Adsorption 6, 61–71 (2000)

Toward a Better Understanding on the Adsorption Behavior of Aromatics in 12R Window Zeolites

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Received May 28, 1999; Revised August 13, 1999; Accepted September 2, 1999

Abstract. Benzene adsorption behavior in a large family of 12R window zeolites (X, Y, EMT, Beta and LTL) has been examined by means of in-situ FTIR spectroscopy and correlated with the zeolite structure, the type and number of counter-ions, and the negative charge on framework oxygen atoms of zeolites. The effect of coadsorption of HCl, NH_3 and CH_3NH_2 on the benzene location has also been studied. The present work illustrates that besides the benzene adsorption on counter ions of zeolites, the 12R windows could also be the adsorption sites for benzene. Upon adsorption of coadsorbates such as HCl, NH_3 and CH_3NH_2, the migration of preadsorbed benzene molecules from one type of adsorption sites towards another, i.e. from 12R windows towards the cations for HCl and opposite direction for NH_3 and CH_3NH_2, has been evidenced. The lack of adsorption of benzene on 12R windows of NaBeta even upon coadsorption of a series of basic molecules reveals that benzene adsorption on 12R windows is most likely governed by a molecular recognition effect where benzene molecule and 12R window should have the adapted chemical and structural properties like in enzyme-substrate system and zeolites can be referred to as solid enzymes or zeo-enzymes. This paper indicates also that the adsorption properties of zeolites can be modified and accommodated by introduction of a co-adsorbate.

Keywords: benzene adsorption, 12R window zeolites, coadsorption of HCl, NH_3, CH_3NH_2, FTIR, molecular recognition

Introduction

Zeolites, a class of microporous crystalline materials, are often involved in the catalytic production, transformation and separation processes of aromatics and, in particular, the 12R window zeolites have mostly been selected. It is well known that the separation of aromatics in a mixture by adsorption processes and the catalytic processes of aromatics must be preceded by selective adsorption of molecules. Hence, the adsorption of molecules in the cavities of zeolites is a central step which influences strongly the selectivity and activity of the reaction and the efficiency of separation processes. A better understanding of the adsorption behavior of aromatics in zeolites is therefore of important interest to describe the catalytic and adsorptive properties of zeolites and to develop advanced catalysts and adsorbents.

The present paper deals with the location of aromatics using benzene as probe molecule in a large series of 12R window zeolites with different Si/Al ratios,

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compensating ions and structures and its change upon coadsorption of acid and basic molecules. We try to elucidate on a molecular level the dominating factors for benzene location.

Experimental

Materials

NaX (Si/Al = 1.2), NaY (Si/Al = 2.4) and KL (Si/Al = 3.0) were provided by Union Carbide and other alkali cations exchanged X and Y zeolites were prepared by ion exchange from NaX and NaY using the methods reported by Su and Barthomeuf (1995). A series of dealuminated NaY zeolites were made using the procedure reported by Szostak (1991). EMT and Beta zeolites were respectively synthesized using 18-crown-6 and tetraethylammonium hydroxide as template in KULeuven, Belgium (Feijen et al., 1995) and in Instituto de Technologia Quimica, Spain (Camblor et al., 1991). To remove organic templates incorporated in the pores of EMT and Beta zeolites, the as-synthesized samples were first calcined in a dry N_2 flow with a heating rate of around 50 K per hour. When the desired temperature (823 K) was reached, the gas was replaced by O_2 and the temperature was maintained for 5 h. The organic template-free NaEMT and H(Na)Beta zeolites were obtained. To obtain fully Na^+ ions exchanged Beta zeolite, five grams of calcined sample were added in 50 mL of 1M sodium chloride solution. The mixture was stirred and heated in reflux condition for 5 h. After filtration, the obtained solid was washed with distilled water and filtrated until all Cl^- ions were removed. The recovered solid was then dried in an oven at 373 K overnight and labelled as NaBeta. The chemical composition and characteristics of these materials are summarized in Table 1.

Table 1. Chemical composition and characteristics of the zeolites studied.

Zeolite	Chemical composition	Si/Al ratio	$-\delta_O$[a]
NaX	$Na_{86}(AlO_2)_{86}(SiO_2)_{106}$	1.2	0.410
CsX	$Cs_{57}Na_{29}(AlO_2)_{86}(SiO_2)_{106}$	1.2	0.463
HY	$H_{56.4}Na_{0.6}(AlO_2)_{57}(SiO_2)_{135}$	2.4	0.228
LiY	$Li_{37}Na_{18}(AlO_2)_{55}(SiO_2)_{137}$	2.5	0.345
NaY	$Na_{56}(AlO_2)_{56}(SiO_2)_{136}$	2.4	0.350
KY	$K_{54}Na_2(AlO_2)_{56}(SiO_2)_{136}$	2.4	0.380
RbY	$Rb_{45}Na_9(AlO_2)_{54}(SiO_2)_{138}$	2.6	0.382
NaY_{DI}[b]	$Na_{44}(AlO_2)_{44}(SiO_2)_{148}$	3.4	0.320
NaY_{DII}[b]	$Na_{27}(AlO_2)_{27}(SiO_2)_{165}$	6.1	0.275
$NaYD_{DIII}$[b]	$Na_7(AlO_2)_7(SiO_2)_{185}$	26.4	0.212
NaEMT	$Na_{21}(AlO_2)_{21}(SiO_2)_{75}$	3.6	0.317
NaBeta	$Na_{3.5}(AlO_2)_{3.5}(SiO_2)_{60.5}$	17.3	0.240
KL	$K_9(AlO_2)_9(SiO_2)_{27}$	3.0	0.352

[a] Negative charge on oxygen atoms calculated using Sanderson electronegativity equalisation principle (Sanderson, 1976; Mortier, 1978).

[b] Prepared from NaY via NH_4Y by dealumination and then ion exchange.

