

Sorption and activation of hydrocarbons by molecular sieves

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Substantial progress has been made recently in the understanding of sorption and activation of alkanes. This progress reflects the emergence of new theoretical and experimental results, leading to a more quantitative picture of the elementary steps involved in the ordering of alkanes in molecular sieves and their chemical interaction with the acid site. Conversion of *n*-alkanes over various zeolites is now well understood to depend mainly upon the concentration of reactants sorbed. The sorption enthalpy and entropy of these molecules are linearly related and this relationship is characteristic of a particular molecular sieve (compensation effect). The interfacial chemistry that alkanes and alkenes undergo involves ionic species only in their transition state, whereas the stable intermediates are covalently bound. This leads to a description of the chemical transformations that resemble nucleophilic and electrophilic substitutions.

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Introduction

The important role of zeolite based catalysts in many petroleum related processes has always led to significant academic and industrial research efforts. The elementary understanding of the underlying surface/pore chemistry in these materials had to rely for a long time exclusively on conclusions drawn from interpreting reaction product patterns and relatively simplistic theoretical calculations. Most notably, our understanding of these elementary reactions has seen new impulses over the past five years, resulting from markedly improved tools for experimental and theoretical studies. These recent advances have led to a remarkably detailed knowledge of the elementary steps in alkane or alkene conversion, which surely will be used in turn to design new zeolite based catalysts and processes.

While consolidation is observed, the results and discussions still retain a certain controversy. Thus, substantial further progress can be expected over the following years. We will treat here the contributions seen in the past 18 months, regarding the first steps involved in the process of catalytic chemistry, being those of sorption of hydrocarbons and proton transfer. Only a few catalytic reactions will be discussed in order to show support or disagreement with models proposed but an exhaustive

report of the reactions and catalyst performance is not attempted.

Adsorption of hydrocarbons

Structural and energetic aspects of alkane adsorption

It is commonly accepted that alkanes are primarily bound by dispersive interactions to the molecular sieve walls, independently of the presence or absence of Brønsted or Lewis acids sites (see for example [1•]). These dispersive interactions lead to a generally weak perturbation of the alkane C–H bonds; the perturbation has been experimentally observed by IR spectroscopy [2•,3].

The energy of interaction (e.g. represented by the heat of adsorption) between alkanes and molecular sieves increases with the number of carbon atoms of the adsorbate. For molecular sieves that constrain molecule–molecule interactions, this increase is a linear function of the number of carbon atoms, for alkanes with similar structure (e.g. 2-methyl pentane and 2-methyl hexane). During the review period three groups have independently reported an increase in the heat of adsorption for *n*-alkanes [1•,2•,4•]. The stronger heat of adsorption is always accompanied by a lower entropy in the sorbed state, indicating a marked compensation effect exists [2•,4•]. The increase in the heat of adsorption with increasing carbon number does not depend upon the presence of acid sites in the zeolite (as seen in the comparison of the heats of sorption on silicalite and H-MFI [3,5]), underlining the relatively low importance of acid sites for the overall energetics of sorption.

The observed heat of adsorption of a particular hydrocarbon and the increase of the heat of sorption per carbon atom depends upon the nature of the zeolite. For *n*-alkanes it rises with increasing framework density. When correlating this increase to the minimum pore radius of the molecular sieve main channels [3], however, it seems to increase first with decreasing minimum pore radius and then to fall again at 0.4 and 0.5 nm minimum pore diameter, that is, as the pores become too small and repulsive forces (less favourable intermolecular potential) dominate [6]. This is well documented by configurational biased Monte Carlo simulations for all silica zeolites such as MFI, MOR, FAU, RHO, LTA, and FER [1•,6]. Experimentally, values of the heat of adsorption of approximately 6 kJ mol⁻¹ per carbon atom for FAU and 10 kJ mol⁻¹ for H-MFI were reported. The theoretically predicted and the measured values are generally in good agreement [2•,4•,6].

The correlations seem to be simplistic, as they do not account for the location and conformation of the alkanes in

the zeolites. Close inspection of these factors for n-hexane in the small pore zeolites RHO and LTA reveals that the molecule adopts highly coiled conformations localized in regions of maximum void volume. In the case of RHO and LTA [5,6] these maximum void volumes are the α cages (≈ 1 nm diameter) and, thus, the alkane experiences a larger pore diameter, a situation similar to sorption in larger channels. If the location and conformation are taken into account a simpler inverse relation between pore diameter and heat of adsorption is found [5,6] resembling the correlation seen with the molecular sieve framework density [3].

