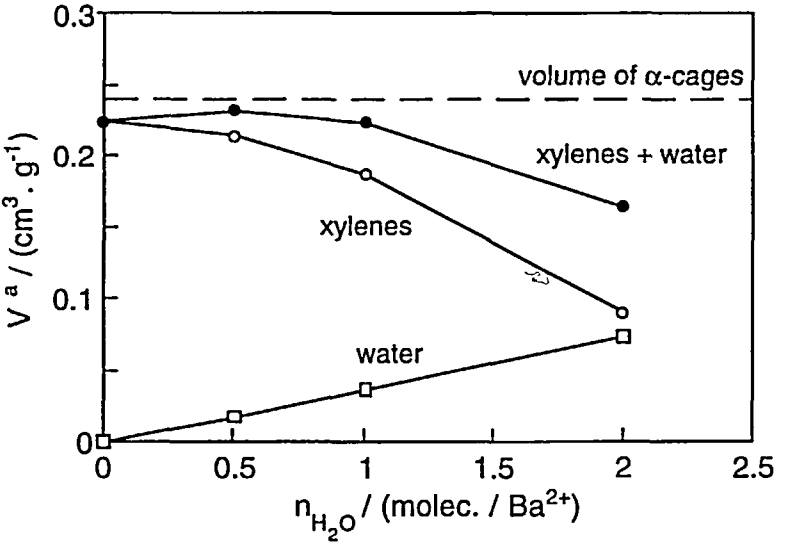

FIG. 5 Volume of adsorbates as a function of the water content of BaY at 150°C.

discerned (Fig. 6). For a filling lower than 2 molec·α^{-1}, the adsorption process is not especially selective. The zeolite preferentially adsorbs the more abundant isomer in the adsorptive mixture, and the selectivity does not change as the filling proceeds. The presence of water does not change the selectivity except for the adsorptive mixtures rich in *p*-xylene (Mixtures 4 and 5), for which the selectivities are higher than those measured on the anhydrous zeolite (Fig. 6). For a filling higher than 2 molec·α^{-1} the adsorption process is selective for *p*-xylene whatever the composition of the adsorptive mixture. With Mixtures 1, 2, and 3 the selectivity increases sharply as the last aromatic molecules are adsorbed in the α-cages. In the presence of water the selectivity for *p*-xylene is sharply increased. It is up to three times as great as with

TABLE 4
Density of Adsorbate (in g·cm^{-3}) at 150°C Following the Assumption of Nikolaev–Dubinin (16). The Density of the Xylenes Mixture Adsorbed Is the Arithmetic Mean of the Densities of Single Xylenes

Water	*p*-Xylene	*m*-Xylene	Xylenes mixture
0.89125	0.7411	0.7531	0.7471

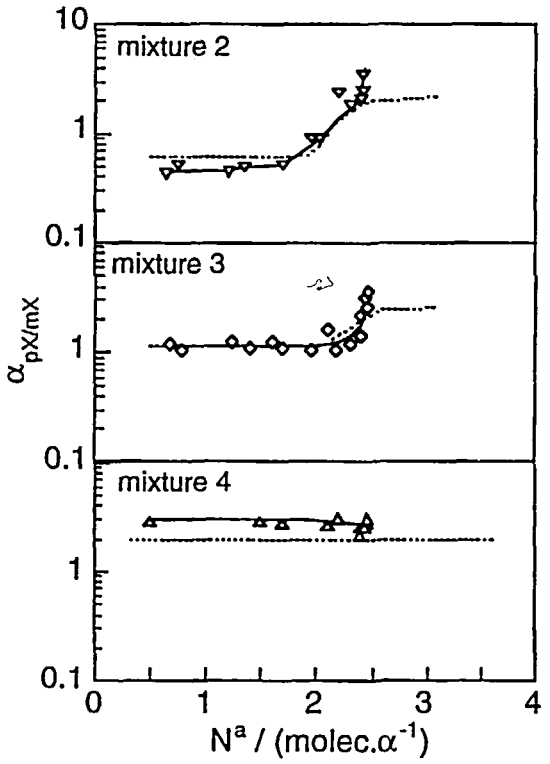

FIG. 6 Dependence of the filling of α-cages on the selectivity $\alpha_{pX/mX}$ of BaY_1 at 150°C (dashed lines: anhydrous BaY).

anhydrous BaY at complete filling of α-cages. However, notice that the selectivity decreases slightly with mixtures rich in *p*-xylene as the last molecules of xylenes are adsorbed (Fig. 6).