Infrared Studies

The adsorption experiments were performed on self-supported zeolite wafers (15 mg/cm^2) prepared with a pressure of 5 tons/cm^2. The zeolite sample wafer locked in a holder was placed in the i.r. cell, which is made of Pyrex with two NaCl windows and directly connected with a vacuum line with primary and turbo molecular pumps, and heated in-situ in a dry oxygen flow from room temperature to 723 K at a rate of 3 K per minute. The temperature was maintained overnight in the same atmosphere. The sample was further treated under vacuum for 4 hours at the same temperature. The i.r. cell was then cooled slowly to room temperature and the spectrum of zeolite phase alone was recorded as a reference at room temperature using a Fourier Transform Bio-Rad FTS-60A or Perkin-Elmer 1750 or Perkin-Elmer Spectrum 2000 Spectometer. It should be noticed that each series of studies was made using the same spectrometer. The adsorption of the increasing and known amounts of benzene was carried out as described by de Mallmann and Barthomeuf (1989), Su and Barthomeuf (1993, 1995) and Su and Norberg (1998) on the pretreated wafer. After each adsorption, the sample was maintained at room temperature for 1 hour for equilibration. Our previous work (Su and Barthomeuf, 1993, 1995) have shown that an equilibration of 1 h at room temperature is sufficient to consider that the system is at the equilibrium, especially for the low weight of zeolite wafers used since no change in i.r. spectra recorded has been noted even after 45 h equilibration at room temperature. The spectra (gas phase of i.r. cell and zeolite phase containing adsorbed species) were then recorded.

The influence of coadsorption of HCl, ammonia and methylamine on the benzene location was performed on the samples having a defined benzene loading (see the text). After recording the spectra of adsorbed benzene, an increasing and known amount of coadsorbate (HCl or ammonia or methylamine) was introduced into the i.r. cell. After 1 h equilibration at room temperature, the i.r. spectra were recorded. The quantities of molecules introduced into the i.r. cell were expressed in molecules per unit cell (molecules/u.c.), although, after saturation of the zeolite, this has no real physical meaning. However, it does facilitate the comparison of the results. The amount of adsorbate introduced into the i.r. cell was controlled by using a calibrated volume and an absolute pressure gauge.

In the present study, only the adsorbed phases on zeolite wafers are reported. The spectrum of zeolite phase and that of gas phase of the i.r. cell have been subtracted.

Results

Effect of the Compensating Ions on the Location of Benzene in Zeolites

The interaction of benzene with zeolite has been studied using several means of investigation in order to characterize the active adsorption sites for benzene and aromatics (Su and Barthomeuf, 1993, 1995; Su and Norberg, 1998; Bull et al., 1993, 1995; Auerbach et al., 1996). In the C—H out-of-plane (o.o.p.) bending vibration range (2200–1700 cm^{-1}), liquid benzene gives a pair of bands at 1960 and 1815 cm^{-1}, belonging to the ($\nu_5 + \nu_{17}$) and ($\nu_{10} + \nu_{17}$) vibrations, respectively. Figure 1 shows the bands of benzene adsorbed on a series of Y zeolites exchanged with different alkali ions or protons. Two pairs of bands are observed on alkali-exchanged Y zeolites (Fig. 1(b)–(e)) while only one main pair is detected on HY (Fig. 1(a)). All these peaks are shifted towards high wavenumbers compared to those of liquid benzene. It is known that the shift of the vibration bands of the C—$\text{H}_{\text{o.o.p.}}$ of adsorbed benzene molecules can provide information on the type of site interacting with benzene. Benzene molecules, interacting with cations or protons of zeolites, give a relatively small shift in wavenumber of around 20–40 cm^{-1} compared to the wavenumbers of the C—$\text{H}_{\text{o.o.p.}}$ bands of liquid benzene since the interaction of the counter ions with the π electron cloud of benzene rings affects indirectly, and only weakly, the C—H out-of-plane bending vibration. This pair of bands was previously referred to as the low frequency bands (LF) (Su and Barthomeuf, 1993, 1995; Su and Norberg, 1998). Adsorption of benzene on the oxygen atoms of the 12R windows induces a relative high shift in wavenumber of around 40–100 cm^{-1} because the hydrogen atoms of benzene molecules interact with the oxygen atoms of zeolites, the C—H vibration is directly and strongly affected. This pair was, hence, referred to as the high frequency bands (HF). However, the exact shift value and the presence of two pairs of bands are strongly dependent on the zeolites used, the Lewis acidity of cations, the basicity of framework oxygen atoms, the number and the type of cations present in zeolite, and the benzene loading. Figure 2 gives a shematic representation of these two kinds of interaction of benzene molecules with zeolite sites.

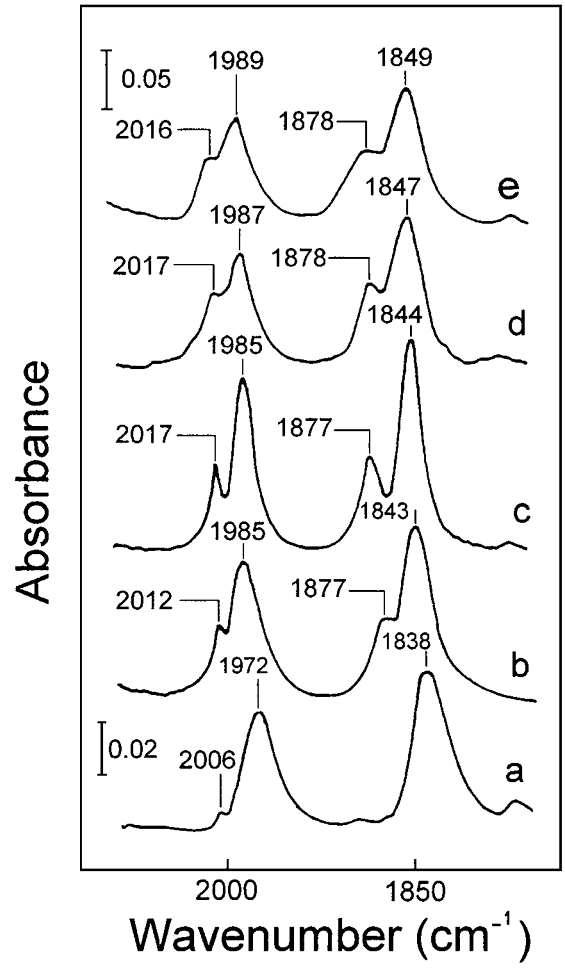

Figure 1. IR spectra of C—$\text{H}_{\text{o.o.p.}}$ vibrations of benzene adsorbed on a series of Y zeolites exchanged with H^+ (a), Li^+ (b), Na^+ (c), K^+ (d) and Rb^+ (e) ions. All these zeolites are saturated by benzene molecules. Note that the absorbance scale for HY is 0.02 and 0.05 for other zeolites.

