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Propylene/propane mixture adsorption on faujasite sorbents

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Abstract The adsorption of propylene and propane on zeolite NaX with and without a saturated (36 wt%) amount of CuCl have been investigated. The single component adsorption isotherms could be well described with a Dual-Site Langmuir model. The dispersion of CuCl results in a decrease of the maximum adsorption capacity of the zeolite for both components. For propylene a strong adsorption via π-complexation with CuCl is present, increasing the adsorption selectivity of the zeolite.

The binary mixture (50 : 50) adsorption was determined via breakthrough/desorption experiments at 318, 358 and 408 K with a partial pressure of the two components between 0.8–54 kPa. For NaX the mixture loading could be well described with the IAS-theory and the single component isotherms, both qualitatively and quantitatively. A transition from an enthalpy controlled adsorption at lower loadings to an entropy affected adsorption at higher loadings was observed. The IAS-theory could only qualitatively describe the trends in the observed mixture adsorption for the CuCl/NaX adsorbent. The dispersion of CuCl in NaX results in a modest improvement of the adsorption selectivity for propylene over propane (from 3–7 to 15–30) but at the expense of a reduced capacity.

Keywords Binary adsorption · Breakthrough · Faujasite · Propylene · Propane · Selectivity

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Abbreviations

$K_{H,i}$	Henry's law constant for component i [$\mathrm{mol\,kg^{-1}\,Pa^{-1}}$]
$K_{i,j}$	Adsorption constant for component i on site j [$\mathrm{Pa^{-1}}$]
P_{tot}	Total pressure at the bottom of the column [Pa]
q_i	Adsorbed amount of component i [$\mathrm{mol\,kg^{-1}}$]
$q_{i,j}^{sat}$	Saturation capacity for component i on site j [$\mathrm{mol\,kg^{-1}}$]
Q^{st}	Isosteric heat of adsorption [$\mathrm{J\,mol^{-1}}$]
Q_0^{st}	Isosteric heat of adsorption at zero coverage [$\mathrm{J\,mol^{-1}}$]
R_g	Universal gas constant [$\mathrm{J\,mol^{-1}\,K^{-1}}$]
T_0	Reference temperature (318 K) [K]
$x_{i,in}$	Mol fraction of component i in the feed [$-$]
$\Delta H_{ads,j}$	Adsorption enthalpy for site j [$\mathrm{J\,mol^{-1}}$]
$\phi_{mol,in}$	Molar flowrate into the column [$\mathrm{mol\,s^{-1}}$]
$\phi_{v,in}$	Volumemetric flowrate into the column [$\mathrm{m^3\,s^{-1}}$]

1 Introduction

The separations of light olefin/paraffin mixtures, like propylene/propane, are amongst the most energy intensive separation processes in the petrochemical industry. This separation, usually done via distillation, requires enormous amounts of energy for the compression of the gases and operates with high refluxes (Eldridge et al. 2005; Humphrey and Keller 1997). Therefore researchers are looking for alternative processes to lower the energy demand of the separation process. An interesting alternative is to perform this separation in an adsorption based process like Pressure Swing Adsorption (PSA) or Temperature Swing Adsorption (TSA) (Ruthven et al. 1994; Thomas and Crittenden 1998).

For these processes it is of the utmost importance to find a cheap and selective adsorbent.

The difference in selectivity can be achieved using a difference in adsorption affinity. Some transition metals, like Cu^+ or Ag^+, can form a π-complex with the double bond of the olefins (Herberhold 1974; Yang and Kikkinides 1995). The paraffins can only adsorb by weak Van der Waals interactions with the adsorbent, and therefore a difference in adsorption affinity between olefins and paraffins is obtained. This π-complex should be weak enough to release the components upon a change in pressure or temperature.

In order to obtain a larger number of accessible selective adsorption sites, transition metals can be dispersed over supports with large surface area as referred to earlier (Van Miltenburg et al. 2006; Van Miltenburg 2007). In this study the single and binary adsorption of propane and propylene were investigated for Faujasite NaX zeolite crystals as such and for CuCl dispersed in this zeolite. The zeolite was synthesized according to our recipe reported elsewhere (Van Miltenburg et al. 2006; Van Miltenburg 2007). By thermal treatment the CuCl was dispersed in the pores of the zeolite. Because of the formation of the π-complex of the olefin with CuCl, the olefin is expected to show a stronger affinity with the zeolite adsorbent after CuCl dispersion. A 36 wt% mixture was chosen as characterizations showed that this appeared to be the saturation capacity; moreover, compared to lower loading, it was more stable during handling in the ambient atmosphere (Van Miltenburg 2007).

In order to be able to model the binary adsorption, single component adsorption isotherm data will be required. Therefore the single component isotherms of propane and propylene on both NaX and 36 wt% CuCl/NaX were determined using the volumetric technique. Compared to the TEOM (Zhu et al. 1998), the volumetric technique allows the measurements of isotherm data at lower pressures and, since the sample is first evacuated before measurement, it is not hindered by the presence of inert gases (e.g. helium or air) inside the pores of the zeolite (Mittelmeijer-Hazeleger et al. 2002).

The isotherm data are correlated by isotherm models, including the Dual-Site Langmuir model. For the adsorption via π-complexation multiple models have been applied and developed in the literature. The adsorption was either described by one of the earlier models, e.g. Langmuir (Huang et al. 1999), or a combination of the UNILAN model with either the Langmuir (Yang and Kikkinides 1995) or the Toth (Grande et al. 2005) model. In these models the physical adsorption of the olefins and paraffins is ascribed with the Langmuir or Toth model and the adsorption constant and adsorption capacity of the olefin is assumed to be equal to those of the corresponding paraffin. The additional adsorption of the olefin via π-complexation is then described by the UNILAN model. The assumption of an equal adsorption constant and equal adsorption affinity is however not (always) valid.

The binary mixture adsorption on the NaX zeolite, with or without dispersed CuCl, was investigated for propylene/propane mixtures using breakthrough/desorption experiments. In a breakthrough setup multiple breakthrough and desorption profiles were recorded at three temperatures (318, 358 and 408 K) and various partial pressures for a 50 : 50 propylene/propane mixture. Based on the breakthrough and desorption profiles, the binary adsorption data were calculated using simple mass balance equations (Malek et al. 1995). The outcome is compared with the Ideal Adsorbed Solution (IAS) theory (Myers and Prausnitz 1965) using the single component adsorption isotherms recorded with the volumetric technique. This theory takes into account that a competition between the two components will occur during binary adsorption. In the 'Ideal' solution it is assumed that each component in the adsorbed phase has an activity coefficient equal to one. Unlike the frequently used multicomponent Langmuir model, the IAS-theory is also thermodynamically consistent in case the saturation capacities of both components in the mixture are not identical.

2 Experimental

2.1 Adsorbents

Faujasite NaX zeolites and 36 wt% CuCl/NaX were synthesized according to the recipe and heat treatment described earlier (Van Miltenburg et al. 2006). For the samples used in the volumetric setup, the CuCl dispersion was performed in a quartz reactor and the samples were stored under nitrogen in the glove box for later use. For the samples used in the breakthrough setup, the dispersion was immediately performed in the breakthrough setup to limit the exposure of the adsorbent to the atmosphere. To remove adsorbed water, a similar heat treatment was applied to the other samples used in the breakthrough setup, viz., NaX and SiC (which is used as inert non-adsorbing reference material). The particles were contained inside the $1/4''$-tube using a stainless steel frit of 1 mm thick, with pore openings of 0.5 µm, fixed in standard Swagelok couplings.

