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Room-Temperature Alkane Reactivity in Zeolites: An H/D Exchange Study

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Abstract: As evidenced by H/D exchange with acidic zeolites, isoalkanes react readily at room temperature whereas linear alkanes do not. The observed regioselectivity of the exchange process demonstrates that the main factor controlling the reaction is not the accessibility to the acid sites, but the intrinsic reactivity of the alkane. The mechanism is best rationalized by classic organic chemistry involving carbocationic intermediates including the Markovnikov rule.

Keywords: alkanes • carbocations • isotopic labeling • reaction mechanisms • solid acids

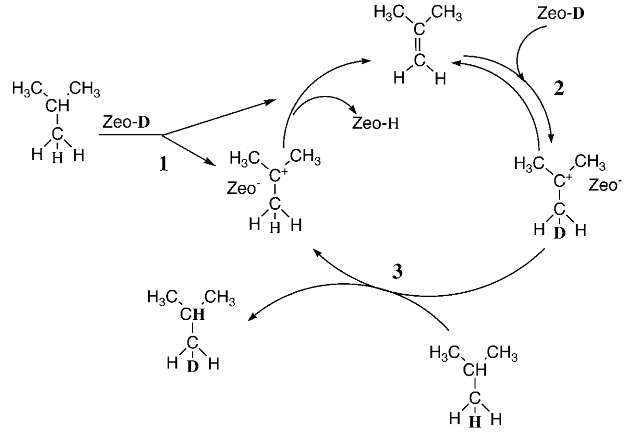
Introduction

The catalytic transformation of alkane C−H and C−C bonds by microporous and mesoporous crystalline solid acids has been industrially exploited in processes such as catalytic cracking, reforming, hydroisomerization, oligomerization, and disproportionation.[1,2] Considering the economic importance of these reactions, a better understanding of the mechanisms should be of interest as it may help to increase selectivity, minimize the formation of unwanted products, and prolong catalyst lifetime.

However, to understand catalytic hydrocarbon conversion over a solid acidic catalyst, we need to focus on generally agreeing on the role of carbocations as intermediates in the process and the lack of experimental information on their mode of formation.[3,4] On the basis of the initial product distribution at high temperature, the Haag–Dessau mechanism[5,6] (σ bond protolysis as in superacids[7–9]) is generally suggested as the first alkane activation step, but hydride abstraction, oxidation, and alkene impurities have also been evoked to account for the formation of the cationic intermediate.[10–12]

Simple carbenium ions are generally considered as transient species (unless they have a large charge delocalization) within the zeolite channels and that the most stable intermediates are the framework-bound alkoxy species.[13–15] The existence of carbenium ions as short-lived reaction intermediates in equilibrium with the alkoxy species is supported by the Koch reaction, the halogen switch reaction,[16–18] single-event microkinetics,[19] and theoretical calculations.[20]

The regioselective H/D exchange that occurs at 150 °C between isoalkanes and acidic silicoaluminates or zeolites has also been rationalized by the existence of carbocationic intermediates (see Scheme 1).[10,21–24] Whereas all the protons of the zeolite can be exchanged by D_2O, as shown by titration experiments, only a very small number of active sites are able to generate a low concentration of carbocations as steady-state reaction intermediates[19]



Scheme 1. H/D exchange via carbocations.

Recently, H/D exchange between perdeuteriated isobutane and the H-ZSM5 zeolite was even observed at room temperature, but a different mechanism was suggested.[22]

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Truitt et al. observed the same regioselective exchange limited to methyl groups, as observed previously at 150 °C,[10,21–24] but suggested that the exchange process at room temperature occurred directly following the model (Scheme 2) proposed earlier for H/D exchange with methane at 400 °C,[23,24] rationalizing the regioselectivity by the easier access of methyl hydrons[25] to the catalyst surface in comparison with the methine hydron.

However, with isobutane it is clear that both direct H/D exchange with the surface (Scheme 2) and indirect exchange via *tert*-butyl carbenium ions (Scheme 1) will lead to the same regioselective exchange on the methyl groups. For this reason, to check whether the mechanism would indeed be different at room temperature, we reinvestigated the hydron exchange that occurs at room temperature between various small alkanes and deuteriated zeolites and herein we describe our results.

