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Effect of Chain Length on the Adsorption Behavior of *n*-Alkanes in Ferrierite

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Zeolites are microporous crystalline materials that are used as catalysts in petrochemical applications because of their acidity and stability.[1] At present there are more than a hundred types of zeolites, each with characteristic pore sizes and pore topologies. One important aim of zeolite science is to use these differences to tune the selectivity of a given reaction.[2] To arrive at a rational design, it is essential to have an understanding on the molecular level of the behavior of the sorbates in the pores of these zeolites.[3] Currently such information is mainly obtained from computer simulations. For example, recent Monte Carlo calculations have allowed many predictions to be made about the behavior of *n*-alkanes in zeolites,[4–8] in particular regarding the preferential adsorption sites of *n*-alkanes in zeolites. To the best of our knowledge, none of these predictions have been confirmed experimentally, since direct information on the siting of *n*-alkanes is difficult to obtain.

Here we present work on the siting of *n*-alkanes in the zeolite ferrierite (FER). FER has ten-ring channels which are interconnected by cages with eight-ring windows. The use of this zeolite as an isomerization catalyst for the production of isobutene, an intermediate in the production of methyl *tert*-butyl ether (MTBE, considered to be an environmentally beneficial fuel), has been studied extensively.[9,10] The comparison of the performance of FER and other zeolites as catalysts for the isomerization of *n*-butene has been mainly focused on the dimensions of the ten-ring channels.[9] We now find that the characteristic pore topology is an important factor as well. One of the questions still open pertains to the distribution of the molecules over these ten- and eight-ring channels.

To study this distribution, we investigated the siting of *n*-alkanes in FER by means of Monte Carlo simulations and ^{13}C NMR spectroscopy. For the simulations we assumed that the zeolite is rigid, and the *n*-alkanes were modeled with a united atom representation; that is, CH_3 and CH_2 groups are considered as "united atoms". Fixed bond lengths, bond angles, and torsion potentials were used.[11] Details on the simulation techniques have already been described.[5,12] The results of Monte Carlo simulations (Figure 1) indicate a surprising effect of the chain length. *n*-Alkanes with more than five carbon atoms prefer the ten-ring channels for all loadings; these molecules are too large to fit into the eight-ring channels. At low loadings propane and butane are distributed over the ten-ring and eight-ring channels. While propane prefers adsorption in the eight-ring channel, butane adsorbs preferentially in the ten-ring channel. The adsorption of pentane is at low loading limited to the ten-ring channel, and adsorption in the eight-ring channel occurs only at higher loadings. These simulations show that the adsorption behavior of even simple *n*-alkanes is quite complex and depends strongly on the chain length. One of the purposes of the present work was to present experimental evidence that the above prediction is indeed correct.

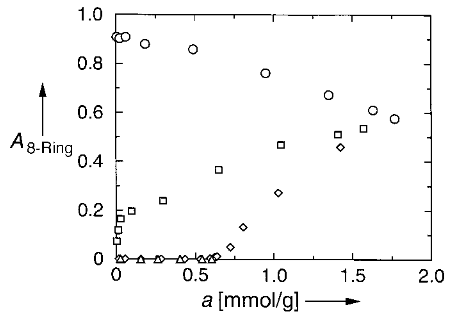

Figure 1. Fraction $A_{8\text{-Ring}}$ of the molecules adsorbed in the eight-ring channels as a function of the loading *a*. The data were obtained from computer simulations with the configurational-bias Monte Carlo method at 333 K. ○ propane, □ butane, ◇ pentane, △ hexane.

An obvious experimental technique to investigate the siting of hydrocarbons in zeolites is ^{13}C NMR spectroscopy. The chemical shifts of *n*-alkanes depend on the local environment

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of the carbon atoms, and one would therefore observe different sets of signals depending on whether the *n*-alkane molecules are adsorbed in the eight-ring or ten-ring channels. To unambiguously assign the NMR signals, we used zeolite ZSM-22 as a reference. Since ZSM-22 has only ten-ring channels similar to those in FER, the NMR spectra of molecules adsorbed in the ten-ring channels of FER will be similar to those obtained in ZSM-22. A vacuum system with a calibrated volume was used to prepare the samples for the ^{13}C NMR measurements. A glass tube with a small capsule containing the sample (15 to 30 mg) was connected to this system. After dehydration by evacuation ($p < 10^{-4}$ kPa) at 773 K for FER and 723 K for ZSM-22 for at least one hour, a certain amount of hydrocarbon was brought into contact with the sample. After adsorption, the sample was cooled in liquid nitrogen, and the capsule closed by melting. This capsule was placed into a magic angle spinning (MAS) rotor (diameter 7 mm) and used in the measurements on a Bruker MSL 400 spectrometer at 9.4 T and room temperature. The MAS spinning rate was 2500 Hz, and cross polarization was performed with a contact time of 1 ms and a repetition time of 5 s. The number of scans accumulated was dependent on the loading of the *n*-alkane. H-FER with a Si/Al ratio of 9 was provided by the Shell Research and Technology Center, Amsterdam. The NaZSM-22 sample with a Si/Al ratio of 35 was donated by Exxon Chemical Europe Inc. (Machelen, Belgium).