2.2 Volumetric method

A Micromeritics ASAP 2010 gas adsorption analyser (stainless steel version) was used to measure the adsorption isotherms of propane, and propylene on NaX, 36 wt% CuCl/NaX and pure CuCl in the pressure range from 0.002 to 120 kPa. The instrument is equipped with turbomolecular vacuum pumps and three different pressure transducers (0.13, 1.33 and 133 kPa) to enhance the sensitivity

Table 1 Dimensions of the breakthrough columns and the total flows and compositions for the breakthrough and desorption experiments. Helium is used as a balance or sweep gas in, respectively, the breakthrough or desorption experiments

	SiC	NaX	36 wt% CuCl/NaX
Outer diameter [inch]	1/4	1/4	1/4
Inner diameter [mm]	4.57	4.57	4.57
Length [mm]	60	60	60
Dry sample mass [g]	1.450	0.82	1.08
Particle diameter [µm]	63–71	63–71	63–71
P_{tot} [kPa]	108	108	108
$\phi_{v,in,adsorption}$ [ml SATP* min^{-1}]	4.0–254	4.0–254	4.0–254
$\phi_{mol,in,adsorption}$ [µmol s^{-1}]	3.0–189	3.0–189	3.0–189
$x_{propane,in}$ [−]	0.500–0.00788	0.500–0.00788	0.500–0.00788
$x_{propylene,in}$ [−]	0.500–0.00788	0.500–0.00788	0.500–0.00788
$\phi_{v,in,desorption}$ [ml SATP* min^{-1}]	20	20	20
$\phi_{mol,in,desorption}$ [µmol s^{-1}]	15	15	15

*SATP = Standard Ambient Temperature and Pressure (298 K and 101 kPa)

in the different pressure ranges. The static-volumetric technique was used to determine the volume of the gas adsorbed at different partial pressures: upon adsorption a pressure decrease was observed in the gas phase, which is a direct measure for the amount adsorbed.

The sample tubes were loaded with a sample of NaX or 36 wt% CuCl/NaX. For 36 wt% CuCl/NaX a larger amount of material was used, to have approximately the same sample amount of NaX. Prior to the adsorption measurements the samples were slowly outgassed in situ in vacuum for 16 h at 383 K followed by 6 h at 523 K. The evacuation at 383 K allowed (most of) the adsorbed hydrocarbons and water to escape from the sample. This should reduce the undesired reactions of the hydrocarbons to form carbon deposits at higher temperatures, and it should prevent the possible reaction of water with CuCl. The adsorption isotherms, which will be presented in the Results section, were based on the amount of dry NaX crystals present in the sample. Adsorption isotherms for propane and propylene were recorded at 318, 358 and 404 K. These temperatures were considered as representative for the range in which a commercial adsorptive separation process would be carried out. The samples were maintained at these temperatures using either a water (318 K) or an oil bath (358 and 404 K) around the sample cell. The equilibration time for each adsorption step was about 12–30 minutes for NaX, while for the CuCl/NaX sample an equilibration time ranging from 12 up to 200 minutes was required.

For comparison, the adsorption of propylene on pure CuCl particles (0.2380 g) was recorded at 358 K. Before measurements the CuCl particles were first pre-treated in the quartz reactor at 623 K for 4 h in flowing argon. Thereafter the sample was installed in a sample tube and slowly outgassed.

At the end of the adsorption measurement at the highest pressure (120 kPa), two points of the desorption isotherms were recorded (at 115 and 110 kPa) to check the reversibility of the adsorption and to check whether equilibrium was reached at 120 kPa. Lower desorption pressures also indicated a reversible adsorption/desorption process, and therefore no further attempts were made to record the complete desorption branch.

2.3 Breakthrough setup

The adsorption of binary (50 : 50) mixtures of propylene/propane in helium (used as a balance) was investigated via breakthrough and desorption experiments in a breakthrough setup at three temperatures (318, 358 and 408 K). Each experiment was performed twice to check the reproducibility. The dimensions of the breakthrough columns and the total flow rates and compositions used in the breakthrough and desorption experiments are summarized in Table 1. For these experiments the exit pressure of the breakthrough column was set at 108 kPa. After each desorption experiment the breakthrough column was flushed for 6 hours with helium at 125 $\text{ml}\,\text{min}^{-1}$ (SATP) at the measurement temperature. A temperature increase after these 6 hours did not result in the desorption of additional adsorbed hydrocarbons, which confirms that all gases have desorbed from the column at that time.

The total analysis time of each breakthrough experiment was approximately 1 h. Since the breakthrough of both components occurred much earlier, this implies an equilibration time of at least 1/2 h. The desorption of the breakthrough column was performed isothermally with a helium flush of 20 $\text{ml}\,\text{min}^{-1}$ (SATP) and was analyzed for 4 h.

In the breakthrough setup the CompactGC (Interscience) is used to determine the mol fraction of both components at the exit of the breakthrough column. The GC is equipped with three parallel 8 meter Rt-QPlot capillary columns (diameter 0.32 mm) and each column is equipped with its own Flame Ionization Detector (FID). Whenever the GC is triggered, 45 samples can be analyzed consecutively, after which 1–1,5 minute is required to allow the detection of the last sample, to save the results and to reset the trigger of the EZChrom Elite software for the next chromatogram. With this configuration and the continuous injection of gas samples in the GC columns, it is possible to analyse the mixture composition every 8 s.

2.4 Adsorptives

Gases were provided by HoekLoos and had following purities: propylene 3.5 (99.95%), propane 3.5 (99.95%) and helium 4.6 (99.996%).

3 Results

3.1 Single component isotherms

The isotherm data of the adsorption of propane and propylene on NaX and 36 wt% CuCl/NaX are presented in Fig. 1a–d. The adsorption isotherm of propylene at 358 K on bulk CuCl particles is included in Fig. 1c for comparison. It clearly indicates that the adsorption capacity of dispersed CuCl is considerably improved and hardly any propylene is adsorbed by bulk CuCl particles and, therefore, its contribution for the CuCl/NaX sample can be disregarded from further analysis.

On both samples the isotherms show a larger adsorbed amount for propylene compared to propane. The adsorbed amount of all components is smaller on the CuCl/NaX sample (Fig. 1c–d) than on the NaX sample (Fig. 1a–b). This effect is larger for propane than for propylene. From a compar-

