Communication

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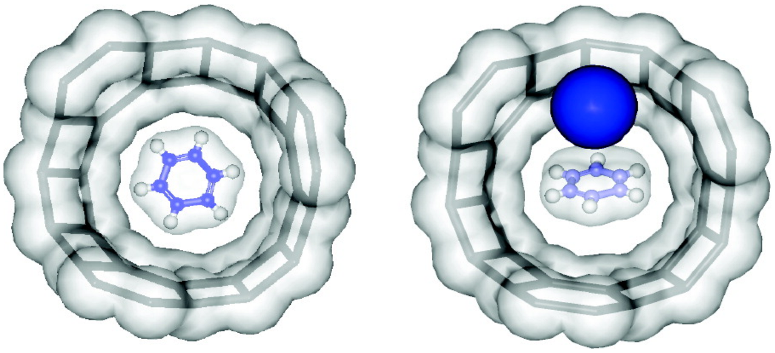

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Unexpected Si:Al Effect on the Binary Mixtures Liquid Phase Adsorption Selectivities in Faujasite Zeolites

Inge Daems,[†] Alain Méthivier,[‡] Philibert Leflaive,[‡] Alain H. Fuchs,[§] Gino V. Baron,[†] and
Joeri F. M. Denayer*,[†]

Department of Chemical Engineering, Vrije Universiteit Brussel, Pleinlaan 2,
B-1050 Brussel, Belgium, IFP-Lyon, Vernaison, France, and Université de Paris-Sud, Orsay, France

Received May 24, 2005; E-mail: joeri.denayer@vub.ac.be

Today's chemical industry has to deal with strict guidelines concerning the removal of harmful components from their products. The carcinogenic component benzene is removed from gasoline by combining extraction and distillation.[1] For other important petrochemical separation processes, such as the separation of aromatic C8 isomers, adsorptive separation is applied.[2] For these large-scale liquid separation processes, zeolites X and Y, belonging to the faujasite (FAU) family, are used. Their structure consists of sodalite cages (β-cages) and hexagonal prisms, connected in such a way that they create an open three-dimensional pore system with large supercages (α-cages) capable of hosting hydrocarbons, accessible via 12-membered ring (12MR) windows[3] (Figure 1). Extra framework cations in the FAU supercages are considered to be the principal adsorption sites for polar molecules.[4]

It is generally accepted that an increase in cation content (decrease in Si:Al) increases the selectivity of adsorption of aromatics, alkenes, and even alkanes in gas-phase conditions.[5−8] Contrarily, the influence of the Si:Al on the adsorption selectivity in liquid phase is poorly investigated, despite its practical importance. In the present work, the liquid-phase adsorption of aromatics, alkenes, and alkanes on Na-containing faujasites with different Si:Al ratios, 1.20 (NaX) and 2.79 (NaY), was studied. To determine the competitive liquid-phase adsorption equilibrium of binary mixtures, a batch technique was used.[9]

Figure 2A shows the liquid-phase adsorption isotherms of benzene from octane on NaX and NaY. Benzene is selectively adsorbed from its mixture with octane on both zeolites. The amount adsorbed increases with the benzene concentration for both zeolites, until a plateau ~5.2 benzene molecules per supercage is reached, which is in close agreement with the generally accepted maximum adsorption capacity of 5 benzene molecules per supercage.[10−11]

Everything occurs, therefore, as if the entire pore volume of NaY and NaX is filled with benzene molecules, at sufficiently high benzene concentration (≥10 mol %).

Unexpectedly, the amount adsorbed increases more steeply for the faujasite with the lowest cation content. At an external concentration of 1 mol %, for instance, ~4.8 benzene molecules are adsorbed per NaY supercage, while only ~3.1 molecules are adsorbed per NaX supercage. The observation that a high-silica zeolite is found to adsorb the aromatic compound more selectively compared to its low-silica counterpart is in clear contrast to what was observed for pure benzene in gas-phase (vide supra).[5,6,8] In these gas-phase experiments, however, the zeolite pores only contain benzene, often at a low degree of pore occupancy. In the present liquid-phase conditions, the pores are always close to saturation and contain benzene as well as solvent molecules since the solvent, present in high concentrations, will show tendency to fill up the free space inside the zeolite.