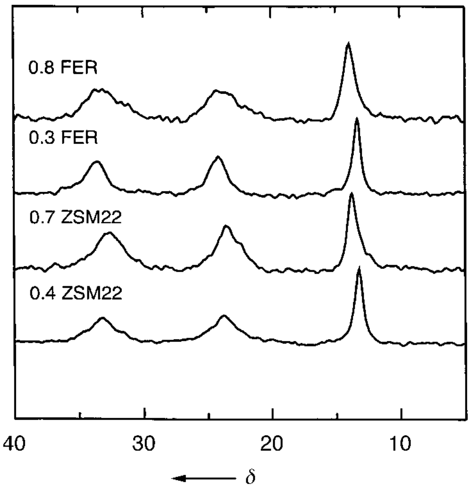

Figure 2. ^{13}C NMR spectra of hexane in ZSM-22 and in FER at different loadings (indicated in mmol g^{-1}).

Figure 2 shows the spectra of hexane in FER and in ZSM-22 at various loadings; the similarity between the spectra is striking. Hexane is too large to fit in the eight-ring channels, and therefore one would expect the spectra to be similar. This indicates that our assumption that ZSM-22 can be used as a reference zeolite is correct.

For pentane we observe (see Figure 3) that at low loadings in FER the spectra are similar to those in ZSM-22, indicating adsorption in the ten-ring channels of FER only. At high loadings, however, additional peaks appear in the spectra in FER that are not present in the spectrum of ZSM-22. This shows that at high loadings the molecules also adsorb in the eight-ring channels. In the case of butane there is adsorption in both the eight- and ten-ring channels at all loadings. For propane we find very different spectra in ZSM-22 and in FER at low loadings, but at high loadings an additional peak appears in the spectrum in FER at a similar position as the peaks in the spectrum in ZSM-22. This implies that at low loadings the propane molecules adsorb in the eight-ring channels and at high loadings also in the ten-ring channels. This behavior of the *n*-alkanes in FER is exactly what has been predicted based on the computer simulations. In addition, these observations are consistent with the pore volumes occupied by the different *n*-alkanes (Table 1). Table 1 shows that the longer molecules, such as hexane and heptane, occupy significantly less of the FER pore volume than the shorter *n*-alkanes. This observation can be explained by noting that both the NMR spectra and the simulations indicate that hexane and the longer *n*-alkanes do not adsorb in the eight-ring channels.

The implications of our results for the isomerization of *n*-butene in FER are interesting. One of the most striking features of FER as a successful catalyst for the isomerization of *n*-butene to isobutene is the low yield of long-chain molecules,[9] which is required to obtain a high selectivity for the desired isobutene. A surprising observation is that this suppression of the production of long-chain molecules only

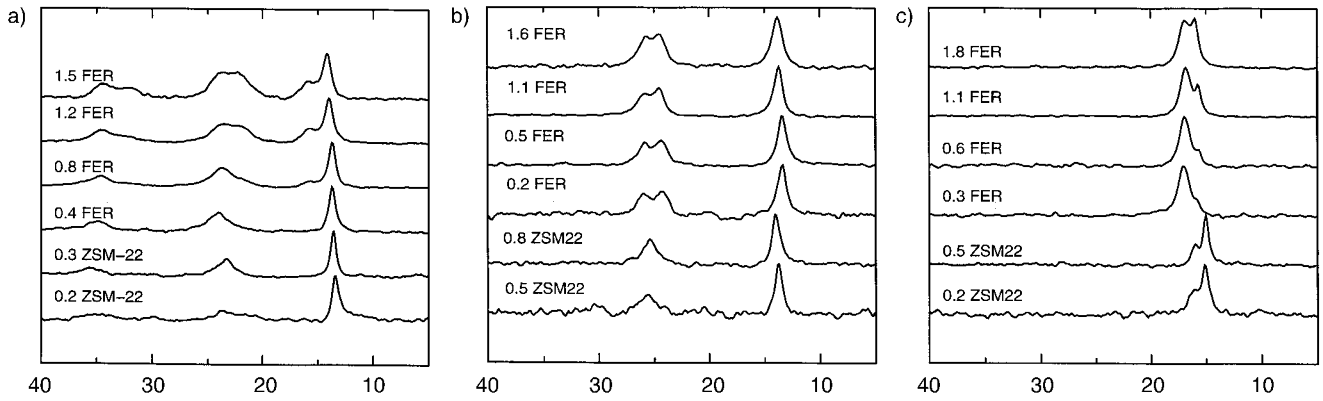

Figure 3. ^{13}C NMR spectra of a) pentane, b) butane, and c) propane in ZSM-22 and in FER at different loadings (indicated in mmol g^{-1}).

