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Commensurate freezing of hydrocarbons in silicalite

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Normal hexane and normal heptane exhibit a two step desorption profile from silicalite while shorter and longer normal alkanes desorb in a single step. The two step desorption profiles are explained by, and give evidence for, commensurate freezing of the hydrocarbon molecules in the zig-zag channels of silicalite. The freezing results in an additional loss of entropy upon adsorption in silicalite. Also linear alkenes with appropriate chainlength display a two step, but less pronounced, desorption profile. The less pronounced desorption profiles are the result of the lower energetic interaction of the alkenes with the silicalite lattice.

1. INTRODUCTION

The interaction between hydrocarbons and zeolites is of major importance for heterogeneous catalysis and is therefore a widely studied subject. Several experimental techniques like calorimetry, adsorption isotherm measurement, IR and NMR spectroscopy and Temperature Programmed Desorption (TPD) have been used to study this interaction. Most of these studies are focused on the energetic interaction between zeolite and sorbate, the entropy of adsorption has attracted much less attention.

Besides these experimental methods, computational techniques have become available for the calculation of the heats of adsorption and of adsorption isotherms. From the calculation of the adsorption isotherms of n-alkanes in silicalite, a kind of phase transition was predicted to occur upon the filling of silicalite with n-hexane and n-heptane [1]. At approximately half the saturation loading, the n-hexane and n-heptane molecules become commensurately frozen in the zig-zag channels. This as a result of the good fit of the n-hexane and

n-heptane molecules in the zig-zag channels. The commensurate freezing results in an efficient packing of the silicalite lattice and is accompanied by an additional loss of entropy. To overcome the additional loss of entropy, an increased pressure is needed which is reflected as a step in the adsorption isotherm. Therefore, the simulations explain the experimentally measured adsorption isotherms which also showed the occurrence of a step in the isotherm for n-hexane and n-heptane while shorter and longer n-alkanes exhibit a normal type I isotherm [2-4]. The additional loss of entropy is furthermore confirmed by the temperature dependence of the occurrence of the step in the adsorption isotherm of n-hexane [2,3,5].

We will present here our study on the sorption of n-alkanes and linear alkenes in silicalite by means of Temperature Programmed Desorption. A comparison will be made between the sorbates for which commensurate freezing was predicted to occur with sorbates of shorter and longer chainlength. Besides comparing different adsorbates, also the adsorption of n-hexane and n-heptane at different temperatures will be compared.

2. EXPERIMENTAL

2.1. Materials
The synthesis of the used silicalite sample is described in reference [6]. The sample was calcined *in-situ* in a Setaram TG-DSC 111 apparatus (in which also the adsorption and desorption experiments were performed) in a mixture of helium and air (25% air) at 943 K for 1 hour. According to X-ray diffraction, the sample was highly crystalline and chemical analysis revealed a Si/Al ratio greater than 4000. Scanning Electron Microscopy showed the average particle size of the sample to be around 3µm. From Hoek Loos (Schiedam, The Netherlands) n-butane 3.5 (purity 99.95%) was obtained, the other n-alkanes ranging from n-pentane to n-decane had a purity of at least 99% and were obtained from Janssen Chimica (Geel, Belgium). The alkenes, 1-heptene and 1,5-hexadiene were obtained from Aldrich (Steinheim, Germany) with a purity of 97% respectively 98%. The other 1-alkenes had a purity of 97% and were obtained from Janssen Chimica.

2.2. Temperature programmed desorption
First, adsorption was performed by mixing a helium flow saturated at room temperature with adsorbate or a gaseous adsorbate flow with a pure helium flow of about 1.8 l/h. Since the adsorbate flows amounted approximately 0.6 l/h, adsorption at room temperature was performed at a relative pressure of at most 0.25. Saturation of the silicalite sample was reached within a few minutes for n-butane while adsorption during 24 hours was needed for n-decane. After saturation, the adsorbate flow was switched off and the temperature program was started. The temperature was raised by 5 K/min to 723 K. A blank run of

the clean sample was subtracted from all TPD-curves to correct for temperature effects on the mass.

2.3. Variation of adsorption temperature

The equilibrium loadings of n-hexane and n-heptane on silicalite at different temperatures were determined in these experiments. Again, one fourth of the total helium flow was saturated at room temperature with adsorbate. This means that adsorption at temperatures higher than room temperature is performed at a relative adsorbate pressure of less than 0.25. The absolute adsorbate pressure is, of course, equal in all the adsorption experiments: *maximal* 4 kPa for n-hexane and *maximal* 1.5 kPa for n-heptane.