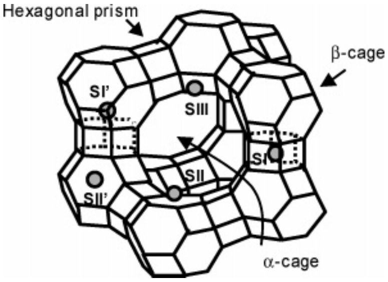

Figure 1. Structure of zeolite X and Y with cation positions SII and SIII in the supercages (α-cage), SI′ and SII′ in the β-cages, and SI in the centers of the hexagonal prisms.

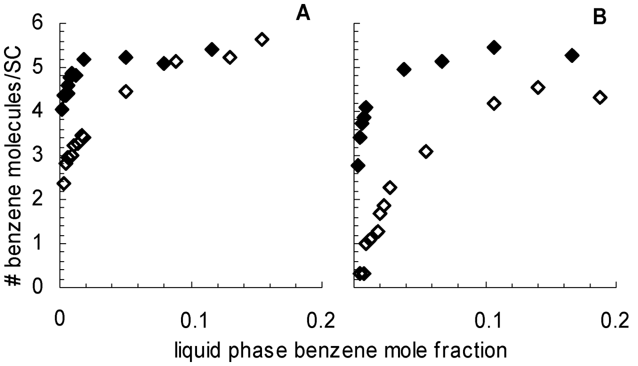

Figure 2. Liquid-phase adsorption of benzene from a (A) benzene/octane mixture and (B) benzene/octene mixture on NaY (closed symbols), and NaX (open symbols) at room temperature (SC: supercage).

An explanation for the higher adsorption selectivity of NaY compared to that of NaX is provided by spectroscopic studies.[10,12−14] It has been recognized that benzene is distributed between two types of adsorption sites in NaY: (i) inside the supercage, near the cation positioned at site II (SII) in front of the six rings of the sodalite cage, and (ii) in the 12MR window between the supercages on a noncationic site. On SII, benzene is bound facially to the cation, with its aromatic ring plane nearly parallel to the six-membered ring. On the noncationic 12MR site, the benzene molecule is essentially bound to the framework by van der Waals forces. The 12MR window site thus is energetically much less favorable compared to the SII site.[15] The NaY zeolite used here contains four SII Na cations per supercage.[16] One may then conclude that, at full loading, four benzene molecules are adsorbed on SII, leading to a tetrahedral conformation around the center of the supercage. Since each supercage is connected to four other supercages, at maximum loading, the fifth benzene is positioned in the 12 MR window between two adjacent supercages without sterically hinder-

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[†] Vrije Universiteit Brussel.
[‡] IFP-Lyon.
[§] Université de Paris-Sud.

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ing the other benzenes inside the supercage. This optimized configuration in the window is possible because of the lower energetic interaction with this noncationic site, enabling free positioning of the fifth benzene molecule.

The main difference between NaX and NaY is that NaX also contains, besides cations on SII, four cations per supercage on sites III or III′ (SIII/SIII′).[17] SIII is located near the four ring of the sodalite cage, close to the 12MR window (Figure 1). SIII′ is closely related to SIII, but positioned inside the 12MR window.[18] Cations on site III or III′ will have an orienting effect on benzene molecules adsorbing in or near the 12MR window as a result of specific electrostatic interactions between the π-electrons of benzene and Na. Complete filling of the pore volume with benzene therefore becomes more difficult as the benzene molecule in the 12MR window can no longer be freely positioned without energy cost. Thus, it could be argued that, in NaX, at low benzene concentration, benzene adsorbs on the SII Na cations. Addition of a benzene molecule in the 12MR window requires a higher external concentration to overcome the energy barrier needed to allow positioning of benzene in the 12MR window. The presence of SIII/SIII′ cations can indeed interrupt the close fitting of benzene inside the 12MR window, thereby hampering the interaction of the negatively charged oxygen atoms of the window aperture with the hydrogen atoms of benzene. This is in agreement with neutron diffraction experiments by Vitale et al.,[13] showing that no benzene could be located in the 12MR window of NaX at moderate benzene loading because of the presence of SIII/SIII′ cations in the same 12MR plane. The present experiments (Figure 2A) demonstrate that at sufficiently high benzene concentration, the NaX host−guest system finds its way to accommodate five benzene molecules per supercage, in agreement with NaY.