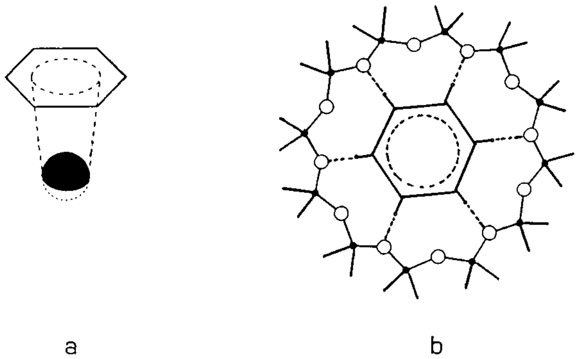

Figure 2. Schematic representation of the experimentally determined binding sites for benzene in 12R window zeolites. Interaction of counter ions with π-electrons of the benzene ring (a), and the interaction of benzene molecule through its six hydrogen atoms with the six oxygen atoms of the 12R window. Counter ions (●), oxygen atoms of the 12R window (O) and hydrogen atoms of benzene (o).

The two pairs of bands observed on alkali-exchanged Y zeolites give the shift values of ca. 28 and 60 cm^{-1}, corresponding therefore respectively to the interaction of π electron cloud of benzene with alkali ions (LF bands) and that of hydrogen atoms of benzene with oxygen atoms of 12R windows (HF bands). The pair of band observed on HY, according to the shift value of ca. 20 cm^{-1}, can be attributed to the interaction of benzene with the protons of this zeolite. The results just presented show that in alkali-exchanged Y zeolites, not only the compensating ions are the adsorption sites for benzene, the 12R windows can also interact with benzene molecules while in HY, solely the protons interact with benzene molecules.

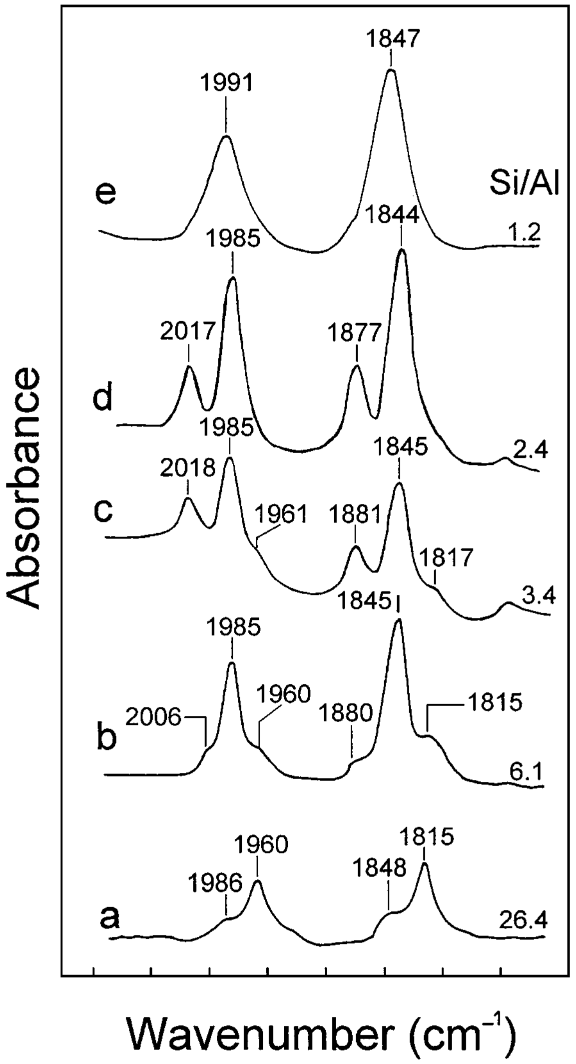

Figure 3. IR spectra of benzene adsorbed on a series of faujasite zeolites with different Si/Al ratios: 26.5 (a), 6.1 (b), 3.4 (c), 2.4 (d) and 1.2 (e). All these zeolites are saturated by benzene molecules.

Effect of Si/Al Ratio on the Location of Benzene

Figure 3(a)–(d) report the IR spectra of benzene adsorbed on a series of Na^+-exchanged Y zeolites with different Si/Al ratio. The adsorption of benzene on NaX (Fig. 3(e)) gives one pair of broad bands at 1991 and 1847 cm^{-1}. Because of the shift value of ca. 30 cm^{-1}, this pair can be attributed to the interaction of benzene with Na^+ ions. Two pairs of bands are detected on NaY (Si/Al = 2.4) and NaY_{DI} (Si/Al = 3.4). These two pairs of bands are generated from the adsorption of benzene on Na^+ ions (LF bands) and 12R windows (HF bands) according to their shift values of ca. 27 and 60 cm^{-1}, respectively. A pair of shoulders at 1961 and 1817 cm^{-1} is also seen on NaY_{DI} (Fig. 3(c)) and can be ascribed to the condensation of benzene in zeolites (referred to as pseudo-liquid phase: PL bands). The wavenumbers of this pair of bands are similar to those of liquid benzene as previously described by Su and Barthomeuf (1993). As the Si/Al ratio increases, the intensity of HF and LF bands decreases while that of PL bands increases. This is because the number of adsorption sites (counter ions) decreases as Si/Al ratio increases while the void space of the supercages in which benzene molecules can be condensed remained inchanged. Hence, less benzene molecules interacting with adsorption sites but more benzene molecules condensed in the cavities of zeolites can be found. On

NaY_{DIII} (Si/Al = 26.4) (Fig. 3(a)), HF bands disappear completely and PL bands are most intense. The above results demonstrate clearly that the location of benzene on 12R windows depends strongly on the Si/Al ratio. Both very high or very low Si/Al ratio disfavor the location of benzene on 12R windows.