3. RESULTS AND DISCUSSION.

3.1. Temperature programmed desorption of n-alkanes

The saturation loadings of the silicalite sample at room temperature with the different n-alkanes are given in table 1.

Table 1
Saturation loadings and occupied pore volumes of n-alkanes on silicalite at room temperature (U.C. = unit cell)

n-alkane	maximum loading (molec./U.C.)	maximum loading (mmol/g)	micropore volume (ml/g)
n-butane	9.3	1.8	0.16
n-pentane	8.7	1.5	0.17
n-hexane	8.1	1.4	0.18
n-heptane	7.3	1.3	0.18
n-octane	5.4	0.93	0.15
n-nonane	5.1	0.89	0.16
n-decane	5.1	0.87	0.17

The micropore volume occupied by the adsorbate was calculated by using the liquid density of the adsorbate at 293 K. All loadings compare very well with the maximum loadings reported in literature, indicating that the crystallinity of the used sample is very good. Further it can be seen that the efficiency of packing the silicalite lattice increases from n-butane to reach a maximum at n-hexane and n-heptane. The efficiency decreases significantly for n-octane and increases again for the larger adsorbates.

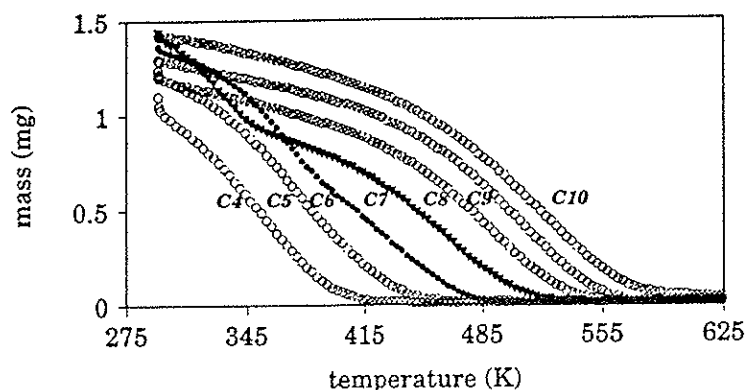In figure 1, the Temperature Programmed Desorption curves for the n-alkanes are given.

Figure 1. TPD curves of n-alkanes from silicalite (10.39 mg silicalite).

The figure shows that n-hexane and n-heptane desorb in two steps from silicalite while longer and shorter n-alkanes desorb in a single step. This can also be seen in figure 2 which displays the differential mass loss (-dm/dT) during the TPD for n-pentane to n-octane. The differential mass loss curves for n-butane, n-nonane and n-decane are similar to the curves of n-pentane and n-octane and are not displayed here for the sake of clarity in the figure. Also for the sake of clarity, the curves are separated from each other. It should be noted that the results reported in figure 1 and 2 were verified by measurements on two different silicalite samples with larger particles of 50 x 20 x 20 µm and of 100 x 40 x 40 µm using heating rates of 5 and 7 K/min. The temperatures at which the differential mass losses are at a maximum are given in table 2.
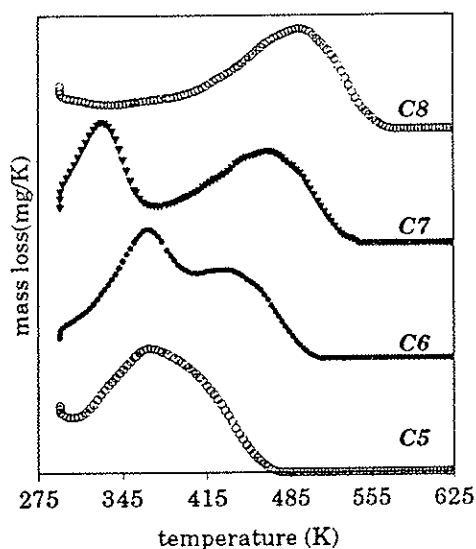

Figure 2. Differential mass loss (-dm/dT) of n-alkanes during TPD.