Table 1. Pore volume occupied by the different *n*-alkanes at 293 K.[a]

	propane	butane	pentane	hexane	heptane
V_{ads} [mL g^{-1}]	0.15	0.16	0.17	0.10	0.10

[a] The values were calculated by using the density of the liquid *n*-alkane at 293 K relative to that of water at 277 K. A Setaram TG-DSC 111 instrument operating under a helium flow of about 3.8 L h^{-1} was used in these adsorption experiments. The FER samples were dehydrated at 723 K for 10 min. After cooling, adsorption was performed by either saturating 20% of the helium flow with the liquid *n*-alkanes or by replacing 20% of the helium flow by the gaseous *n*-alkanes. This means that the adsorption pressure of the liquid *n*-alkanes was 20% of the saturation pressure, while the propane and butane pressure was 20 kPa.

occurs after the formation of coke residues in the FER pores.[9,10,13] The results presented here imply that FER behaves as a one-dimensional pore system for long-chain molecules, while its full two-dimensional pore system can be exploited only by the shorter molecules. Pore blocking due to the formation of coke will therefore have a large inhibiting effect on the movements of the long-chain molecules, which are limited by one-dimensional (single-file) diffusion; the movements of shorter molecules are far less restricted. The resulting long residence time of the long-chain molecules causes them to crack. The combination of ten-ring channels with intersecting eight-ring channels, from which the longer molecules are excluded, is a unique feature of the FER pore structure. The results presented provide an excellent demonstration of the importance of understanding adsorption effects in zeolites for predicting differences in catalytic performance of zeolites.

Received: November 11, 1997 [Z 11139IE]
German version: *Angew. Chem.* **1998**, *110*, 1142–1144

Keywords: alkanes · heterogeneous catalysis · molecular modeling · NMR spectroscopy · zeolites

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The First Delocalized Phosphole Containing a Planar Tricoordinate Phosphorus Atom: 1-[Bis(trimethylsilyl)methyl]-3,5-bis-(trimethylsilyl)-1,2,4-triphosphole**

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The generally accepted view that phospholes are not aromatic[1, 2] must now be revised in light of the first example of a fully delocalized 1,2,4-triphosphole containing a planar tricoordinate phosphorus atom, which is described here. Theoretical calculations predict that a planar phosphole would be strongly aromatic,[3, 4] and that planarity can be achieved by partial[5, 6] or full replacement[6–8] of CH groups by dicoordinate phosphorus atoms in the five-membered phosphole ring. Both the sum of the bond angles (342°)[9] and the complexing behavior[10, 11] of the recently described 1-[bis(trimethylsilyl)methyl]-3,5-di-*tert*-butyl-1,2,4-triphosphole (**1**), indeed show the expected increase in the planarity of the tricoordinate phosphorus atom and the enhanced aromaticity of the ring system. Likewise, the incorporation of bulky substituents[12–15] at the tricoordinate phosphorus atom of a phosphole resulted in characteristic changes both in the photoelectron spectrum[16] and in the chemical reactivity,[15] providing the first example of a phosphole that undergoes electrophilic substitution. Schmidpeter et al. recently reported phospholes substituted by electron-withdrawing cationic moieties,[17, 18] which exhibited NMR spectroscopic characteristics[17] or structural features (sum of bond angles at the tricoordinate phosphorus atom 338°),[18] which is in accordance with partial flattening of the phosphorus pyramid. However, a totally planar phosphole which would lead to full aromaticity has not been previously achieved.

Treatment of the recently reported[19] 3,5-bis(trimethylsilyl)-1,2,4-triphospholide anion (**2**) with $(SiMe_3)_2CHBr$ in 1,2-dimethoxyethane (DME) readily affords yellow 1-[bis(trimethylsilyl)methyl]-3,5-bis(trimethylsilyl)-1,2,4- triphosphole [**3**, Eq. (a)]. As anticipated, the compound exhibits a molecular ion at *m/z* 422 in the mass spectrum, four expected resonances in the ^{1}H NMR spectrum, and three resonances in the ratio 2:1:1 in the ^{29}Si NMR spectrum. The $^{31}P\{^1H\}$ NMR spectrum of **3**, however, is completely different from that of the corresponding 1,2,4-triphosphole **1**.[9] Whereas the latter

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[**] Financial support from EPSRC, the British Council and DAAD, the Royal Society, and OTKA (T 014555) is gratefully acknowledged.