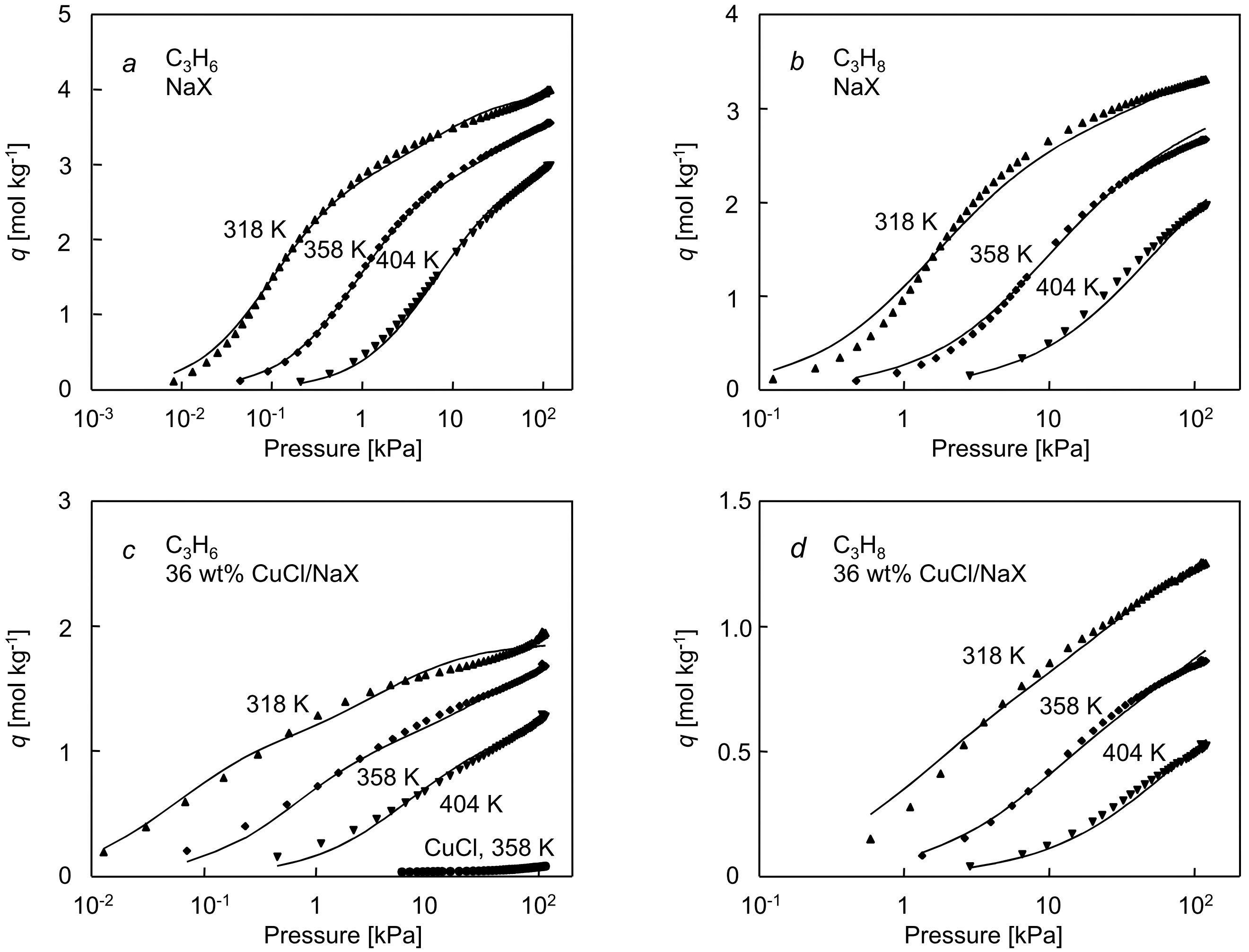

Fig. 1 Adsorption isotherms of (**a**) propylene on NaX, (**b**) propane on NaX, (**c**) propylene on 36 wt% CuCl/NaX and (**d**) propane on 36 wt% CuCl/NaX at 318 K (▲), 358 K (♦) and 404 K (▼). (**c**) For comparison the adsorption isotherm of propylene on CuCl (•) at 358 K is included. The *lines* correspond to the selected model correlation. The adsorbed amounts are based on the dry amount of NaX present in the sample

Table 2 Adsorption isotherm parameter values for propylene and propane on NaX and 36 wt% CuCl/NaX

	q_i^{sat} [mol kg^{-1}]	$q_{i,A}^{sat}$ [mol kg^{-1}]	$K_{i,A}(T_0)$ [10^{-5} Pa^{-1}]	$-\Delta H_{ads,A}$ [kJ mol^{-1}]	$q_{i,B}^{sat}$ [mol kg^{-1}]	$K_{i,B}(T_0)$ [10^{-5} Pa^{-1}]	$-\Delta H_{ads,B}$ [kJ mol^{-1}]
NaX							
Propylene	3.99	2.94	1007	51.9	1.05	13.2	51.9
Propane	3.76	2.83	62.5	43.1	0.93	1.20	43.1
36 wt% CuCl/NaX							
Propylene	1.87	1.11	1870	59.2	0.76	23.9	54.5
Propane	1.41	0.75	77.9	47.8	0.66	2.97	47.8

ison of the desorption branch (not shown) with the adsorption data it can be concluded that the adsorption is reversible. In all cases desorption occurred immediately when the pressure was decreased, except for CuCl/NaX at the lower temperatures, that showed a small increase, compared with the loading found at 120 kPa, indicating that equilibrium was not yet completely reached at these temperatures.

The experimental isotherm data at multiple temperatures were correlated by the isotherm models by non-linear least squares fitting, minimizing the sum of squared residuals of the adsorbed amounts. In order to obtain the combined fitting results, first estimates for the saturation loading(s) and adsorption constant(s) were obtained by fitting the isotherm at 318 K (T_0). Thereafter, the isotherms at 358 K and 404 K were added to the fitting procedure and all parameters were allowed to vary in this combined fitting, except T_0.

The Toth and UNILAN model did not result in a considerable improvement of the sum of squared residuals compared to the Dual-Site Langmuir model. The application of the combined UNILAN-Langmuir model to describe the adsorption of the olefin via the π-complex did not result in an improved fitting and/or resulted in the heterogeneity parameter(s) to be equal or close to zero. In that case the UNILAN-Langmuir model is identical to the Dual-Site Langmuir model. Based on these results the Dual-Site Langmuir model was chosen to correlate the experimental data.

For propane on CuCl/NaX (Fig. 1d) and for propane and propylene on NaX (Fig. 1a–b), the adsorption enthalpy of the two adsorption sites were kept equal. In case the adsorption enthalpies of both adsorption locations were allowed to vary independently, the fitting convergence was very slow and the outcome depended strongly on the starting values chosen. Restricting the adsorption enthalpy for these cases to a single value resulted in more realistic and less extreme values. Furthermore the fitting of these three sets of adsorption isotherms was hardly affected by this restriction. For propylene on CuCl/NaX (Fig. 1c) two adsorption enthalpies were used, since on this adsorbent the olefin can also adsorb via the π-complex with CuCl, which is expected to result in a larger adsorption enthalpy than for the physical adsorption. The obtained parameter estimates for all isotherms are listed in Table 2. If we compare these parameters no direct relation between the A-sites (or the B-sites) on the NaX and on the CuCl/NaX samples can be drawn, though the values for the latter adsorbent are higher than for NaX, as was expected. The designation of site A or B is purely arbitrarily and does not necessarily correspond to the same location on the two samples.

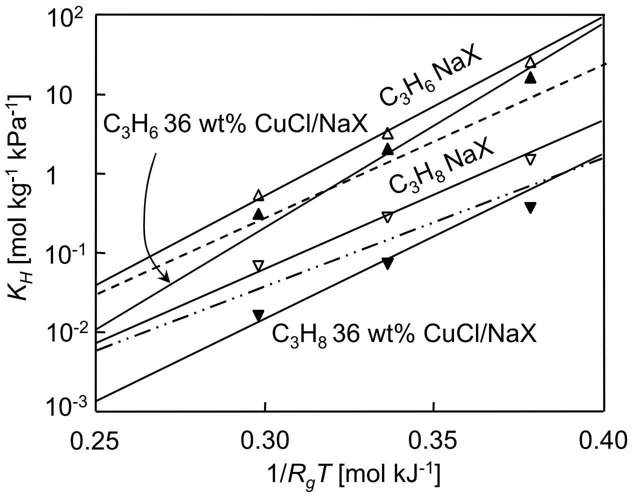

Fig. 2 K_H obtained from individual isotherm fits vs. $1/R_gT$ for propylene (△, ▲) and propane (▽, ▼) on NaX (▽, △) and 36 wt% CuCl/NaX (▼, ▲).The *solid lines* represent the combined isotherm fitting results. Literature data of propylene and propane on NaX is represented by (- - - - -) and (–··–··), respectively (Da Silva and Rodrigues 1999)

3.2 Thermodynamics

The Henry's law constants, based on the individual fit of the isotherm data at every temperature (Table 3) are plotted versus $1/R_gT$ in Fig. 2. Literature values for NaX are also included (Da Silva and Rodrigues 1999). The isosteric heat of adsorption at zero coverage is calculated for both the individual and the combined isotherm fitting results and included in Table 3 together with the literature values.

