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Evaluation of Experimental Methods for the Study of Liquid-Phase Adsorption of Alkane/Alkene Mixtures on Y Zeolites

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Abstract. Liquid phase adsorption of alkane/alkene mixtures on NaY was studied using different methods. It was shown that the presence of traces of water in the feed, has a tremendous influence on subsequent measurements during continuous flow through experiments. The hydrophilic character of the adsorbent combined with the inevitable presence of water inside the mobile phase made the application of the pulse chromatographic technique impossible. The influence of water became neglectable in an optimized batch technique allowing to determine binary adsorption isotherms of alkane/alkene mixtures in the low alkene concentration range (0–15wt%). 1-octene was shown to adsorb more selective from decane and dodecane than from its mixture with hexane or heptane on NaY. This unexpected selectivity effect was attributed to molecular packing in the supercages of NaY.

Keywords: liquid, adsorption, faujasites, alkane, alkene

1. Introduction

Today's industry is confronted with strict guidelines concerning the removal of harmful components from their products. The demand of high quality products leads to the search of alternative and very specific separation processes like adsorption. In recent years some industrial scale liquid phase adsorptive separations were developed in which zeolites X and Y play an important role (Kulprathipanja and Johnson, 2002). These zeolites posses an open 3 dimensional pore structure with large α-cages (diameter 13 Å) accessible through 12 MR windows (diameter 7.3 Å) (Fig. 1). This leads to a low mass transfer resistance, what makes them very suitable for application in large scale separations.

Liquid phase adsorption of hydrocarbons on faujasite type zeolites, is still an unexploited field, since most academic studies were performed in gas phase. Both static or flow through methods can be applied to investigate adsorption in liquid phase. The static method (cfr. batch or immersion method), is the most used experimental technique (Rouquerol, 1999). When using an inert, non adsorbing solvent, this technique allows to determine the adsorption capacity and the competitive adsorption of a binary mixture in a straightforward way (Choudhary et al., 1989). Flow through methods contrarily are much less labor intensive and require only one adsorbent sample. Depending on the required information, different types of flow trough experiments can be performed: (1) breakthrough experiments

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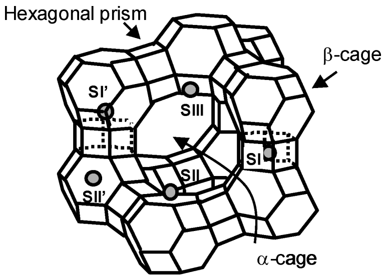

Figure 1. Structure of zeolites X and Y with cation sites SII and SIII in the supercages, SI′ and SII′ in the β-cages and SI in the centers of the hexagonal prisms.

(Santacesaria et al., 1982), (2) pulse chromatographic experiments (Denayer et al., 1998) and (3) zero length chromatography (Brandani and Ruthven, 1995; Boulicaut et al., 1998). Determination of the energies involved in liquid phase adsorption occurs with calorimetric methods (Messow et al., 1983). In this work, the applicability of both a flow through method (liquid pulse chromatography) and the static method to study the competitive adsorption of alkane/alkene mixtures on NaY is investigated.

2. Experimental Section

All experiments were performed with Na containing Y zeolites. The Dubinin micropore volume and surface area were determined by means of N_2-porosimetry and are presented together with other zeolite properties in Table 1.

Table 1. Properties of NaY zeolites used in this study.

Commercial/ reference name	Source/ manufacturer	Si/ Al-ratio	Micropore volume (cm^3/g)	Surface area (m^2/g)
CBV100	Zeolyst	2.55	0.347	976
ACL0009	IFP	2.79	0.346	975