The situation becomes even more complex for molecular sieves containing a larger main channel which has smaller side pockets or connecting channels, such as in mordenite. Alkanes, with the exception of methane, do not enter the side pockets of mordenite [2*,3,7] and, thus, do not utilize approximately two thirds of the acid sites located there.

Localized sorption on acid sites is energetically preferred as is seen by IR spectroscopy [2*]. The interaction between the apolar alkane and the zeolite Brønsted acid site occurs via dipole-induced hydrogen bonding that contributes an almost constant energy, independent of the number of alkane carbon atoms. This hydrogen bonding involves the induction of polarity in the alkane by the proton of the hydroxyl group in the zeolite. This interaction increases with the polarizability of the C-H bond and the acid strength of the bridging hydroxyl group and this is manifested by increasing perturbations of the OH stretching frequency as the size of the alkane increases [2*]. The contribution of these variations to the overall sorption enthalpy are, however, very small (≈ 1 kJ mol⁻¹). Interactions between molecules may lead to a further stabilization, whenever the pores or cavities are large enough to accommodate more than one molecule, as can be seen from the increase of enthalpy of sorption with loading (concentration of alkanes per unit volume) for FAU and AFI structures [3]. Intermolecular interactions, however, also seem to play a role in the adsorption of alkanes in the pores of an all-silica MFI. Heats of adsorption for the n-alkanes and single branched alkanes (2-methyl or 3-methylpentane) were independent of the coverage, but for 2,2-dimethylpentane, methyl cyclopentane and cyclohexane, heats of adsorption increased with coverage [8]. This suggests that only these bulkier molecules populate the channel intersection and hence are able to interact. Support for this interpretation is obtained by earlier molecular modeling [9]. It is interesting to note that Eder [2*] found evidence for adlineation of two n-alkanes (not for iso-alkanes) at the acid site of MFI which is only likely to occur at the intersection of the MFI channels.

Comparison of the data in [9] and [2*] indicates, that molecules that interact such that the heat of adsorption increases do not share the same acid site. Due to the

spacial constraints, an increase in the heat of adsorption by such interactions can therefore only be expected in cage/intersection-containing microporous structures. The second conclusion to be extracted from the work of June *et al.* [9] is that, for a given molecular size, the rigidity of the sorbate lowers the heat of sorption. The absolute values have to be interpreted cautiously, as the trend in the heat of adsorption, that is, the trend that a branched alkane has a lower heat of adsorption than a linear alkane, reverses in the case of large pore zeolites [3], leaving the branched alkane to be more strongly adsorbed.

The chemical composition of molecular sieves has been assumed to strongly influence their interaction with alkanes (for discussion see [2*], references [4*,5,7] and [10]). In contrast, Eder and Lercher [11*] showed unequivocally for an aluminum phosphate and an all-silica form of the AFI structure that the different chemical composition and, thus, the different polarity of the lattice did not influence the sorption enthalpies and entropies of alkanes.

Highly ordered structures of alkanes in zeolites have now been demonstrated for at least two molecular sieves, MFI and FER. It was first predicted theoretically by Smit and Maesen [12*], and was subsequently verified experimentally by Elder [3] and van Well *et al.* [13]. Experimental evidence (a kink or step in the adsorption isotherm) indicates that ordering occurs at a loading when intermolecular repulsion becomes critical, that is, when the physical presence of one molecule at a particular position hinders the adsorption of another. It is, thus, confined to molecules that match the microdimensions of (intersecting) channel structures. With MFI, the most pronounced ordering occurred for hexane and heptane, while it was butane and pentane with FER [3,12*]. For molecules with a smaller size, ordering does not lead to an improved packing (so that a higher volume of sorbate can be accommodated); for larger molecules it does not help to avoid mutual sorption constraints exerted by the sorbate (leading to a lower total uptake).

Effects of the adsorption upon the kinetics for alkane conversion

Two reports demonstrate independently that the rate of cracking of alkanes is primarily governed by adsorption of the alkane. For light n-alkanes Narbeshuber *et al.* [14*] showed that the decrease in the apparent activation energy of protolytic cracking with increasing alkane chain length was compensated for by an increase in the heat of adsorption, resulting in a constant true energy of activation, independent of the carbon chain length. Thus, the higher reactivity of larger hydrocarbons is due to their higher abundance in the molecular sieve pores and not to their intrinsically higher reactivity. Wei [4*] shows that increasing the heat of adsorption with increasing chain length leads to negative apparent activation energies for alkanes larger than n-hexadecane. As this strictly holds only for the protolytic cracking of alkanes, the paper by

Wei also gives first results of monomolecular cracking for alkanes as large as hexadecane.