The Henry's law constants and the slopes in Fig. 2 are higher for propylene compared to propane. Smaller Henry's

Table 3 Calculated adsorption properties of the adsorptives on the adsorbents

	$K_{H,318\text{ K}}$ [mol kg^{-1} kPa^{-1}]	$K_{H,358\text{ K}}$ [mol kg^{-1} kPa^{-1}]	$K_{H,404\text{ K}}$ [mol kg^{-1} kPa^{-1}]	Q_0^{st} [kJ mol^{-1}]		Q_0^{st} (Literature data) [kJ mol^{-1}]
				Ind.*	Comb.*	
NaX						
Propylene	26.0	3.28	0.542	48.1	51.9	42.5[a]; 46.1–52.7[b]
Propane	1.50	0.282	0.0686	38.4	43.1	35.8[a]; 32.9[c]; 34.4[d]
36 wt% CuCl/NaX						
Propylene	16.6	2.09	0.316	49.2	59.2	
Propane	0.375	0.0732	0.0163	38.9	47.8	

*Based on the individual fit of each isotherm at each temperature (Ind.) or based on the combined fitting of each set of isotherms at different temperatures (Comb.)

[a] (Da Silva and Rodrigues 1999)

[b] (Costa et al. 1991; Ghosh et al. 1993; Huang et al. 1994; Järvelin and Fair 1993)

[c] (Loughlin et al. 1990)

[d] (Siperstein and Myers 2001)

law constants and a larger slope is observed, when the CuCl/NaX sample is compared with NaX.

The isosteric heats calculated from Fig. 2 correspond well to the literature values for NaX. The isosteric heats on NaX obtained from the individual fits correspond well with the combined fitting results, though a slightly lower value, closer to the reported literature data, is obtained. For the CuCl/NaX sample there is a larger difference between the isosteric heat calculated from the individual fits and that from the combined fitting. The main cause for this difference is that the saturation capacities (q^{sat}) were allowed to decrease at the higher temperatures in the individual fitting procedure, while it was assumed to be one fixed value over the entire temperature range in the combined fitting procedure.

Figure 3 shows the results of the isosteric heat of adsorption as a function of the loading for the two adsorbents. At zero loading the same isosteric heats of adsorption are obtained as those presented in Table 3. The isosteric heat remains (relatively) constant for propane on both adsorbents and for propylene on NaX. This also follows from the Dual-Site Langmuir adsorption modelling for these systems, *cf.* Table 2. On the CuCl/NaX adsorbent a transition is observed in the isosteric heat of propylene. The transition occurs at values corresponding with the capacities for the sites with the highest heats of adsorption in the Dual-Site Langmuir modelling, ~1.1 mol/kg for propylene (q_A^{sat} in Table 2).

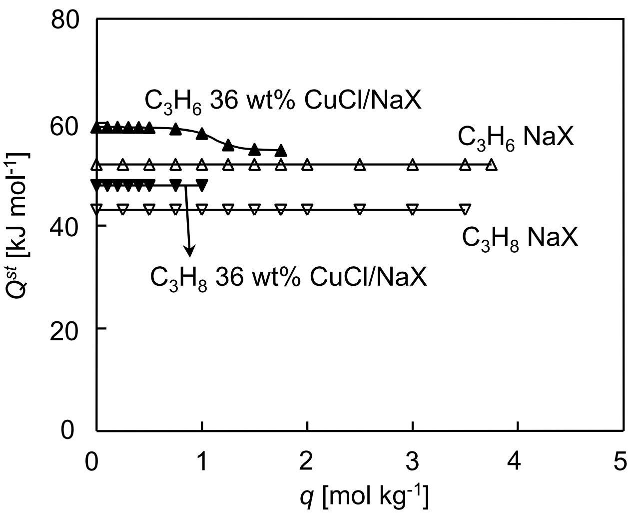

Fig. 3 Isosteric heat of adsorption (Q^{st}) as a function of the amount adsorbed (q) for propylene (△, ▲) and propane (▽, ▼) on NaX (▽, △) and 36 wt% CuCl/NaX (▼, ▲)

3.3 Breakthrough curves

In Fig. 4a–f the breakthrough profiles of a binary mixture of propylene and propane in helium (25 : 25 : 50) are shown at the three temperatures on CuCl/NaX (Fig. 4a–c) and NaX (Fig. 4d–f). The breakthrough curves of the two duplicate experiments overlap with each other, indicating a good reproducibility of the experiments. In all figures first propane breaks through, followed by propylene, which indicates that both adsorbents selectively adsorb the olefin at all temperatures. The propane mol fraction even increased beyond 1/3 on both adsorbents. This roll-up indicates a displacement of adsorbed propane by propylene.

The breakthrough times of propylene and propane were considerably longer on the NaX-column compared to those observed on the CuCl/NaX column. On the CuCl/NaX col-

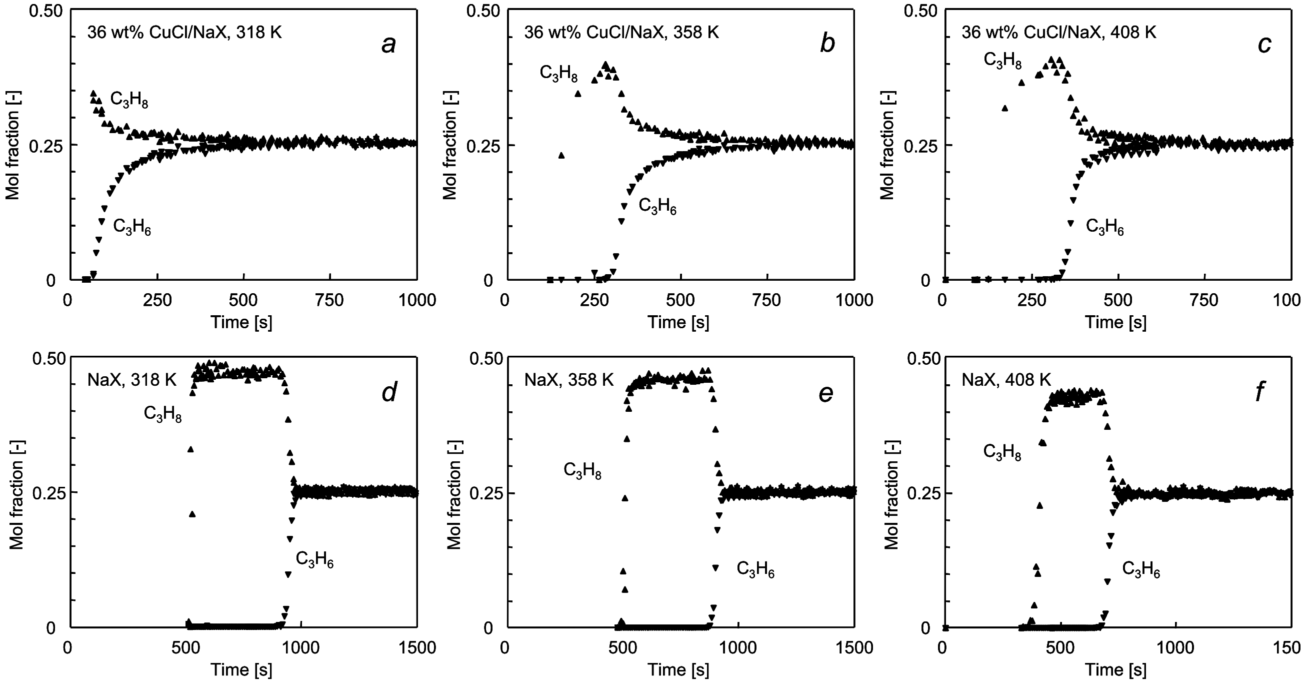

Fig. 4 Breakthrough profiles of propane (▲) and propylene (▼) mixture in helium (25 : 25 : 50) over 36 wt% CuCl/NaX (**a**–**c**) or NaX (**d**–**f**) at 318 K (**a** and **d**), 358 K (**b** and **e**) and 408 K (**c** and **f**)

umn only a minor time difference between the first breakthrough points of propylene and propane was observed at 318 K, whereas on the NaX-column the breakthrough time of propylene was almost two times longer as that of propane. Curiously, at 318 K a shorter breakthrough time of both components was observed on CuCl/NaX than at higher temperatures.