Table 2
Temperatures of the differential mass loss maxima

n-alkane	T1 (K)	T2(K)
n-butane	-	355
n-pentane	-	369
n-hexane	367	429
n-heptane	329	467
n-octane	-	493
n-nonane	-	512
n-decane	-	520

Figure 1 and 2 show that the second desorption peak of n-hexane and n-heptane, and the desorption peaks of the other n-alkanes are ordered according to their increasing chainlength. However, the first desorption peak of n-hexane and n-heptane occurs at relatively low temperatures. These low temperatures indicate that at high loadings a part of the adsorbed n-hexane and n-heptane molecules desorbs more easily from silicalite than the other n-alkanes do. Further it is remarkable that the first desorption peak of n-heptane occurs at a lower temperature than that one of n-hexane, while the second desorption peaks are ordered in accordance with their increasing chainlength.

Since the first desorption peaks of n-hexane and n-heptane are not ordered according to their increasing chainlength, the first mass loss of these two adsorbates should not be determined by energetic but by entropic effects. This means that the low temperature desorption of n-hexane and n-heptane should be the result of a relatively high gain of entropy upon desorption. This high gain of entropy can only be the result of an extra low entropy value, a constrained position, of the adsorbed n-hexane and n-heptane molecules. The constrained position can be explained by the commensurate freezing of the molecules in the zig-zag channels. Due to the larger chainlength, n-heptane will have a more constrained position and therefore a lower entropy value than the n-hexane molecules adsorbed in the zig-zag channels. This will result in a higher gain of entropy upon desorption of the adsorbed n-heptane molecules and causes the first n-heptane mass loss to occur at a lower temperature than the first mass loss of n-hexane. The more constrained position of the n-heptane molecules in the zig-zag channel is confirmed by the simulated [1] and measured [2-5] adsorption isotherms of n-hexane and n-heptane. These isotherms show that the step in the adsorption isotherm is more pronounced for n-heptane than for n-hexane.

After partial desorption of n-hexane and n-heptane, rearrangement of the molecules takes place resulting in an ordering similar to the ordering of the shorter and longer n-alkanes, adsorbates with a normally low entropy value. This similarity in ordering is reflected in the second desorption peak of n-hexane and n-heptane and the desorption peaks of the other n-alkanes which are ordered according to their increasing chainlength. The occurrence of a rearrangement during the desorption agrees with the interpretation of Richards and Rees of a two step desorption profile of n-hexane from silicalite [7].

A similair feature as displayed by the presented TPD curves, was found in the uptake rate of n-hexane in silicalite [8]. It was shown that for a quantitative description of the diffusion of n-hexane, a combination of intracrystalline diffusion with a molecular rearrangement is needed. The rearrangement was denoted as intracrystalline immobilization in this context.

Not only the desorption curves presented here are in agreement with the concept of commensurate freezing, also the maximum loadings of the different n-alkanes on silicalite are in agreement. As can be seen in table 1, the packing of

n-alkanes in the silicalite lattice is most efficient for the n-alkanes which can be frozen in the zig-zag channels. The efficiency drops significant when the lattice is filled with n-octane, the adsorbate which chainlength is too large to be commensurately frozen in the zig-zag channels.

3.2. Temperature programmed desorption of alkenes

Saturation of the silicalite sample with 1-alkenes ranging from 1-pentene to 1-octene results in occupied pore volumes which are similar to the pore volumes occupied by the corresponding n-alkanes. Also the desorption profiles are similar to the profiles found for the n-alkanes, a two step desorption profile for 1-hexene and 1-heptene while 1-pentene and 1-octene desorb in a single step. Hence, it can be concluded that also linear alkenes with chainlengths matching to the length of the zig-zag channel can be commensurately frozen in these channels. However, the temperature difference between the two desorption peaks of 1-hexene is smaller than for n-hexane leading to a less pronounced two step desorption profile. In figure 3, the desorption of n-hexane, 1-hexene and 1,5-hexadiene is compared.
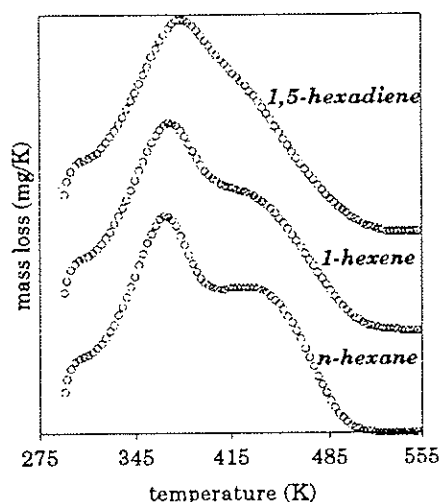

Figure 3. Differential mass loss of n-hexane, 1-hexene and 1,5-hexadiene from silicalite.