Effect of Zeolite Structure on the Location of Benzene

Figure 4 depicts the spectra of benzene adsorbed on a series of zeolites with different structures. The adsorption of benzene on cations is observed for all four zeolite structures studied. However, only on NaY_{DI} (Si/Al = 3.4) (Fig. 4(c)), the location of benzene on 12R windows is detected. Although NaEMT and KL zeolites have similar Si/Al ratio to that of NaY_{DI} zeolite, no benzene adsorption on 12R windows is observed. A pair of intense bands at 1962 and 1818 cm^{-1}, corresponding to PL bands, is seen on NaBeta (Fig. 4(d)). This is because of the high porosity and the low number of counter-ions of NaBeta. Only part of benzene molecules which penetrates into the pores of this zeolite interacts with counter-ions. The other part condenses in the pores or interacts with the large number of silanols present in this zeolite after pretreatment (Su and Norberg, 1998).

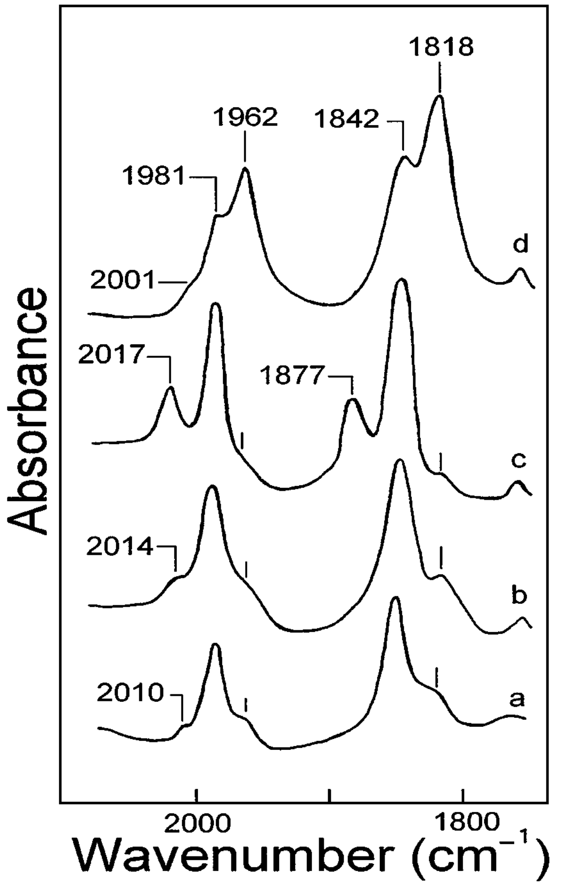

Figure 4. IR spectra of benzene adsorbed on a series of zeolites with different structures, KL (a), NaEMT (b), NaY_{DI} (c) and NaBeta (d) at benzene saturation condition (a pressure of around 2.7 kPa of benzene is present in the i.r. cell and in contact with zeolite wafers).

Effect of Coadsorbates on the Location of Benzene

Coadsorption of HCl. This was performed on a CsX wafer in contact with 1.1 molecules of benzene per supercage. Figure 5 demonstrates the spectra of benzene adsorbed on CsX upon coadsorption of HCl. Both the LF and HF bands are observed on this zeolite in the presence of benzene alone and HF bands are most intense (Fig. 5(a)). Upon coadsorption of HCl, the intensity of HF bands decreases while that of LF bands increases. In the presence of high numbers of HCl

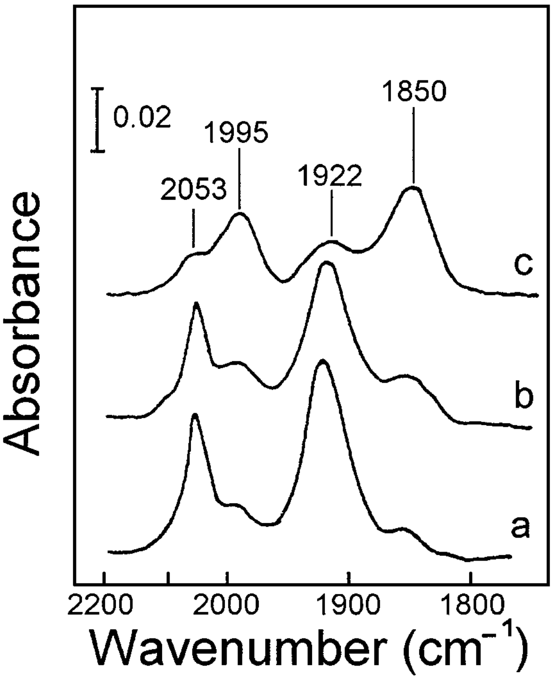

Figure 5. Change in IR spectra of $C{-}H_{o.o.p.}$ vibrations of benzene adsorbed on CsX zeolite upon coadsorption of different amount of HCl molecules per surpercage: 0.0 (a), 1.2 (b) and 3.5 (c). The experiment was carried out on a sample wafer adsorbed around 1.1 molecules of benzene per supercage.

molecules in the IR cell (Fig. 5(c)), LF bands become most intense. The above observation shows clearly a migration of benzene from the 12R windows towards the ions upon coadsorption of HCl.