3.4 Binary mixture adsorption and selectivity

Based on the breakthrough and desorption profiles the adsorbed amounts of both components were calculated using mass balance equations (Malek et al. 1995). The results of these calculations are shown in Fig. 5a–b and Fig. 6a–b for propane and propylene mixtures on CuCl/NaX and NaX, respectively. The predictions, based on the single component isotherms (Fig. 1a–d) and the IAS-theory, are shown in, respectively, Figs. 5c–d and 6c–d for binary mixtures of propylene/propane. The propylene selectivity calculated from the experimental adsorbed amounts or the modelling data are shown in Fig. 7a–b and 7c–d, respectively.

The calculation of the adsorbed amounts using the breakthrough profiles instead of the desorption profiles in many cases resulted in a similar outcome, though at the lower pressures, and especially for propane on CuCl/NaX, the calculations based on the breakthrough profiles yielded higher amounts than those based on the desorption profiles. Unfortunately, at the end of the breakthrough profile the (small) absolute analytic error of the GC made it difficult to distinguish the propane mol fraction from its equilibrium value at these lower partial pressures. In Fig. 8 the relative standard deviation of the (integrated) adsorbed amounts and selectivity, calculated from the two duplicate experiments, are shown for propane and propylene on CuCl/NaX at 358 K (Fig. 8). Similar trends in this relative analytical error were observed for the other adsorptive-adsorbent combinations at the various temperatures. Because of this, primarily the data points obtained from the desorption profile were used. Fortunately, the breakthrough profiles yield valuable information about the phenomena occurring during the binary adsorption and give insight in the reliability of the adsorbed amounts obtained from the desorption profiles. At the higher pressures the obtained loadings and trends from the breakthrough profiles were almost equal to those obtained from the desorption profiles, in agreement with the smaller experimental error at these pressures.

In agreement with the modelling predictions, the adsorbed amounts for propylene on both adsorbents are higher than those for propane at all the investigated temperatures and pressures, resulting in a selective adsorption of propylene. The adsorbed amounts on NaX are larger than those on CuCl/NaX, while the opposite is seen for the selectivity. Almost all components show an increase in the adsorbed amount when their partial pressure is increased.

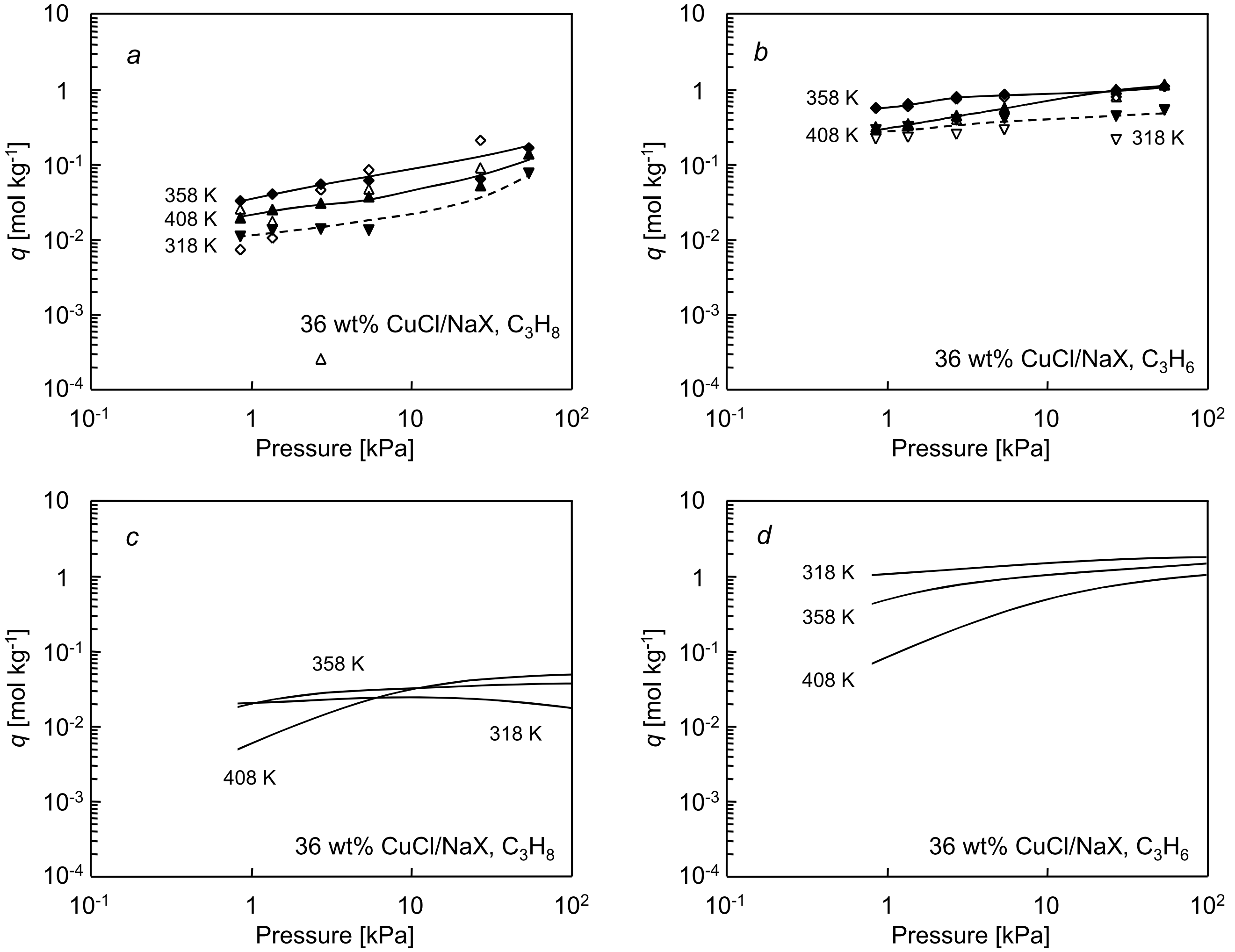

Fig. 5 (**a**–**b**) Loadings of propane (**a**) and propylene (**b**) for binary mixture (50 : 50) adsorption at 318 K (▼, ▽), 358 K (♦, ◇) and 408 K (▲, △) on 36 wt% CuCl/NaX. (*Open symbols* based on breakthrough profile, *closed symbols* based on desorption profile.) *Lines* follow the *closed symbols* and are to guide the eye; a *dashed line* indicates the unreliable low temperature data (see Discussion). (**c**–**d**) IAS-theory prediction for the loading of propane (**c**) and propylene (**d**) for a (50 : 50) mixture on 36 wt% CuCl/NaX

An increase in the temperature shows different effects for the two adsorbents. Similarly as the curious shorter breakthrough time at 318 K (Fig. 4a), the adsorbed amounts of both components on CuCl/NaX at 318 K are often lower than those determined at higher temperatures. For this adsorbent, the modelling predictions show therefore a larger deviation to the experimental data. The IAS-theory predictions are more in line with the expectations of a shorter breakthrough time and lower adsorbed amounts at higher temperatures. To indicate this lower reliability a dotted line was used to guide the eye along the data at 318 K.

On NaX a temperature increase results in an increase in the adsorbed amount of the propane at higher partial pressures, while the reverse is observed at lower partial pressures. For this adsorbent a large similarity with the experimental data is seen, both qualitatively and quantitatively.