The figure shows that for 1,5-hexadiene the two step desorption profile is even less pronounced than for 1-hexene. Since the energetic interaction between the adsorbed hydrocarbons and the all-silica lattice of silicalite is only determined by dispersive interactions, the energetic interaction with the silicalite lattice will decrease from n-hexane via 1-hexene to 1,5-hexadiene [9]. The decrease in energetic interaction causes a significant shift of the second desorption peak to lower temperatures. Besides a decrease in the energetic interaction with the lattice, the chainlength will decrease and the rigidity of the chain will increase from n-hexane to 1,5-hexadiene. This results in a smaller entropy loss when the molecules get commensurately frozen in the zig-zag channels and, therefore, in a

lower gain of entropy upon desorption. At high loadings, the net result of the lower energetic interaction with the lattice and the smaller entropy loss when the molecules become frozen in the zig-zag channels is a first desorption peak of 1,5-hexadiene which is shifted to slightly higher temperatures compared to n-hexane. Also for 1-heptene, a smaller temperature difference between the two desorption peaks (125 K) is found than for n-heptane.

3.3. Variation of adsorption temperature

The equilibrium loadings of n-hexane and n-heptane on silicalite at different temperatures are given in table 3. The loadings are expressed in mmol of adsorbate and as mmol of carbon to make a comparison of the loading of the two adsorbates at different temperatures possible.

Table 3
Equilibrium loading of n-hexane and n-heptane at different temperatures

	n-hexane (mmol/g)	n-hexane (mmol C/g)	n-heptane (mmol/g)	n-heptane (mmol C/g)
298 K	1.4	8.2	1.2	8.3
323 K	1.3	8.0	1.0	7.0
348 K	1.2	7.2	0.86	6.0
373 K	0.97	5.8	0.79	5.5
398 K	0.78	4.7	0.74	5.2
423 K	0.65	3.9	0.66	4.6

The loading of silicalite with n-heptane is slightly higher than the n-hexane loading at 298 K. In contrast, the loading with n-heptane becomes lower than the n-hexane loading at higher adsorption temperatures. Increasing the adsorption temperature means that commensurate freezing of n-hexane and n-heptane becomes more difficult. Therefore, it will be impossible to overcome the additional loss of entropy accompanying the commensurate freezing at higher temperatures. Due to the larger loss of entropy of n-heptane, freezing of n-heptane in the zig-zag channels becomes at lower temperatures (compared to n-hexane) impossible which results in a less efficient packing.

The n-heptane loading becomes again higher than the loading with n-hexane at 398 K. This implies that at 398 K also commensurate freezing of n-hexane is not possible anymore. We can compare this result with the calculated adsorption isotherm of n-hexane at 398 K [1]. According to this isotherm, a n-hexane pressure of 3 to 7 kPa is needed for commensurate freezing at this temperature. This is in agreement with the absence of commensurate freezing of n-hexane at this temperature and the experimentally used n-hexane pressure (maximal 4 kPa).

4. CONCLUSIONS

The presented temperature programmed desorption results show that besides the heat of adsorption, also the entropy of adsorption can play an important role in the filling of zeolites. The desorption profiles give evidence for the occurrence of commensurate freezing of hydrocarbons in the zig-zag channels of silicalite. In full agreement with the computational results, the freezing behaviour is only found for molecules which just fit in the zig-zag channels. For longer and shorter hydrocarbons this behaviour is not found.

The temperature difference between the two desorption peaks is smaller for linear alkenes than for the corresponding n-alkanes. This is caused by the lower energetic interaction of the alkene molecules with the silicalite lattice as a result of the lower adsorbate molecular weight.

The equilibrium loadings of n-hexane and n-heptane at different temperatures confirm the results obtained by temperature programmed desorption. At temperatures between 323 and 398 K, commensurate freezing of n-hexane is still possible at the used experimental conditions while freezing of n-heptane is not possible anymore. At higher temperatures, freezing of both n-hexane and n-heptane is impossible which agrees again with the computational results.

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