Figure 2B shows the adsorption isotherms of benzene from octene (instead of octane) on NaY and NaX. As in the preceding case, benzene is shown to be selectively adsorbed from its mixture with octene on both zeolites. Again, NaY, with the highest Si:Al, appears to be the most selective adsorbent. Its double bond allows octene to compete more efficiently with benzene for the adsorption sites than octane, resulting in a lower selectivity for benzene on NaY and especially on NaX compared to the previous case (Figure 2A). At an external benzene concentration of 1 mol %, the number of benzene molecules adsorbed per NaY supercage decreases from 4.8 to 4.1 when the solvent is changed from octane to octene. For NaX, the presence of a double bond in the solvent even causes a more drastic decrease from 3.1 to 0.9 benzene molecules per supercage. This larger effect of octene on the adsorption of benzene in NaX versus NaY is in line with the more difficult hosting of benzene in the supercages of NaX as explained above.

In this case, the theoretical maximal adsorption capacity of five benzene molecules per supercage is not reached for NaX within the investigated concentration range, and only about four molecules are adsorbed per supercage, in contrast to NaY. In view of the above, the adsorption of four benzene molecules on the most favorable SII sites is suggested on both NaX and NaY. In NaY, the fifth benzene adsorbs in the 12MR window. In NaX, contrarily, benzene cannot be accommodated as easily in the 12MR window because of the orienting effect of Na in SIII/SIII′. Octene, with its higher conformational freedom, can interact strongly with the Na cations in SIII/SIII′ via its double bond, without distorting the arrangement of the benzene molecules adsorbed inside the supercage. Thus, energetically and entropically, it is unfavorable to replace the octene adsorbed on SIII/SIII′ with benzene.

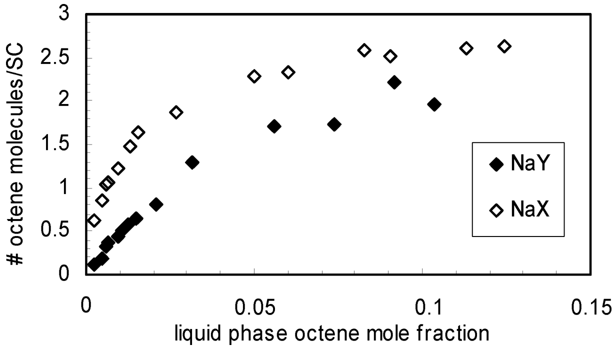

Figure 3. Liquid-phase adsorption of octene from an octene/heptane mixture at room temperature (SC: supercage).

For both mixtures, it was found that a decrease in Si:Al (increase in cation content) results in a decrease in selectivity toward the more strongly adsorbed component (benzene in this case). On the basis of a simple reasoning in terms of zeolite cation content and adsorption measurements in gas-phase,[5,6,8] this was rather unexpected. This "reverse" behavior is not a rule. There are cases in which the Si:Al effect goes the other way around. We report in Figure 3 the liquid-phase adsorption of octene from heptane on NaY and NaX. Octene is found to be selectively adsorbed from heptane in both cases, but here, the selectivity increases in going from NaY to NaX.

We may conclude from this work, that liquid-phase binary mixture selectivity predictions cannot simply rely on the amount of cations present in the zeolite framework, but that it has to take into account the details of the location and energetics of the available molecular adsorption sites. The gained insights are important to a more rational design of industrial liquid-phase separation processes.

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