In agreement with the modelling predictions, the propylene selectivity on CuCl/NaX remains relatively constant up to a partial pressure of 10–27 kPa (Fig. 7b). Thereafter a curious decrease to a mixture selectivity of 7–8 is seen in the experimental data, while the modelling (Fig. 7d) shows a rising trend. Because of this curious difference a dotted line was used to guide the eye along the data above this partial pressure. At the lowest temperature (318 K) the highest mixture selectivity for propylene (25–30 compared to 50 based on modelling) was obtained for this adsorbent. At the other temperatures the mixture selectivity for propylene is approximately 15–20 (compared to 15–30 based on modelling).

On NaX the experimental propylene mixture selectivity shows a small increase at 318 K and a decrease at 408 K with

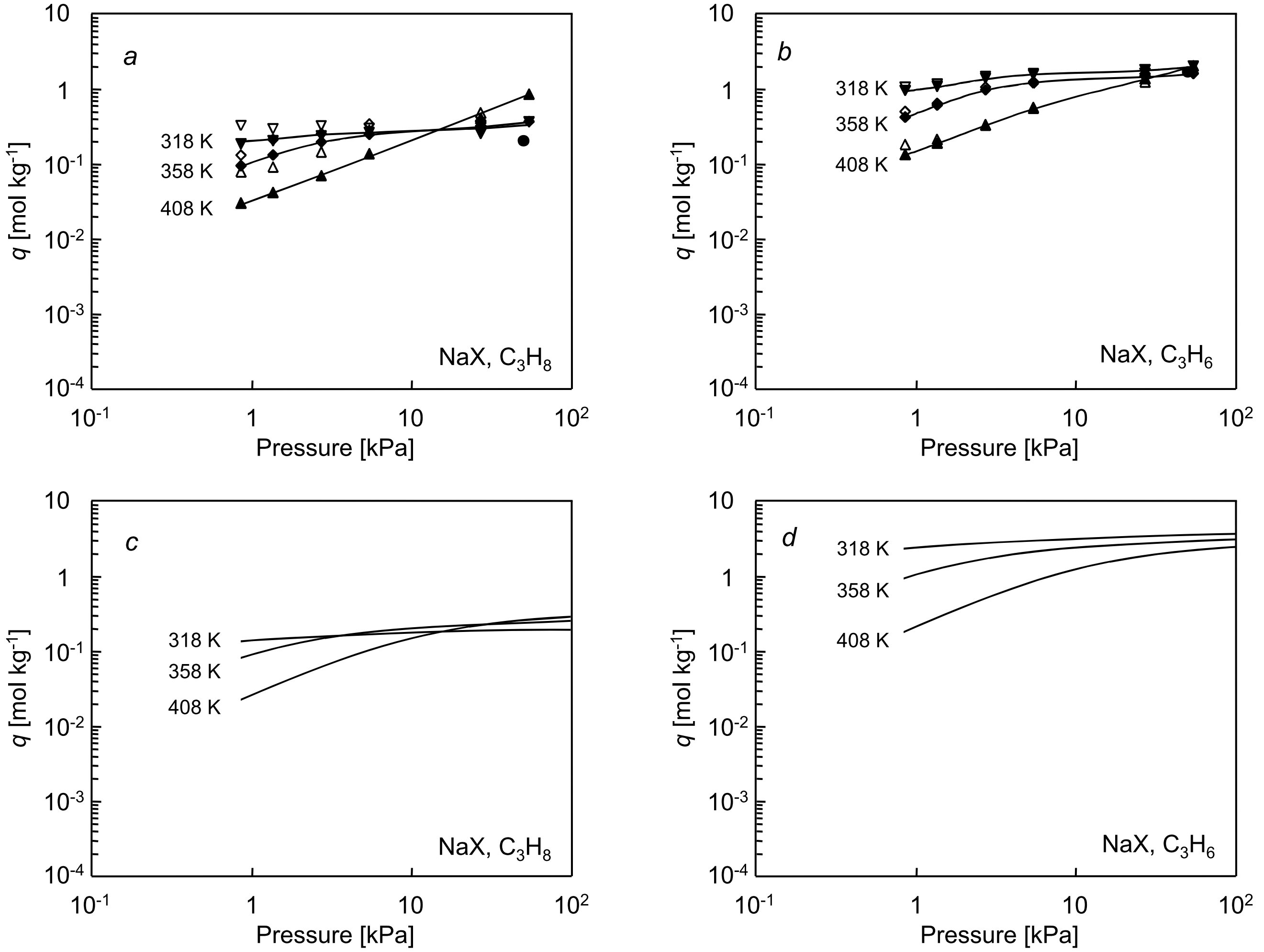

Fig. 6 (**a**–**b**) Loadings of propane (**a**) and propylene (**b**) for binary mixture (50 : 50) adsorption at 318 K (▼, ▽), 358 K (♦, ◊) and 408 K (▲, △) on NaX. Literature data (•) for a binary propane and propylene mixture on NaX at 343 K (Huang et al. 1994). (*Open symbols* based on breakthrough profile, *closed symbols* based on desorption profile.) *Lines* follow the *closed symbols* and are to guide the eye. (**c**–**d**) IAS-theory prediction for the loading of propane (**c**) and propylene (**d**) for a (50 : 50) mixture on NaX

increasing partial pressure (Fig. 7a), while the IAS-theory predictions (Fig. 7c) show an almost constant selectivity. Within the experimental pressure and temperature range the mixture selectivity for propylene varies between 2,5 and 7 (compared to 8–20 based on the modelling).

4 Discussion

4.1 Single component isotherms

The adsorption isotherms of propylene and propane on NaX and CuCl/NaX can be well described by the Dual-Site Langmuir isotherm model (Fig. 1a–d and Table 2). For both materials the adsorbed amounts of propylene is larger than propane which suggests a larger affinity of the olefins with the adsorbents. The presence of CuCl results in a reduction of the capacity and in a slower diffusion, both ascribed to a reduction in the pore volume. Therefore longer equilibration times in the volumetric setup were required for propane and propylene on the CuCl/NaX sample. The reduction in the adsorbed amount for propane is larger than for propylene, since the later benefits from the π-complexation with CuCl.

The isotherm models show some deviations from the experimental data. For CuCl/NaX, these deviations occur at the higher pressures (10–100 kPa) and lower temperatures. At these pressures the increase in adsorbed amount is relatively small in each step of the analysis and due to the presence of the adsorbed gas and CuCl in the pores of NaX, the diffusion of the adsorptives is hindered and therefore slow. As a consequence, the equilibrium between the surface and the center of the zeolite may not have been fully established. Since the diffusional time is proportional to the squared particle size, these diffusion limitations inside the