Activation of alkanes by proton transfer or hydride abstraction

Activation of alkanes to carbonium (addition of a proton) or carbenium ions (hydride abstraction) is strongly endothermic. Thus, the concentration of carbocations in molecular sieve pores will be low under all practical conditions. Actually, the main question arising is if these carbocations only exist as transition states.

All theoretical studies addressing this problem use model clusters that simulate the bridging hydroxyl group between a Si-O and an Al-O tetrahedron. Some of these clusters are, however, so large that one could argue that they only reflect particular zeolite structures. Hydrogen (deuterium) exchange between such an acidic cluster and methane (the reversible protonation of methane) occurs via a carbonium ion in the transition state [15], as suggested by the density functional theory [16]. During the exchange a symmetric transfer of the proton from the zeolite and to the methane molecule occurs. Two oxygen atoms of the zeolite (attached to Al) are involved, one in accepting the proton (acting as a base), the other in donating the proton (acting as an acid) [16]. *Ab initio* calculations by Kramer and van Santen [17] have confirmed this view, reporting the rate of exchange to be determined solely by the difference in acid/base strength between the two oxygen sites involved in the process and not by the intrinsic acidity of the zeolite. Hartree-Fock-type quantum-chemical calculations indicate that the transition states and the surface chemistry of these reactions depend on the sign of the bond polarization [18,19]. Protolytic attack of the C-H bond results in the heterolytic splitting of this bond with abstraction of a hydride ion. The transition state for this reaction step resembles a carbenium ion and the reaction leads to one molecule of hydrogen and the formation of a surface alkoxy group. Only when a proton is split off from the paraffin is hydrogen exchange observed, as discussed above.

Active intermediates and transition states

Carbonium ions

The results from Kazansky *et al.* [18,19] marked a boundary between calculations on the protonated complex and a more complete potential surface in protolytic light alkane cracking. Collins and O'Malley [20,21] suggested that protolysis of alkanes by zeolite Brønsted acid sites occurs via insertion of a hydrogen at or near the centre of a C-C bond. They also demonstrated that the results of theoretical calculations depend subtly upon the method used and the model for the acid site. The resulting carbonium ion is formed directly over the acid site at a significant distance from the zeolite surface. The carbonium ion exists in a highly excited, but stable, ion pair. The collapse of the carbonium ions leads to an alkane

and an alkene (carbenium ion). Note that this contrasts with the model of Lercher *et al.* [22], who proposed that an alkane and a surface alkoxide were formed in that step.