The dependence of the equilibrium composition of the adsorbate on the selective adsorption process at constant pressure is shown in Figs. 7 and 8. At low pressure, i.e., low filling, the *x*–*y* diagrams $y_{pX} = f(x_{pX})_{T,p}$ for BaY and BaY_1 have the same shape, but in the presence of water the mole fraction of the gas is more dependent on the composition of the adsorbate (Fig. 7). Both *x*–*y* diagrams have an azeotropic point at a mole fraction of adsorbate close to 0.5. As the mole fraction of the adsorbate is below this value, BaY and BaY_1 have almost the same selectivity and preferentially adsorb the *m*-xylene. On the contrary, as the adsorbate becomes rich in *p*-xylene, the zeolites are selective for *p*-xylene and the selectivity of the hydrous zeolite be-

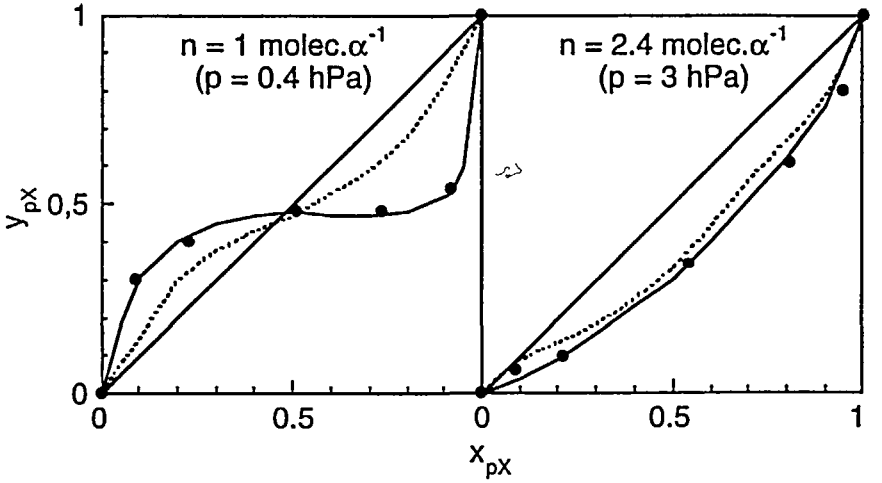

FIG. 7 x–y diagram of BaY_1 at 150°C for low and high filling with xylenes (dashed lines: anhydrous BaY).

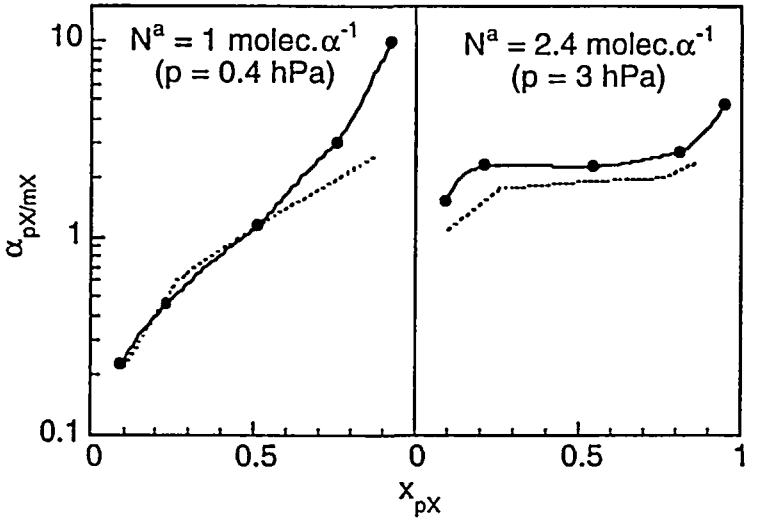

FIG. 8 Dependence of the composition of the adsorbate at equilibrium on the selectivity $\alpha_{pX/mX}$ at 150°C (dashed lines: anhydrous BaY).

