Change in Location of Benzene in Faujasite upon Coadsorption of NH_3 or HCl

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The distribution of benzene between cations and 12 R-windows in faujasites, which depends on the acid–base character of the zeolite, may be strongly modified upon adsorption of a basic or of an acidic compound; the benzene is displaced and moves to the type of site, cation or oxygen, not poisoned by the coadsorbate.

Faujasite type zeolites in the alkaline cation form may be used in processes for catalysis or separation by adsorption. It has been shown that the selectivities in acid–base catalysis[1] or separation of aromatics[2,3] can be changed by specifically poisoning some zeolite sites. The present paper shows how the coadsorption of an aromatic (benzene) and of a basic or acidic compound changes the location of benzene in the zeolite structure.

A NaY zeolite from Union Carbide and a CsNaX sample[4] obtained by extensive exchange of NaX with a CsCl solution were used. The X-zeolite has the unit cell formula $Cs_{57}Na_{29}X$. Benzene adsorption was followed by i.r. spectroscopy as previously[4—6] in the absence or presence of a coadsorbate.

Figures 1 and 2 give the i.r. spectra of benzene adsorbed on NaY and CsNaX, respectively in the CH out-of-plane vibrations range (1800—2200 cm^{-1}) and the C–C stretching range (1400—1550 cm^{-1}). Curves (a) are the spectra of benzene alone for a loading close to 1 molecule per unit cell, *i.e.* approximately one quarter of the adsorption capacity.

As described previously in those conditions benzene on NaY gives only one pair of CH bands at 1848 and 1986 cm^{-1}, assigned to benzene interacting with the Na cations in S_{II} sites (LF pair).[5,6] The further addition of ammonia in ratios $NH_3:C_6H_6$ increasing from 3.8 to 36 progressively modifies the spectra. A second pair of bands at higher wavenumbers (HF) grows while the absorbance of the initial LF pair decreases. The HF pair of CH bands in the presence of pure benzene is usually observed in NaY at loadings higher than 2—3 molecules per supercage after the stronger cationic sites are filled. It is assigned to benzene sitting in the 12 R-windows and weakly interacting with the basic framework oxygen.[5,6]

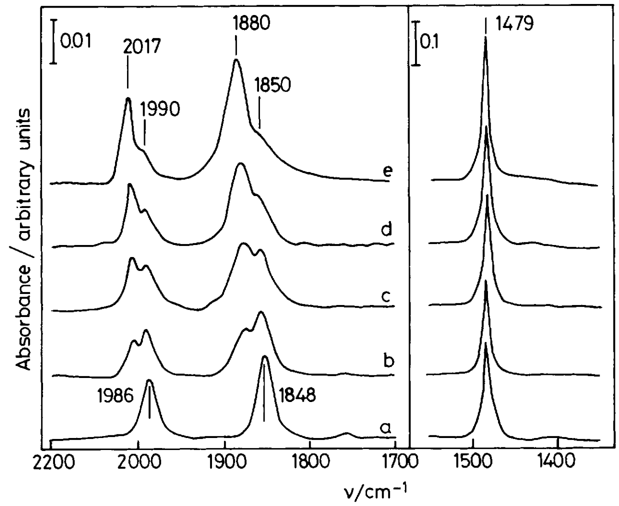

Figure 1. CH Out-of-plane vibration bands of benzene adsorbed on NaY for pure benzene (1 mol/unit cell) (a) and after addition of NH_3 so that $NH_3:C_6H_6$ in the cell equals 3.8 (b), 4.8 (c), 6.7 (d), and 36 (e).

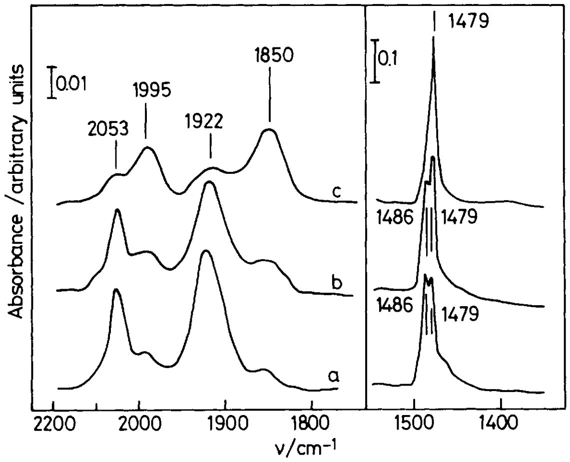

Figure 2. CH Out-of-plane vibration bands of benzene adsorbed on CsNaX for pure benzene (1.1 mol/unit cell) (a) and after addition of HCl so that HCl : C_6H_6 in the cell equals 1.2 (b) and 3.5 (c).

The present results suggest that ammonia, which is known to interact strongly with zeolite cations,[7] displaces benzene from the Na ions in the supercage. The benzene molecule moves to the zeolite sites which have a sufficiently attracting character to retain the aromatic, *i.e.* the 12 R-window.

In order to check such displacement of benzene according to the preferred location of the coadsorbate, CsNaX was studied. In contrast to NaY, this zeolite adsorbs pure benzene at low loading preferentially on the 12 R-window, generating an intense HF pair of bands as seen in Figure 2a. This arises from the higher oxygen basicity in CsNaX than in NaY.[8] An acidic compound, gaseous HCl, is then adsorbed (Figure 2b,c), giving rise to new hydroxyls, weakly acidic, due to the interaction of the proton with framework oxygen. Simultaneously the absorbance of the HF pair decreases while that of the LF pair at 1850, 1995 cm^{-1} increases, indicating a rise in the benzene cation interaction. This is corroborated by the decrease in the ν_{19} 1486 cm^{-1} band (C–C bond) associated with benzene interacting with oxygen[4] and an increase in the usual 1479 cm^{-1} band for benzene in the liquid phase or in interaction with the cations. Benzene is displaced by HCl and moves to the second type of site, the cations, which are not usually preferred in CsNaX at that loading.

Both experiments show that a coadsorbate able to interact more strongly than benzene with the cations (Lewis acid sites) or the framework oxygen (basic sites) can displace benzene to the other sites. The extent of such displacement depends, of course, on the zeolite considered. It is most important upon adsorption of a base like NH_3 on a rather acidic zeolite like NaY, or of an acidic compound (HCl) on basic zeolites (CsNaX), as seen in Figures 1 and 2.

It has also to be considered that during the process of benzene and coadsorbate interaction with the zeolite the charges on framework atoms and cations may be redistributed.[9,10] This may modify at each step the adsorption strengths involved.

The displacement of an adsorbate-like benzene upon selective poisoning of its preferred adsorption site, is exemplified here. It may explain in catalysis or separation by adsorption processes the decrease in the reactivity caused by poisoning of the preferred type of site. An enhancement of the reactivity of another type of site not initially involved may also be found.

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