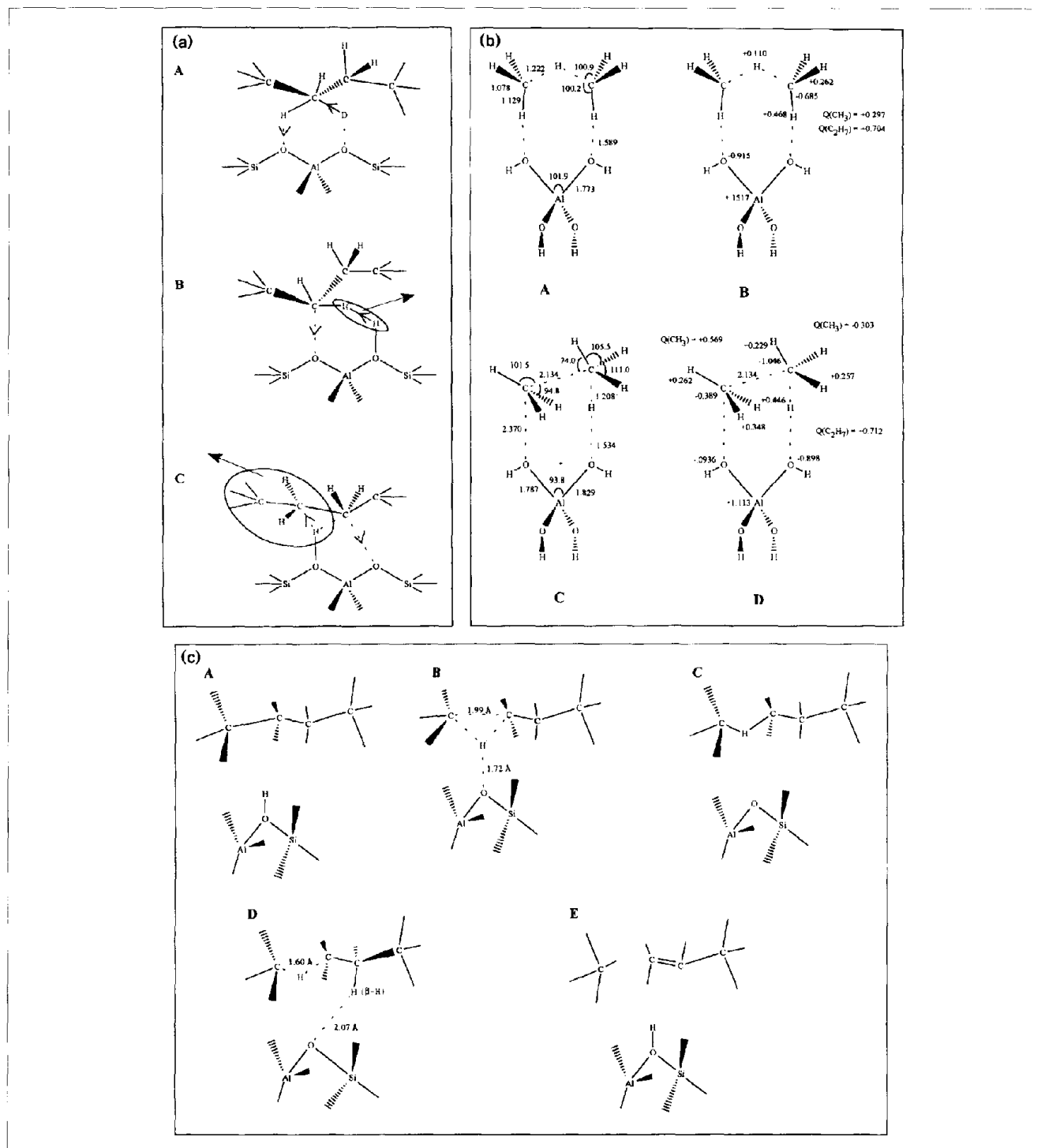
Blaskowski *et al.* [23] took a different view. By means of density functional theory the energy barriers calculated for ethane conversion were 118 kJ mol⁻¹ for hydrogen exchange, 202 kJ mol⁻¹ for hydride transfer, 292 kJ mol⁻¹ for cracking and finally 297 kJ mol⁻¹ for dehydrogenation [14*,24]. Considering the different heats of adsorption, the calculations are in remarkably good agreement with the data of Narbeshuber *et al.* [24] and Lercher *et al.* [22] for hydrogen/deuterium exchange of perdeuterated n-butane. However, the two latter energies of activation (dehydrogenation and cracking) are significantly higher than those reported experimentally. Carbonium or carbenium ions involved in the reactions are claimed to exist only as transition states [18,19,22,25]. In agreement with the previously discussed studies the calculations indicated that the stable species involved in hydrogen exchange were rather covalent in character. The species in the transition state resembled a carbonium ion for the hydrogen exchange reaction and carbenium ions for cracking and dehydrogenation. Similar conclusions with respect to the nature of the carbonium ions were reached by Kazansky [18,19,25], Lercher [22] and their co-workers.

Common to all these models is the fact that alkane activation involves the simultaneous interaction of the alkane with the acid hydroxyl group and a neighboring basic oxygen atom, which finally leads to cleavage of the alkane into a saturated fragment and a covalently bound alkoxide. To show the differences in the various pathways proposed, we compiled three graphic representations in Figure 1. Note that especially models (a) and (b) in Figure 1 suggest carbenium and carbonium ion chemistry in terms of concerted nucleophilic/electrophilic substitutions. Proton accepting and proton donating sites share importance in that scenario.

Carbenium ions

Similar experimental and theoretical approaches as described in the previous section were used to understand the nature of the carbenium ions. Kazansky and co-workers [18,19,26] used diffuse reflectance IR spectroscopy to establish the covalent character of the ground state of the zeolite hydroxyl groups. Interaction of these acidic hydroxyl groups with olefins led to the formation of covalent surface alkoxides. This was in perfect agreement with an earlier review by Farneth and Gorte [27*] on the formation of alkoxy groups by reacting alcohols with zeolite hydroxyl groups using ¹³C NMR spectroscopy. The (adsorbed) carbenium ions are, thus, the energetically excited transition states formed from these covalent precursors. Despite claims that a small fraction of 1-octene adsorbed at ambient temperature on H-MFI exhibits carbenium ion properties, evidence from IR [28] and NMR [29] experiments has shown that the proton was