2.1. *Flow Through Method: Liquid Pulse Chromatography*

The experiments were performed with the experimental setup presented in Fig. 2. Before starting the experiment, the mobile phase was dried with zeolite 3A (CECA). To ensure permanent dryness of the mobile phase, a dry N_2 flow was maintained above the liquid level in the solvent reservoir. Zeolite crystals were packed into a 1/4″ stainless steel column (5 cm). Before starting the experiment, the adsorbent was regenerated *in situ* by flushing with nitrogen and gradual increasing the temperature to 450°C at a rate of 0.5°C/min. The mobile phase was pumped through the filled column using an isocratic pump (Agilent 1100 Series). Before entering the column, the mobile phase passed a guard column of 90 ml filled with 3A and a vacuum degasser. The column was connected to the sample injector and the detector by means of 1/16″ capillary tubes. A small pulse (typically 0.1 to 0.2 μl) of the tracer component was injected into the mobile phase using an automated sample injector (Agilent 1100 series). A chromatogram was recorded at the end of the column using a refractive index detector. The first moment of the response curve (μ) was determined by integration and corrected for the dead time of the system. The column was kept at a temperature of 30°C.

The partition coefficient (K) of a component injected into a pure mobile phase was calculated based on the following equation (Ruthven, 1984):

$$\mu = \frac{L}{v_f}(\varepsilon_{\text{ext}} + (1 - \varepsilon_{\text{ext}})K) \tag{1}$$

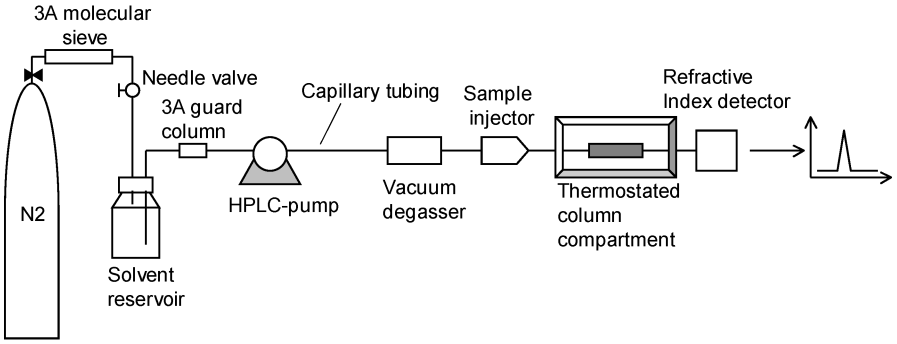

Figure 2. Experimental setup for the liquid pulse chromatographic technique

in which v_f presents the superficial velocity and ε_{ext} the external packed bed porosity. K is defined as the ratio of the concentration of the tracer compound in the adsorbed phase and in the mobile phase.

2.2. *Static Method: Determination of Binary Adsorption Isotherms (Without Use of Inert Solvent Molecule)*

Two component liquid mixtures were used to investigate the competitive adsorption of alkanes and alkenes on NaY in the liquid phase. Alkanes served as solvent, and the preferentially adsorbed alkenes acted as the adsorbate.

Zeolite samples (~0.2 g) were put in 10 or 20 ml glass vials and slowly heated (0.5°C/min) in a ventilated oven until a maximum temperature of 450°C was reached, which was kept overnight. The applied temperature program allowed the removal of water and impurities present inside the zeolite pores, without the creation of mesopores as checked by N_2-porosimetry. After regeneration, the vials were immediately sealed with a cap with septum in order to avoid water uptake from the air. Before preparing the binary mixtures, the solvent (alkane) was dried and purified by adding molecular sieves 13X (Zeosorb 13X, Tricat) and 3A. Immediately after sealing the cap and determining the regenerated zeolite mass (m_{zeolite}), the liquid mixture was injected through the septum. A certain amount (300 μl) was kept aside at 4°C (avoids evaporation), to be used as blank. Meanwhile the vials were stirred continuously at room temperature and liquid samples were taken after 24 h, when equilibrium was reached. All blanks and samples were analyzed using a GC with flame ionization detector. An Agilent HP-5 column (5% Phenyl Methyl Siloxane, 30 m × 320 μm × 0.25 μm film thickness) was used to separate the mixture.