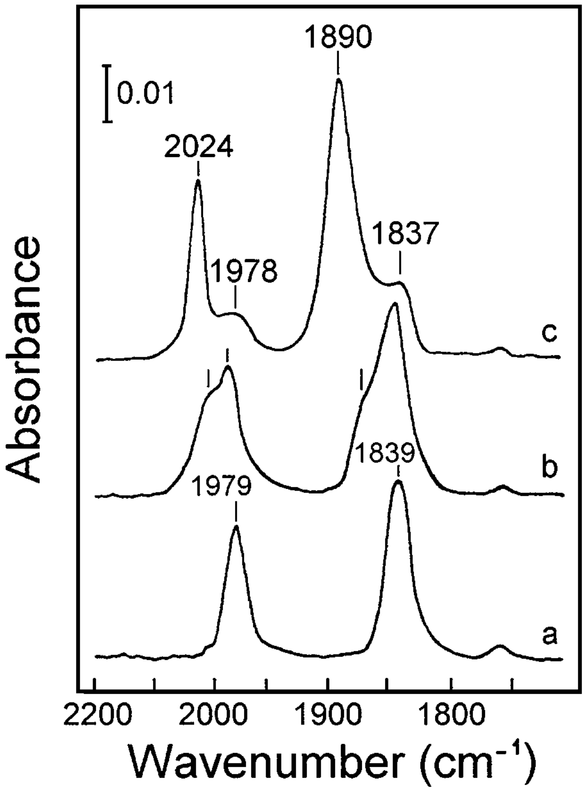

Figure 6. Change in IR spectra of C—$H_{o.o.p.}$ vibrations of benzene adsorbed on HY with introduction of increasing and known amounts of ammonia molecules per supercage: 0.0 (a), 32.8 (b) and 120 (c). The benzene loading used for this study is 8.0 molecules of benzene per unit cell of HY.

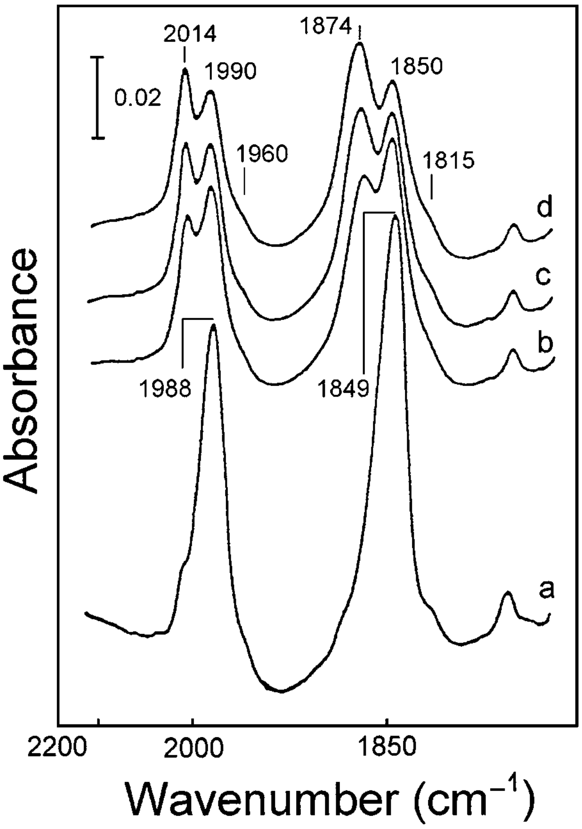

Figure 7. Change in IR spectra of C—$H_{o.o.p.}$ vibrations of benzene adsorbed on NaEMT with introduction of increasing and known amounts of ammonia molecules per unit cell: 0.0 (a), 99.6 (b), 153.2 (c) and 215.3 (d). The benzene loading used for this study is 20.5 molecules per unit cell.

Coadsorption of NH_3. The study was made on HY, NaEMT, KL and NaBeta zeolite wafers with benzene loading of 8.0, 20.5, 2.5 and 6.0 molecules per unit cell, respectively. At the benzene loading used, all the adsorption sites of these four zeolites are occupied by benzene molecules according to Su and Barthomeuf (1993, 1995) and Su and Norberg (1998). Figures 6–9 show the spectra of benzene adsorbed on HY (Fig. 6), NaEMT (Fig. 7), KL (Fig. 8) and NaBeta (Fig. 9) upon coadsorption of NH_3. In the presence of benzene alone (spectrum a of Figs. 6–9), only one pair of bands, assigned to the adsorption of benzene on counter-ions (LF bands) is observed in these four zeolites. Upon coadsorption of NH_3, both on HY (Fig. 6) and NaEMT (Fig. 7) zeolites, the HF bands appear while the LF bands decrease simultaneously in intensity. The HF bands become most intense in the presence of a high number of NH_3 in the IR cell (Figs. 6(c) and 7(d)). This indicates clearly that the 12R windows become adsorption sites for benzene and benzene molecules migrate from cations towards the 12R windows upon coadsorption of NH_3. However, none of this migration is observed either in KL (Fig. 8) or in NaBeta (Fig. 9). Only the LF bands are present upon coadsorption of NH_3 and their intensities decrease due to the adsorption of NH_3 on those zeolites which desorbs benzene molecules. A large band at 1935 cm^{-1} is observed on NaBeta zeolite and has been ascribed to the framework overtones modification (Zecchina et al., 1995), which indicates an increase in lattice parameter and the deformation of the framework. This deformation of zeolite framework observed in NaBeta zeolite in the presence