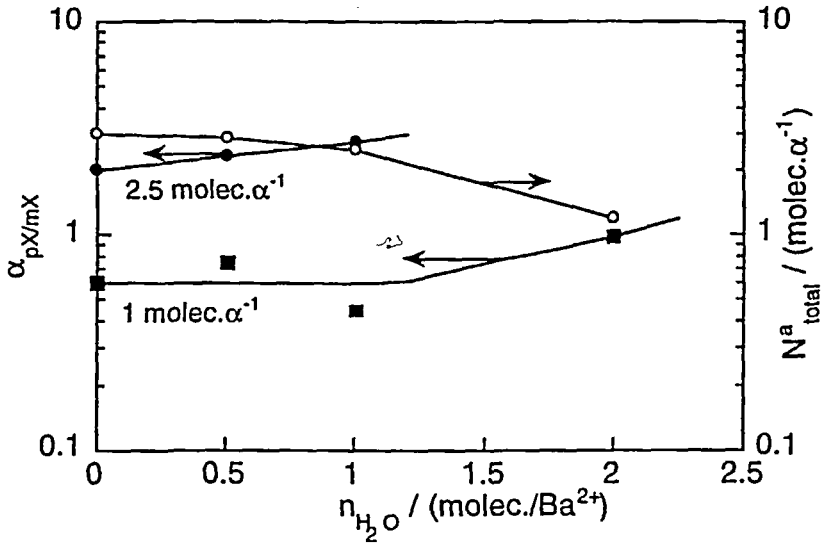

FIG. 9 Dependence of the water content on the xylenes' adsorption capacity and on the selectivity $\alpha_{pX/mX}$ of BaY at 150°C.

comes much higher than that of anhydrous BaY (Fig. 8). At high pressure, i.e., high filling ($N^a > 2$ molec·α^{-1}), the x–y diagrams of BaY and BaY_I are the same (Fig. 7). The selectivity favors *p*-xylene and is rather constant over a wide range of composition ($0.2 < x_{pX} < 0.8$). It is only when the adsorbate is excessively rich in one isomer or the other that the selectivity varies with the composition (Fig. 8).

The effect of water content on the selectivity is shown in Fig. 9, where the evolution of the adsorption capacity of BaY is also reported. Results obtained from the adsorption of Mixture 2, which is rich in *m*-xylene, on the three partially hydrated BaY samples (Table 2) show that, at low filling, the selectivity for *p*-xylene does not change with the water content. Nevertheless, at filling close to the saturation of α-cages, the higher the water content, the higher is the selectivity for *p*-xylene. Obviously, this increase of selectivity is to the detriment of the adsorption capacity owing to the preadsorption of water.

CONCLUSION

This work shows that the selectivity of adsorption of *p*-xylene with respect to *m*-xylene of BaY zeolite, which depends on the exchangeable cation, the

composition of the mixture, and the filling of α-cages, is also a function of the water content of the zeolite.

The preadsorbed water molecules are probably located in the α-cages around the exchangeable cations in Sites II. The presence of water in the cavities leads to a decrease of the xylene adsorption capacity and to a weakening of the interactions between the aromatic ring and the compensation cation.

Water preadsorption has no significant effect on the selective adsorption process at low filling of α-cages except for mixtures rich in *p*-xylene. On the other hand, at high filling the selectivity for *p*-xylene is strongly enhanced by the presence of water.

The effect of water content on the selectivity is attributed, on the one hand, to the important steric hindrance caused by water molecules in the α-cages and by the displacement of Ba^{2+} cations. Indeed, it is well known that the occupancy of cation sites in faujasite-type zeolites depends on the degree of hydration (15). Moreover, neutron and RX diffraction experiments carried out on anhydrous NaX, BaX, NaY, and YbNaY zeolites in the presence of xylenes showed that the cations could move inside or outside the zeolitic framework according to the filling (13, 14, 17). Such a phenomenon probably occurs during the adsorption of xylenes on hydrated BaY. On the other hand, the presence of a polar guest molecule like water changes the molecular interactions, especially those which occur with other polar molecules like *m*-xylene. The strong dipolar moment of water is probably part of the reason that at high filling the preadsorbed water seems to prevent access of *m*-xylene to α-cages.

ABBREVIATIONS USED

T	temperature of adsorption
p	pressure of gas at equilibrium
N^a	amount of xylenes adsorbed expressed in molecules of xylene per α-cage (molec·α^{-1})
N^a_{total}	total amount of xylenes mixture adsorbed (molec·α^{-1})
V^a	volume of adsorbate at 150°C ($cm^3 \cdot g^{-1}$)
m_{H_2O}	amount of water preadsorbed ($g \cdot g^{-1}$)
V_{H_2O}	volume of water preadsorbed at 150°C ($cm^3 \cdot g^{-1}$)
n_{H_2O}	water content (molecules of water per Ba^{2+} in one unit cell)
$\alpha_{pX/mX}$	selectivity of adsorption of *p*-xylene with respect to *m*-xylene, the so-called separation factor: $\alpha_{pX/mX} = x_{pX}y_{mX}/x_{mX}y_{pX}$
y_i^0	mole fraction of Component *i* in the initial adsorptive mixture
y_i	mole fraction of Component *i* in the gas at equilibrium
x_i	mole fraction of Component *i* in the adsorbate at equilibrium

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