For every binary mixture, a calibration line was obtained by analysis of the blanks. This approach guaranteed a high precision in the calculation of the amount adsorbate adsorbed, obtained by calculation of the mass balance:

$$q_{\text{alkene}} = \left(\frac{(\text{wt}\%_{\text{blank}} * M_{L,0}) - (\text{wt}\%_{\text{sample}} * (M_{L,0} - 0.3^{*} m_{\text{zeolite}} * \rho_{\text{alkene}}))}{100 * \rho_{\text{alkene}} * m_{\text{zeolite}}} \right) \tag{2}$$

with $\text{wt}\%_{\text{blank}}$ and $\text{wt}\%_{\text{sample}}$: the concentration (wt%) of the alkene in the blank and sample; ρ_{alkene}: density of the alkene (sorbate molecule) at room temperature, and $M_{L,0}$ the total mass of external liquid phase before adsorption.

The experimental technique did not allow to investigate binary mixtures that contained more than 15 wt% alkenes. This upper limit was caused by the fact that the amount alkene added to the zeolite could not largely exceed the zeolite micropore volume, in order to detect changes in the alkene concentration upon adsorption in an accurate way. Furthermore, this technique did not allow to detect changes in alkane concentration before and after adsorption, since the alkane solvent was always present in high concentrations.

3. Results and Discussion

3.1. *Application of the Liquid Pulse Chromatographic Technique*

When investigating the adsorption of alkane/alkene-mixtures on zeolite NaY (2.55), alkanes were used as a mobile phase. During the course of the experiments, the retention time of a certain injected alkene tracer decreased with the amount of mobile phase pumped through the adsorbent column. The chromatograms, showing a decreasing retention time for subsequent decene injections on zeolite NaY (2.55), are depicted in Fig. 3. The origin of this degeneration was tracked down in a systematic way. Comparison of the N_2-micropore volume of the adsorbent before and after a liquid pulse chromatographic experiment, showed that the adsorbent underwent no structural changes.

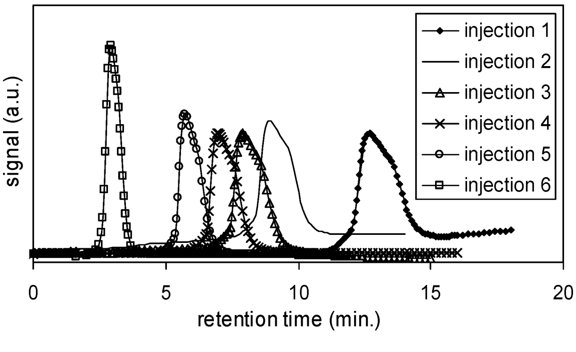

Figure 3. Chromatograms of subsequent decene injections on NaY (2.55) with heptane as a mobile phase.

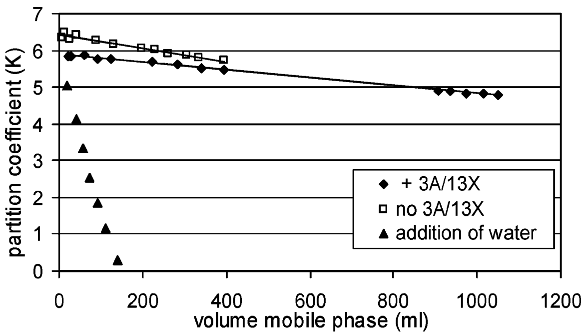

Figure 4. Decrease of K-value of 1-decene on NaY (2.55) with (1) dried/purified, (2) not dried/purified heptane as a mobile phase or (3) injection of water before each 1-decene injection.