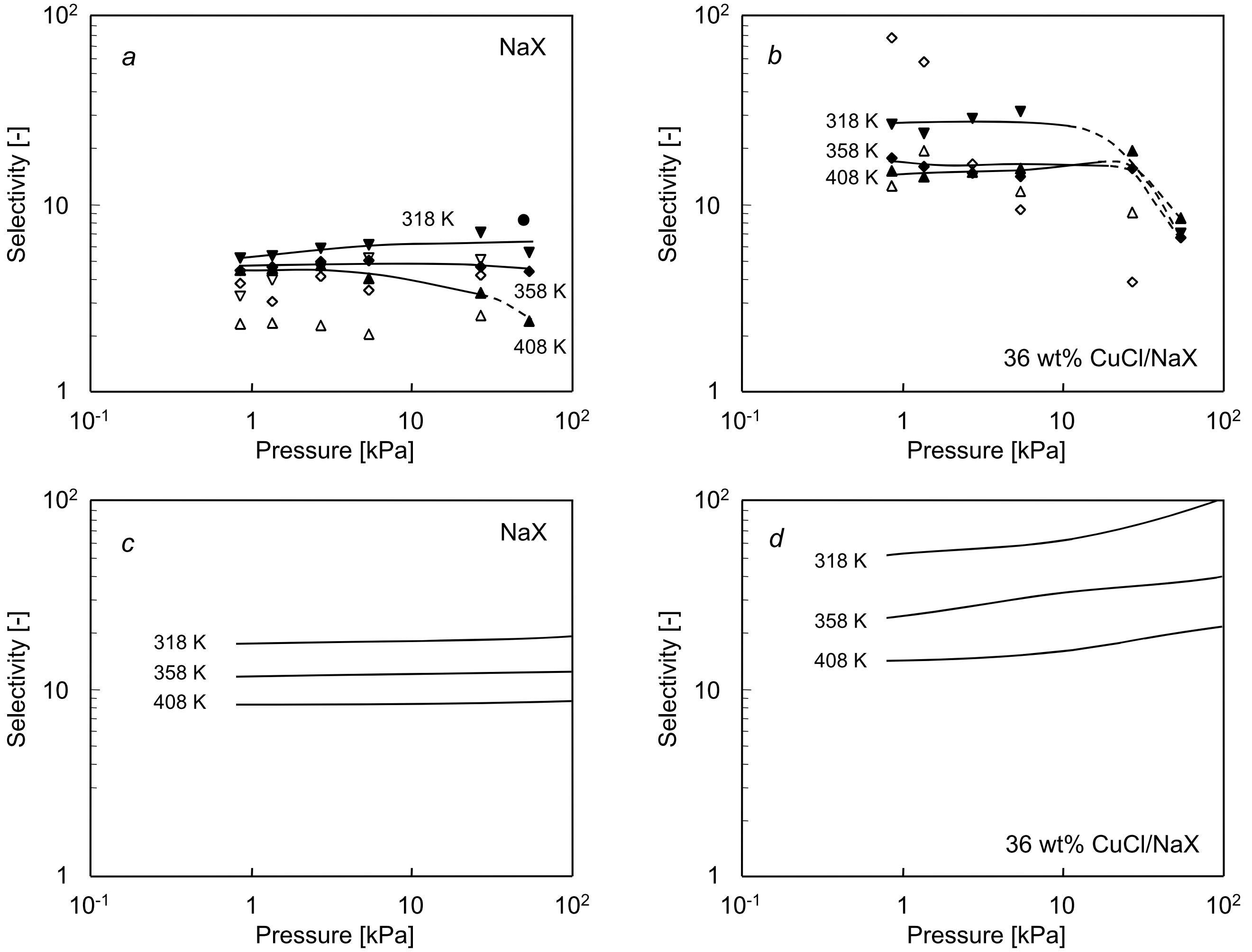

Fig. 7 (**a**–**b**) Selectivity for propylene over (**a**) NaX and (**b**) 36 wt% CuCl/NaX at 318 K (▼, ▽), 358 K (⧫, ◊) and 408 K (▲, △). (●) Literature data for propylene on NaX at 343 K (Huang et al. 1994). (*Open symbols* based on breakthrough profile, *closed symbols* based on desorption profile.) *Lines* follow the *closed symbols* and are to guide the eye, a *dashed line* for unreliable data (see Discussion). (**c**–**d**) IAS-theory estimation for the selectivity for propylene over (**c**) NaX and (**d**) 36 wt% CuCl/NaX for a (50 : 50) mixture with propane

crystal will be smaller when smaller (industrial) zeolite crystals are used.

After the dispersion of CuCl, the adsorption constants (Table 2) of propane on the zeolite adsorbent hardly change. Only a small increase in the adsorption enthalpy and isosteric heat (Tables 2 and 3) are observed, probably due to the increased density of the adsorbent by the coverage of the zeolite surface with CuCl, resulting in larger attractive forces (Tümsek and Inel 2003). Literature data is limited for the CuCl/NaX adsorbent. The adsorption enthalpy and isosteric heat are in the range of values reported for CuCl on pillared clays (Cheng and Yang 1995). Isosteric heats of adsorption between 45–54 kJ mol^{-1} have been reported for propylene, and for propane the reported values are between 22–29 kJ mol^{-1}.

The adsorption enthalpies, isosteric heats and loadings on NaX correspond well with literature data. For propane and propylene isosteric heats of adsorption on NaX of 33–36 and 43–53 kJ mol^{-1} (Table 3) were reported, respectively. The combined fitting on the Dual-Site Langmuir model yields a larger difference with the literature data for the isosteric heat of adsorption for propane on NaX. This may be the result of the larger deviation at lower pressures of this fit from the experimental data. The individual isotherm fits result in an isosteric heat closer to the reported range in the literature for the isosteric heat, but this fitting procedure uses a variable adsorption capacity at each temperature. A temperature dependency of the adsorption capacity is expected to be relatively small, since the pore volume would be (almost) the same at each temperature. A large change in the adsorption capacity is therefore not considered realistic.

The Henry's law constants (Fig. 3 and Table 3) were larger than those reported in the literature, although the global trend is similar. As was often noticed, the literature

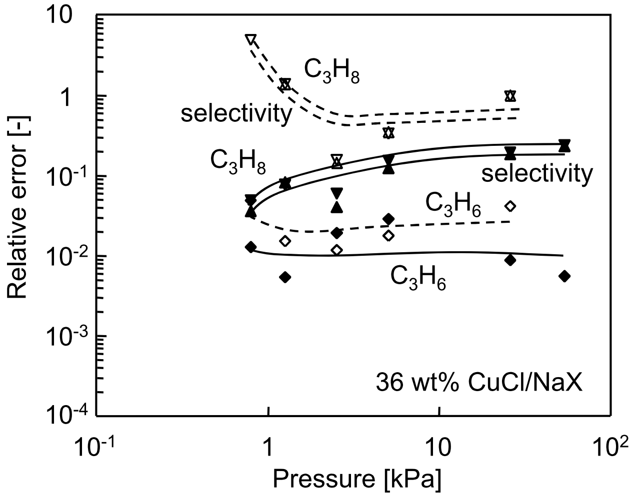

Fig. 8 Relative standard deviation of the loading of propane (▲, △) and propylene (♦, ◇) and relative standard deviation of the selectivity (▼, ▽) for the breakthrough profile (△ , ◇, ▽ and *dotted line*) and the desorption profile (▲, ♦, ▼ and *solid line*) on 36 wt% CuCl/NaX at 358 K. *Lines* are indicative and to guide the eye

is rather vague about the sample pretreatment, which hampers a good comparison of the absolute values, especially since the 'wet' zeolite contains approximately 23 wt% water, which results in a 30% higher uptake for the dry sample mass compared to the 'wet' sample mass.

The isosteric heat of adsorption as a function of loading is (relatively) constant for propane on both adsorbents and for propylene on NaX (Fig. 3), which indicates an energetically homogeneous sorbent, for which the Dual-Site Langmuir model with equal heats of adsorption is applicable. For propylene on CuCl/NaX a transition is observed around about 1 mol/kg, which suggests that specific interactions are involved, the π-complexation of propylene with CuCl. This value corresponds on average with 1.7 propylene molecules complexing with CuCl per supercage. Since on average 10 molecules of CuCl are present per supercage of NaX, not all Cu^+ is involved in the complexation possibly the result of partial blockages of pores and/or Cu^+-sites by CuCl and/or adsorbed propylene.