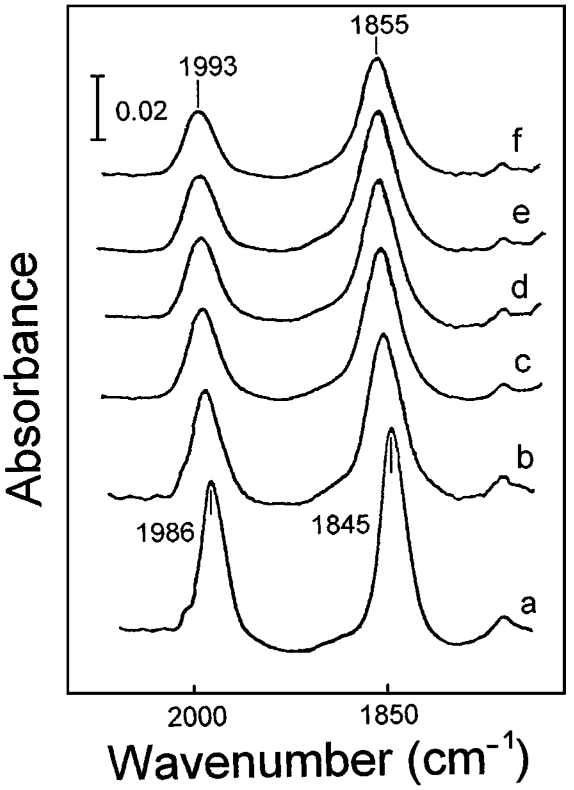

Figure 8. Change in IR spectra of C—H$_{o.o.p.}$ vibrations of benzene adsorbed on KL with introduction of increasing and known amounts of ammonia molecules per unit cell: (a): 0.0, (b): 12.3, (c): 30.4, (d): 48.4, (e): 75.5 and a pressure of 4.2 kPa of ammonia present in the cell (f). The benzene loading used for this study is 2.5 molecules per unit cell.

of NH_3 does not modify the benzene adsorption behaviour of this zeolite.

Coadsorption of CH_3NH_2. Figures 10 and 11 depict the spectra of benzene adsorbed on KL (Fig. 10) and NaBeta (Fig. 11) upon coadsorption of CH_3NH_2. These studies were made equally on the KL and NaBeta wafers in contact with 2.5 and 6.0 molecules of benzene per unit cell, respectively, i.e. the saturation of zeolite adsorption sites by benzene according to the previous work of Su and Barthomeuf (1993) and of Su and Norberg (1998). In the presence of benzene alone (spectrum a of Figs. 10 and 11) only the LF bands are present. Upon coadsorption of CH_3NH_2 on KL, the HF bands appear and their intensities increase with an increasing amount of CH_3NH_2 introduced whereas the intensity of LF bands decreases simultaneously. In the presence of high amount of CH_3NH_2 in the IR cell, the HF bands become most intense. A large band at 1935 cm^{-1} is also observed, indicating the deformation of the framework in the presence of CH_3NH_2 in the IR cell. However, this is not observed on KL zeolite upon coadsorption of NH_3. This leads us to suggest that the appearance of benzene adsorption on 12R windows of KL zeolite is very likely related to this deformation of zeolite structure. However, on NaBeta, only the LF bands are detected and broaden upon coadsorption of CH_3NH_2, no HF bands appear. The large band at 1935 cm^{-1} is also present, indicating the deformation of the framework of NaBeta zeolite upon coadsorption of CH_3NH_2, however no change in benzene adsorption behaviour is observed.

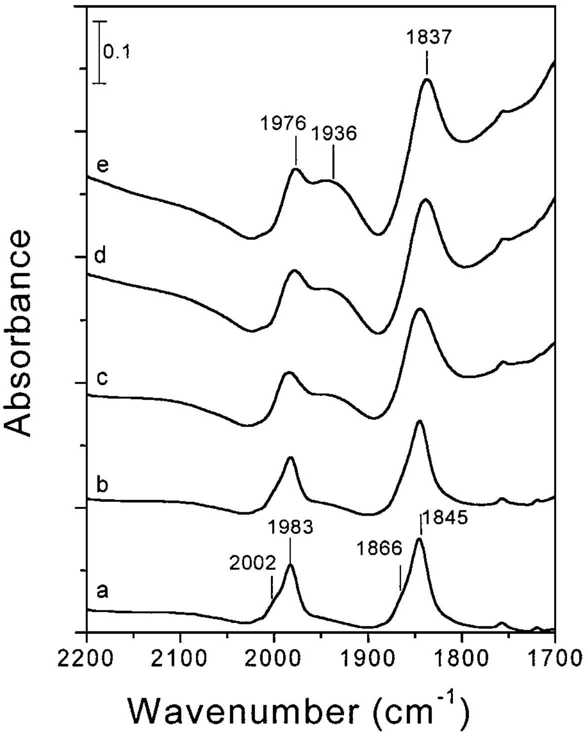

Figure 9. Change in IR spectra of C—H$_{o.o.p.}$ vibrations of benzene adsorbed on NaBeta with introduction of increasing and known amounts of ammonia molecules per unit cell: 0.0 (a), 1.0 (b), 3.0 (c), 5.0 (d), 8.0 (e), 10.0 (f), 15.0 (g) and a pressure of 2.7 kPa of ammonia present in the cell (h). The benzene loading used for this study is 6.0 molecules per unit cell.

Discussion

The benzene adsorption behavior in above zeolites is correlated with the negative charge on framework oxygen atoms ($-\delta_O$), the zeolite structure, and the type

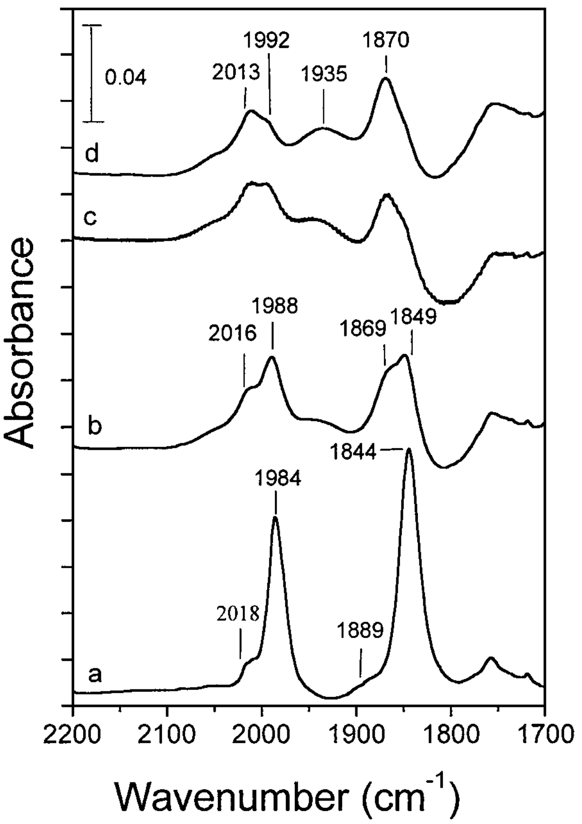

Figure 10. Change in IR spectra of benzene adsorbed on KL zeolite upon coadsorption of different amount of CH_3NH_2 molecules per unit cell: 0.0 (a), 3.5 (b), 5.0 (c), 7.0 (d). This experiment was made on a KL sample wafer in contact with 2.5 molecules of benzene per unit cell.