Furthermore, there was no loss of adsorbent out of the column during the experiment. Next, it was investigated whether the degeneration was caused by permanent occupation of the adsorption sites by impurities present either in (1) the mobile phase or (2) the injected tracer compounds. According to GC-analysis, unpurified heptane had a purity exceeding 99.8 wt%. The main impurities being iso-octane (0.007 wt%) and dimethylcyclopentane (0.143 wt%). These impurities could not be removed by the addition of 13X beads, so they were not considered as strongly adsorbing on faujasite type zeolites. Figure 4 depicts the partition coefficients (K-values) of subsequent 1-decene injections as a function of the total volume of mobile phase (heptane) pumped through the column. Three experiments were performed: (1) heptane was dried/purified, (2) heptane was not dried/purified and (3) heptane was dried/purified but before each decene injection 40 μl of water was manually injected. During both experiments without water injection, an almost linear decrease of the partition coefficients as a function of the volume of mobile phase was observed. However, the rate of degeneration was smaller when dried/purified heptane was used according to the slope of the linear trendline. The hypothesis that injected tracers permanently occupied the adsorption sites was rejected, because the degeneration continued without further injection of tracers (see Fig. 4; +3A/13X; between 400 & 900 ml). KF-titration showed a remaining amount of 17.6 ppm water present in heptane after addition of molecular sieves 3A and 13X. Furthermore the importance of water for the hydrophilic NaY (2.79) zeolite is shown by the third experiment. Most probably water present in heptane causes the degeneration. These water molecules permanently occupy all adsorption sites, until no specific adsorption remains. Even extreme precautions to remove water from the mobile phase and to avoid its reentrance into the system, could not prevent degeneration of the adsorbent. To avoid the influence of water, a suitable method, putting a limited amount of liquid in contact with the adsorbent, had to be developed.

3.2. *Application of the Batch Experimental Technique*

3.2.1. Investigating the Adsorption of Alkane/Alkene Mixtures with Use of Inert Solvent. The use of an inert solvent molecule, not capable of entering the zeolite pores, nor influencing the adsorption of alkenes and alkanes, would allow to determine the maximum adsorption capacities of both type of molecules in a straightforward way. Besides, determination of complete binary adsorption isotherms of alkane/alkene mixtures in an inert solvent, would allow to investigate the competitive selectivity of different mixtures.

The suitability of 1,3,5-triisopropylbenzene (TIPB), as inert solvent was tested by adding a mixture containing a small amount heptane (1.5 $*$ pore volume) in an excess of TIPB to the zeolite (NaY (2.79)) at 4°C and at room temperature. TIPB has a kinetic molecular diameter of 8.4 Å ($r_{\min}$) (Breck, 1974), which should theoretically be too large to pass through the windows of NaY. Complete pore filling of the zeolite with heptane would confirm the inert character of TIPB. Figure 5 shows the heptane uptake from TIPB on NaY as a function of time at room temperature and at 4°C. Initially, about 0.12 ml of heptane is adsorbed in the zeolite, which is less than half of the pore volume. With time the amount heptane adsorbed decreases, which should be attributed to a slow uptake of TIPB in the zeolite pores at 4°C, and an even faster uptake at room temperature.

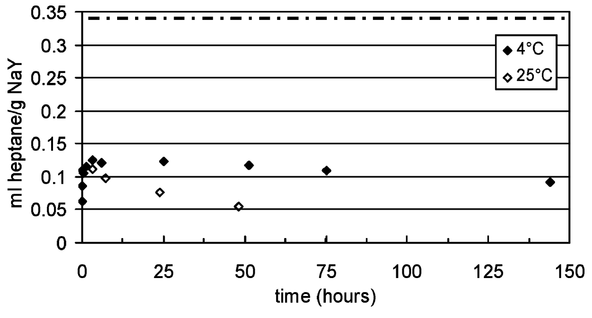

Figure 5. Adsorption of heptane from TIPB on NaY (2.79) (dotted line: N_2-micropore volume)

Thus, TIPB does not only hamper the adsorption of heptane, but in spite of its size it also slowly enters the zeolite pores, where it replaces the adsorbed heptane molecules. Since the existence of an inert mobile phase was not obvious for these large pore faujasite type zeolites, a batch method without the use of an inert solvent, had to be searched for.