Figure 1



Models representing the transition states for the conversion of hydrocarbons at the Brønsted hydroxyl group of the zeolite. **(a)** A, H/D exchange; B, butane dehydrogenation (note that the C-C bond stretches and H_2 and σ -bonded carbenium ion is generated); and C, cracking (note that the C-C bond stretches, ethane and σ -bonded carbenium ion is generated). Reproduced with permission from [22]. **(b)** Protolytic cracking of ethane on a high silica zeolite, A, geometry and B, charge distribution, in the most stable adsorbed ethyl carbonium ion, C, geometry and D, charge distribution, in the transition state for protolytic cracking. Reproduced with permission from [18,19]. **(c)** Representation of the collapse of the carbonium ion by protonation of the outer C-C bond in butane. A, alkane situated above the acid site, B, approach of the proton to the C-C bond; C, stable minimum and formation of the carbonium ion; D, collapse of the transition state; and E, olefin production. Restoration of the acid site leads to two of the primary products, methane and propene. Reproduced with permission from [20,21].

transferred from the solid to the sorbate, and yet the alkylsilyl ethers were the most abundant species.

In the framework of such a model the role of the (basic) oxygens surrounding the acid site is significant. Formally, the Brønsted acid part protonates the adsorbed alkene, forming a carbenium ion, whose strong interaction with the neighboring basic oxygen converts it into the more stable covalently bound alkoxy group. As this simultaneous interaction with acid-base pairs strongly depends on their steric arrangement, the dual nature of active sites may cause the manifestation of apparent inhomogeneities in the acid strength. Note that in this context the differences in the acid strength are often related to subtle structural differences in zeolites, which, however, can always be translated to the direct role of the T-O-T bond angle in determining the acid strength of the hydroxyl group.

Apparently controversial spectroscopic evidence for carbenium ions has been claimed by several authors [30–32], who used IR, UV-visible and NMR spectroscopy. This evidence includes studies by Demidov and Davydov [30] and Xu and Haw [31] on the formation of carbocations. The formation of carbocations has been deduced from the appearance of CCC stretching bands at 1490–1530 cm⁻¹ in the IR spectra and bands at 290–310 nm (allyl), 350–380 nm (dienyl) and 430–450 nm (trienyl cations) in UV-visible spectra [30]. *In situ* ¹³C MAS-NMR identified carbocations during the reactions of α -¹³C styrene, [β -¹³C] styrene, and [α -¹³C]- α -methylstyrene on the acidic zeolites H-ZSM-5, HY and H-mordenite. Less sterically constrained molecules seemed not to produce carbenium ions. Neither the methylphenylcarbenium ion (from styrene) nor the dimethylphenylcarbenium ion (from α -methylstyrene) were observed as stable species by NMR [31].

The results indicate that (as in the presence of acid in solutions) larger carbocation species are stable enough over zeolites to be observed using NMR. This evidence for carbenium ions suggests that, depending on the size of the reactant, different states can be observed that resemble either tightly (covalently) bound or weakly bound (ionic) species. In general, it seems that ion pair formation occurs when significant steric constraints prevent tight bonding and/or when stabilization in a conjugated system is possible. In this context it is important to note that carbenium ions (in the specific case from alkylhalides) are seemingly more readily formed on salt structures (e.g. on ZnCl₂ surfaces) than in zeolite pores [32].

Conclusions

The understanding of the adsorption of alkanes and their transformation into carbocations is approaching a level that allows clear predictions with respect to catalyst performance to be made. We have shown that acid sites play a minor role in the adsorption step. The match

between pore structures and the size of the hydrocarbons dominates the adsorption behavior and entropy is seen to play a major role, particularly at higher loadings. The chemistry during the transformation from the alkane to the carbocation involves steps that resemble nucleophilic and electrophilic substitution reactions. For most structures the carbonium and the carbenium ions are only transition states. Only in the case of bulky carbenium ions does steric separation of the carbon atom bearing the positive charge and the basic lattice oxygen seem to allow the existence of stable carbenium ions.

For hydrocarbon catalysis the implication is that we have to consider the lifetime of the ground states, that is, the hydrogen-bonded alkanes (for carbonium ions) and the alkoxy groups (for carbenium ions), when discussing reaction pathways and selectivities of catalysts. In particular, the chemistry of these latter species may involve bimolecular steps that are only beginning to be explored by theoretical calculations and model experiments. Understanding these details will open new routes for catalyst and process design and surely help to overcome some of the bottlenecks currently experienced in hydrocarbon processing.

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