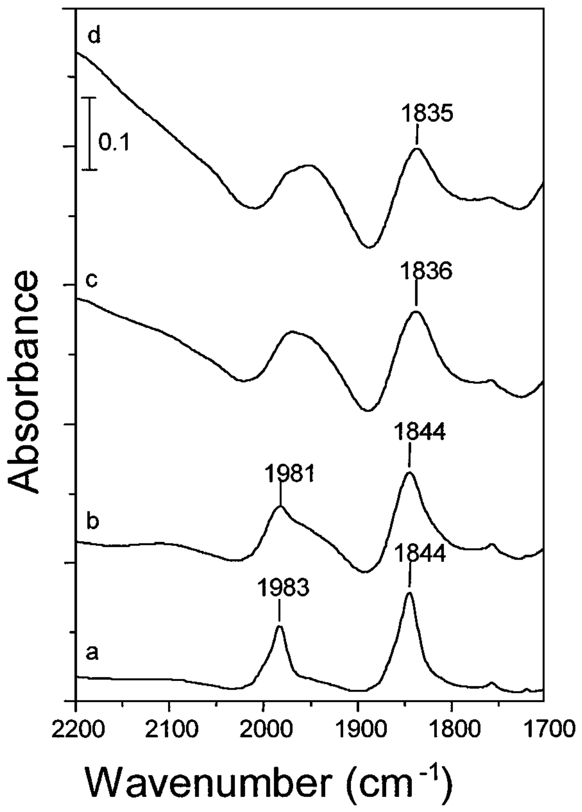

Figure 11. Change in IR spectra of benzene adsorbed on NaBeta zeolite upon coadsorption of CH_3NH_2 molecules per unit cell: 0.0 (a), 2.0 (b), 6.0 (c) and a pressure of 20 torr present in the cell (d). This experiment was made on a NaBeta sample wafer in contact with 6.0 molecules of benzene per unit cell.

and number of counter-ions. The negative charge on framework oxygen atoms of all zeolites studied here was calculated by using Sanderson electronegativity egalisation principle (Sanderson, 1976) which was first introduced in the field of zeolites by Mortier (1978) and is listed in Table 1. The adsorption behavior of benzene in the series of zeolites studied here in the presence of benzene alone and upon coadsorption of HCl, NH_3 and CH_3NH_2 is summarized in Table 2. The correlation between the benzene adsorption behavior in these zeolites and their physico-chemical characteristics including the calculated average negative charge of framework oxygen atoms of these zeolites shows that the adsorption of benzene on counter-ions is a general trend, however, the location of benzene on 12R windows is strongly dependent on the negative charge on oxygen atoms. The high $-\delta_O$ value can enhance the interaction of hydrogen atoms of benzene with the oxygen atoms of 12R windows. The lack of adsorption of benzene on 12R windows in the presence of benzene alone in HY, NaBeta, NaY_{DII} and NaY_{DIII} should be related to their low $-\delta_O$ value. Although the $-\delta_O$ value of NaEMT and KL zeolites is very similar to that of NaY_{DI} and NaY, no benzene adsorption on their 12R windows is observed. This suggests that the negative charge on oxygen atoms is not the only factor dominating the location of benzene on 12R windows. Other factors such as the shape and the flexibility of 12R windows are believed to strongly affect the benzene adsorption on 12R windows. On the other hand, in this calculation the negative charge calculated is only based on the chemical composition of zeolites, the structural factors such as bond angle and length are not taken into account in calculation.

NaX has a very high $-\delta_O$ value and the same structure as NaY. However, no benzene molecules are found on its 12R windows at least at high benzene loadings. This is because in NaX, there are S_I, $S_{I'}$, S_{II}, $S_{II'}$, S_{III}

Table 2. Benzene adsorption behavior observed in the zeolites studied.

	Benzene adsorption							
			Upon coadsorption					
	Benzene alone		HCl		NH_3		CH_3NH_2	
Zeolites	C	12R	C	12R	C	12R	C	12R
NaX	xxx[a]	–	–	–	xx[b]	xxx[b]	–	–
CsX	x	xxxx	xxxx	x	–	–	–	–
HY	xxxx	*	–	–	*	xxxx	–	–
LiY	xxx	xx	–	–	x	xxxx[b]	–	–
NaY	xxx	xx	–	–	x[b]	xxxx[b]	–	–
KY	xxx	xx	–	–	–	–	–	–
RbY	xxx	xx	–	–	–	–	–	–
NaY_{DI}[a]	xxx	xx	–	–	x[b]	xxxx[b]	–	–
NaY_{DII}[a]	xx	x	–	–	x[b]	xx[b]	–	–
NaY_{DIII}[a]	x	*	–	–	–	–	–	–
NaEMT	xxxx	*	–	–	x	xxxx	–	–
NaBeta	xxxx	*	–	–	xxxx	*	xxx	[b]
KL	xxxx	*	–	–	xxxx	*	x	xxx

– No data.

*Trace or no observable.

[a]Number of x represents relative amount of benzene adsorbed.