3.2.2. Investigating the Adsorption of Alkane/Alkene Mixtures Without Use of Inert Solvent. The adsorption of 1-octene from several alkanes with different chain length on NaY (2.79) was investigated. The adsorption isotherms, representing the volume octene adsorbed (ml) versus its concentration in the liquid phase (wt%), are depicted in Fig. 6. Octene was adsorbed preferentially from all alkane molecules, which is in agreement with the higher heats of immersion of 1-octene compared to that of alkanes (C6-C12) on NaY (2.6) at 30°C (Messow et al., 1983). Apparently the length of the alkane molecules influenced the adsorption behavior of octene. The amount octene adsorbed from the 'long' solvent molecules decane and dodecane is higher compared to the amount adsorbed from the 'short' alkane molecules hexane and heptane. This was the opposite of what was expected from interaction energies presented in literature. Previous gas phase investigations concerning the adsorption of *n*-alkanes point out that larger alkanes interact more strongly with faujasites than shorter molecules (Kiselev and Lopatkin, 1967; Atkinson and Curthoys, 1981; Denayer and Baron, 1997; Eder and Lercher, 1997). So, application of longer alkane molecules was expected to lead to a decreased selectivity for 1-octene. Probably, molecular packing effects and not energetic effects are mainly responsible for the selectively adsorption phenomena detected in liquid phase. During liquid phase adsorption, all supercages are completely filled with hydrocarbons. Small alkane molecules, like hexane and heptane, might experience less steric constraints when occupying adsorption sites in the same supercage as octene. The void spaces probably can be more easily filled with smaller alkane molecules, which leads to a lower selectivity for the alkene. This is in agreement with the results obtained by Satterfield and Smeets (1974), who showed that in liquid phase alkane molecules with a lower molecular weight are preferentially adsorbed compared to those with a higher molecular weight.

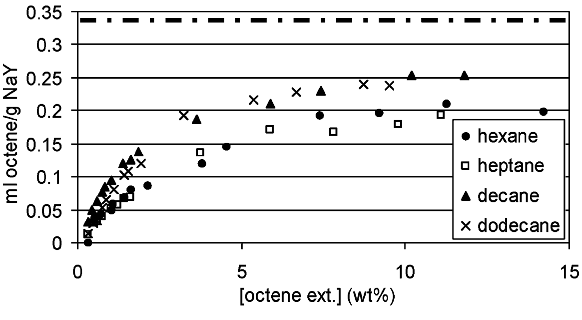

Figure 6. Adsorption of octene on NaY (2.79) from alkanes with different chain length (dotted line: N_2-adsorption volume).

Previous investigations concerning the influence of the alkane chain length on the adsorption of alkenes showed conflicting results. According to data shown by Herden et al. (1982) the selectivity for adsorbing tetradecene on NaX at room temperature was higher for tetradecene/hexane than for tetradecene/dodecane, corresponding to a decrease of the separation factor with increasing chain length of the alkane solvent. On the other hand, Andreev et al. (1985) investigated the adsorption of dodecene out of pentane and dodecane on NaY. Here was concluded that the selectivity for adsorbing 1-alkenes increased with increasing molecular weight of the alkane solvent.

The adsorption isotherms of octene from dodecane and heptane were determined in duplicate and no differences between both isotherms were observed, demonstrating the reproducibility of the method. Furthermore water present inside the dried alkane solvents did not influence the adsorption of octene because of the limited amount of solvent added to the adsorbent in comparison with the flow through method. A typical batch test corresponds to the point of 50 ml on Fig. 4 (1), and hence there is no appreciable influence of water on the partition coefficient.

4. Conclusion

An experimental method was developed to investigate liquid phase adsorption of alkane/alkene mixtures on low Si/Al-ratio Y zeolites. The influence of water was avoided by using a batch method instead of a flow through method. Application of this batch method lead to the discovery of some surprising adsorption effects, which were rather large given the size of the α-cages. In contradiction to what was expected from the heats of adsorption determined at low coverage, a larger selectivity for 1-octene was obtained for mixtures of

1-octene with long alkanes compared to mixtures of 1-octene with short alkanes. The importance of packing effects during adsorption in liquid phase was clearly demonstrated.

In the near future this technique will be applied to perform a profound and more systematic study of the adsorption of binary alkane/alkene and alkane/aromatic mixtures on faujasite type zeolites with different Si/Al-ratios and compensating cations.

Acknowledgments

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