4.2 Binary mixture adsorption and selectivity

The trends of the adsorbed amounts presented in Figs. 5a–b and 6a–b show a large similarity with those predicted with the IAS-theory (Figs. 5c–d and 6c–d). Both sorbents show a relatively high selectivity for propylene (Fig. 7a–d), which is consistent with the later breakthrough times of propylene compared to propane (Fig. 4a–f). In agreement with the larger analytical error (Fig. 8), the trends and values obtained from the desorption profiles correspond better to the predictions than those obtained from the breakthrough profiles. On NaX larger adsorbed amounts are found, which is consistent with the longer breakthrough times on NaX (Fig. 4d–f) compared to CuCl/NaX (Fig. 4a–c). Also for NaX the quantitative values of the adsorbed amounts and the selectivity correspond well with the predictions of the IAS-theory (Figs. 6a–d, 7a and 7c), which confirms the applicability of breakthrough and desorption curves to determine binary adsorption equilibria. For CuCl/NaX larger differences are observed, though most of the trends are similar (Figs. 5a–d, 7b and 7d).

The calculation of propylene and propane adsorbed amounts and selectivity on CuCl/NaX from adsorption and desorption profiles are however affected by mass-transfer phenomena and small absolute analytical errors. For instance, on CuCl/NaX the adsorption capacity of, especially, propane is very small compared to NaX and, as a consequence, the correction for the inert SiC-column is large. This may explain why for propane model and experiment deviate by a factor 5. For propylene this correction is relatively small and therefore the absolute value of the experimental data is closer to the modelling predictions.

Furthermore, the reduction of the pore volume after the dispersion of CuCl in NaX not only causes a reduction in the adsorption capacity (Table 2 and Fig. 5a–d compared to Fig. 6a–d), but it also affects the mass-transport and the attainment of the adsorption equilibrium. As seen in Fig. 4a–f the breakthrough profiles for CuCl/NaX are less steep than for NaX and the equilibrium appears to be established much slower on CuCl/NaX, which indicates a slower mass-transfer/diffusion. This was also noticed in the determination of the adsorption isotherms (Fig. 1a–d). Attainment of adsorption equilibrium for CuCl/NaX took much longer than for NaX. At higher temperatures, activated diffusion is enhanced and indeed faster equilibration times are seen (Fig. 4a compared to Fig. 4c). The slow mass-transport considerably affects the adsorption of both components at 318 K. Because of this slower mass-transfer, only adsorption at the outer region of the zeolite particles may take place and therefore the apparent adsorption capacity is much lower, resulting in a very early breakthrough at 318 K (Fig. 4a).

Additionally, a roll-up phenomenon during the breakthrough experiments (Fig. 4a–f) was seen. The roll-up is caused by a displacement of adsorbed propane by propylene during the breakthrough experiment. Therefore counter-diffusion takes place in the zeolite crystals. Counter-diffusion in pores approaching molecular sizes can be very slow, and this will be important especially in the smaller pores of CuCl/NaX. Part of the propane could even be locked in the center or a pocket of the zeolite crystals unable to desorb from the zeolite crystal. This locked propane would result in a higher propane loading and a lower mixture selectivity of the adsorbent than expected for a true binary equilibrium (Mittelmeijer-Hazeleger et al. 2002). It can be doubted therefore if equilibrium has been established in all cases for the CuCl/NaX sample. So, because of the slow diffusion, higher values for the adsorbed amount of propane at higher pressure and loadings are found.

In the binary adsorption on NaX an increase in the temperature results in a decrease in the adsorbed amount of propane at lower pressures, whereas it increases at the higher pressures (Fig. 6a). This observation is in agreement with the predictions of the IAS-theory (Fig. 6c). At the lower pressures the adsorption is mainly determined by the adsorption affinity. The exothermal adsorption results in a decreased adsorbed amount at higher temperatures and lower pressures. At higher pressures and loadings the adsorption becomes also affected by entropic effects. The component that has the highest packing efficiency (propylene, see Table 2) on the adsorbent will be favoured to occupy all the adsorption sites, expelling the other component (Kapteijn et al. 2000; Krishna and Baur 2003; Krishna and Paschek 2000). Especially at lower temperatures the loadings are higher and the importance of the packing efficiency becomes more important, and a transition from enthalpy to entropy control will occur at lower pressures (Fox and Bates 2004; Zhu et al. 2005). Indications of such a transition are (i) that the selectivity for propylene on NaX increases with pressure at 318 K, while the total loading hardly changes and (ii) that the selectivity decreases with temperatures at the higher pressures. The loading of propane still increases with pressure at 408 K, while it becomes constant at the lower temperatures (see Figs. 6a–b and 7a). This is exactly what the IAS-theory also predicts (Figs. 6c–d and 7c). For the CuCl/NaX sorbent the results are contaminated with diffusional limitations and no conclusions can be drawn in this respect.

This is one of the first experimental data were this transition in the adsorbed amounts is indeed observed for fairly similar molecules.

On Faujasite (NaY) an entropy/packing effect was observed earlier (Daems et al. 2005; Denayer et al. 2006) for the liquid-phase adsorption of olefin/paraffin mixtures of different lengths (hexene/decane and dodecene/decane mixtures). A larger selectivity for the shorter olefin is similarly attributed to its higher packing efficiency in Faujasite.

Considering the hyperbolic limit of the selectivity to 1, the experimental selectivity of NaX corresponds well to the IAS-theory predictions. Only for CuCl/NaX the selectivity at higher pressures are considerably affected by the erroneous value in the adsorbed amounts due to diffusion limitations. For NaX the propylene selectivity also shows a good agreement with the literature values of 11 (at 298 K), 9 (at 323 K) and 8 (at 343 K) (Huang et al. 1994).

Considering the application of the adsorbents for propylene/propane separation, a choice between the slightly higher selectivity of CuCl/NaX or the higher adsorption capacity and faster diffusion of the NaX adsorbent has to be made. Since the increase in the propylene selectivity is relatively small at higher pressures, the capacity of the adsorbent is reduced after CuCl dispersion, and desorption from NaX is easier, in an industrial pressure swing adsorption (PSA) unit NaX without dispersed CuCl would be the sorbent of choice. Furthermore, the CuCl/NaX sorbent is sensitive to humid air, leading to its deterioration (Van Miltenburg 2007).

5 Conclusions

Adsorption isotherms and mixture breakthrough profiles show a preferential adsorption of propylene over propane on NaX and 36 wt% CuCl/NaX. Their isotherms can be described by the Dual-Site Langmuir model on both materials.

Breakthrough experiments showed that during the loading of the adsorption-column a displacement of adsorbed propane by propylene occurred along the length of the column. This roll-up effect was more pronounced on NaX, because of its higher adsorption capacity.

The dispersion of CuCl in the zeolite results in a lower saturation capacity of propylene and propane by about 60%, but the adsorption constants have increased. For propylene on NaX and propane on CuCl/NaX and NaX the isosteric heats remain constant with loading, while CuCl/NaX shows a transition for propylene at around 1.7 propylene molecules π-complexating with CuCl per supercage. Hence, only 17% of the dispersed CuCl is involved in the π-complexation.

Binary mixture adsorption data confirmed a lower adsorption capacity for CuCl/NaX. The dispersion of CuCl inside the zeolite crystal results in smaller pore sizes and pore volume, lowering the adsorption capacity and causing diffusion limitations. The dispersion of CuCl in the zeolite resulted in an increase of the mixture selectivity for propylene from 3–7 on NaX to 15–30 on CuCl/NaX. On NaX diffusion limitations were not observed and sharper breakthrough profiles were obtained than on CuCl/NaX.

The binary isotherms of propylene and propane on NaX showed that at the lower partial pressures the adsorption is primarily controlled by the adsorption affinity of the adsorbent with propylene. At the higher partial pressure the adsorption is affected by entropy and the molecule with the most effective packing efficiency (propylene) is adsorbed preferentially.

For practical application NaX is preferred over CuCl/NaX in propylene/propane separation units, because it is less affected by a slow diffusion in the zeolite particles, has a higher adsorption capacity and is more stable during handling in the ambient atmosphere.

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