[b]From de Mallmann (1989).

and $S_{III'}$ sites for cations, 64 out of 86 Na^+ ions occupy half of the S_I, $S_{I'}$, S_{II} and $S_{II'}$ sites and 22 others locate on S_{III} and $S_{III'}$ sites which are near the 12R windows. These Na^+ ions interacting with benzene will hinder the adsorption of benzene on 12R windows. At high Si/Al ratio, the number of Na^+ ions is reduced and S_{III} and $S_{III'}$ are not occupied by Na^+ ions, resulting in this hindrance effect not being present. The S_{III} and $S_{III'}$ sites have recently been proved to be adsorption sites for benzene by Auerbach et al. (1996) using H^2 NMR technique and molecular mechanics. We can also notice the great difference of adsorption behavior of benzene in NaX (Fig. 1(c)) and in CsX (Fig. 5(a)). This is due to the difference in the $-\delta_O$ value between these two zeolites (Table 1) and weak interaction between Cs^+ ions and benzene molecules compared to the interaction between Na^+ ions and benzene molecules. The comparison of benzene adsorption behavior in these two zeolites and the effect of the Na content in CsX zeolite have been previously reported (de Mallmann and Barthomeuf, 1989).

It is well-known that the adsorption of an acid or a basic molecule can modify the negative charge on oxygen atoms which will be decreased or increased, respectively. The change in location of benzene on CsX upon coadsorption of HCl and on HY and NaEMT upon coadsorption of NH_3 is related to this modification. The $-\delta_O$ value of CsX is reduced upon coadsorption of HCl, the adsorption of benzene on 12R windows is thus destabilized. Benzene molecules migrate therefore towards the cations. On HY and NaEMT, upon coadsorption of NH_3, the $-\delta_O$ value is increased, the 12R windows which are initially not the adsorption sites for benzene in the presence of benzene alone due to their low intrinsic negative charge on oxygen atoms become indeed the adsorption sites for benzene and benzene molecules migrate from cations towards the 12R windows. However, the $-\delta_O$ value of NaBeta is also strengthened upon coadsorption of NH_3 and further upon coadsorption of CH_3NH_2, a more basic molecule, no benzene adsorption on 12R windows is observed. This suggests that the lack of benzene adsorption on 12R windows results from other factors. The shape of the 12R windows in NaBeta is very likely not compatible with the shape of benzene molecules. In NaBeta, there are two types of 12R windows, one is in saddle shape and too small (5.5 × 5.5 Å) to be host to receive benzene molecules (3.4 × 6.2 × 6.9 Å). However,

Table 3. Classification of zeolites with regards to the location of benzene on 12R windows.

Category	Chemical property	Structural property	Location on 12R windows	Examples
1	Favorable	Favorable	Yes	LiY, NaY, KY, RbY, CsX, NaY_{DI}
2	Unfavorable	Favorable	No[a]	HY, NaEMT, NaY_{DII}, NaY_{DIII}
3	Favorable	Unfavorable	No[b]	KL
4	Unfavorable	Unfavorable	No[c]	NaBeta

[a] Upon coadsorption of a basic molecule, the 12R windows can become adsorption sites for benzene.

[b] The coadsorption of CH_3NH_2 induces the deformation of the framework, the 12R windows become suitable for the location of benzene.

[c] In any case, the 12R windows are not preferential adsorption sites for benzene.

the other one is large enough (6.4 × 7.6 Å). The absence of adsorption of benzene on 12R windows in NaBeta zeolite is probably due to the fact that the 12 oxygen atoms are not in the same plane. Even though coadsorption of CH_3NH_2 induces a deformation of framework, the 12R windows in this zeolite are not suitable for adsorption sites for benzene. In KL, upon coadsorption of NH_3, no benzene adsorption on 12R windows is observed and is probably due to its incompatible shape of 12R windows for benzene as in NaBeta. However, upon coadsorption of CH_3NH_2, the 12R windows become finally the adsorption sites for benzene. This is because of the important deformation of the framework in the presence of CH_3NH_2. The presence of a large band at 1935 cm^{-1} proves this deformation. We will discuss further elsewhere the origin of these broad bands upon adsorption of methylamine. As a result of this important deformation, the shape of 12R windows becomes compatible with the benzene molecule and the adsorption of benzene on 12R windows becomes possible.

It has been observed from this work that the adsorption of benzene on the counter-ions located in the large cavities of 12R window zeolites is a general trend because the chemical properties are often favourable and there is practically no steric hindrance. This is a simple guest-host interaction and not controlled by the molecular recognition effect owing to the concept described by Lhen (1997). However, in the case of the adsorption on the 12R windows, this does not occur in all the 12R window zeolites because it is governed by both the chemical and structural factors. The adsorption or fixation of benzene molecules on the 12R windows, concerning a multiple interactions phenomenon, is through the interactions of six hydrogen atoms of benzene molecules and six oxygen atoms of the 12R windows. The adsorption of benzene on 12R windows is possible only when benzene molecule and 12R windows have the adapted chemical and structural properties. The adsorption of benzene on the 12R windows of the zeolites should be considered as an example of molecule recognition. The chemical properties of 12R windows can be easily modified by the ion exchange and by the isomorphous substitution etc. The structural compatibility can be also accommodated by introduction of a coadsorbate for several zeolite structures.

Regarding the benzene adsorption behavior, 12R window zeolites can be classified into four different categories which are listed in Table 3. This classification should be very useful in the design of new catalysts and adsorbents used in the industrial treatment of aromatics.

Conclusion

The present work reveals that the zeolite structure, the chemical composition of zeolites, the type and number of counter-ions and the coadsorption of an acid such as HCl or a basic molecule such as NH_3 and CH_3NH_2 can affect strongly the benzene adsorption behavior of zeolites. It shows also that the adsorption of benzene on counter-ions is a general trend, however, the location of benzene on 12R windows is dependent on both the negative charge of oxygen atoms and the compatibility of the 12R windows with benzene molecules and is a multi-interaction, i.e., six hydrogen atoms of benzene molecules interacting simultaneously with six oxygen atoms of 12R windows. The adsorption of benzene on 12R windows is probably governed by a molecular recognition effect, in which the substrate and adsorbent should involve the adapted chemical properties and the compatible geometry such as in enzyme-substrate systems. The adsorption of benzene on 12R windows could be an example of zeolites as solid enzyme and zeolites can be referred to as zeo-enzymes.

Acknowledgment

VN thanks the FNRS (Fonds National pour la Recherche Scientifique, Belgium) for a scholarship (FRIA) and the financial support from PAI (IUAP) 4-10 is greatly acknowledged.

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