Results and Discussion

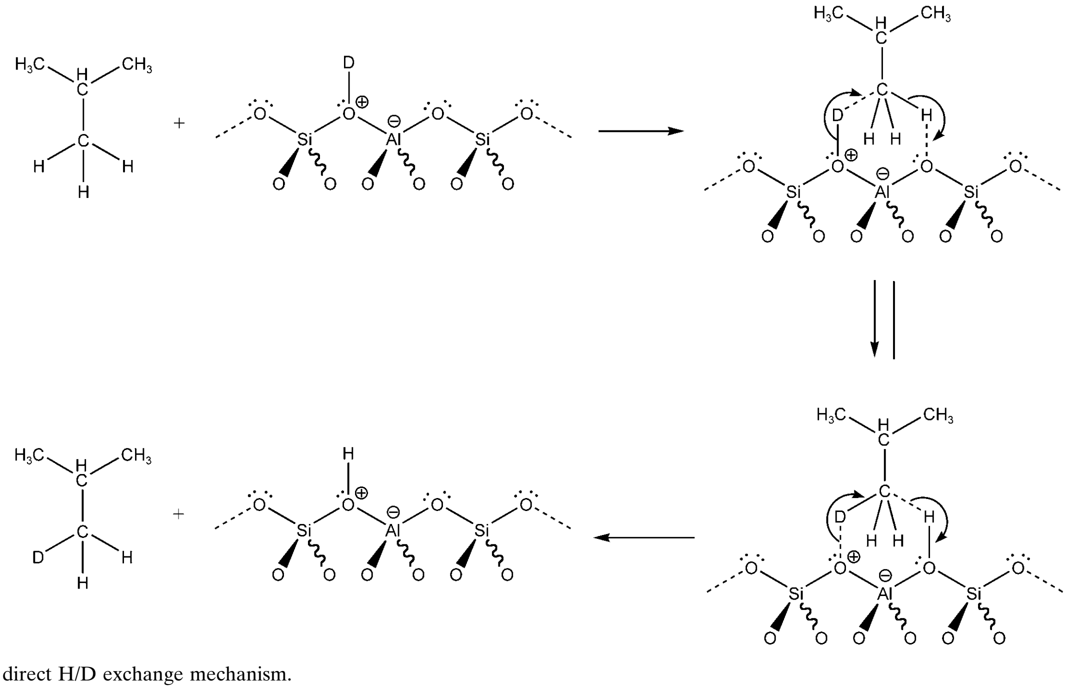
Isotopic-labeling is one of the most efficient tools for gaining an insight into the early interaction between hydrocarbons and acidic catalysts.[26] With this technique, the interaction of hydrocarbons with the acidic protons of the catalyst, which involves fast hydron exchange, can be monitored at an early stage. The regioselective H/D exchange between isobutane and acidic silicoaluminates at 150 °C was first observed as early as 1950 by Hindin et al.[21] using mass spectrometry as the analytical tool. They suggested a mechanism involving a carbocationic intermediate (*tert*-butyl cation), in equilibrium with isobutene, that underwent rapid deprotonation and redeuteriation to give, as expected from the Markovnikov rule,[27] regioselective deuteriation of the methyl groups before hydride transfer from another isobutane molecule induced the desorption. They highlighted the similarity of this process with the regioselective exchange between isobutane and deuteriated sulfuric acid observed the previous year by Otvos and co-workers.[28]

During the last two decades the improvements in high-field multinuclear NMR, MAS-NMR, FTIR, UV/Vis, and MS techniques have facilitated the experimental reinvestigation of H/D exchange between various small alkanes (C_1 to C_7) and deuteriated solid acids. The reaction has been extensively studied with zeolites,[11,29–34] sulfated zirconias,[35–37] and heteropolyacids.[38] The results have consistently shown that, at temperatures around 100–150 °C, hydron exchange occurs readily with branched alkanes whereas linear alkanes are practically unreactive under the same conditions. Independently of the branched alkane and of the acidic catalyst, the exchange takes always place regioselectively at the hydrons vicinal to the branching.

To rationalize the regioselectivity of the exchange process there has been general agreement[11,31,32,34] that with solid acids the mechanism (Scheme 1) is similar to that proposed for the reaction between isobutane and D_2SO_4,[39] that is, the reaction proceeds via carbocationic intermediates.

In contrast, for methane, ethane, or neopentane, in which only primary protons are available, higher temperatures are necessary to observe the exchange process and it was proposed that for these compounds the exchange takes place in a concerted step involving a pentacoordinated carbon as the transition state similar to a carbonium ion, as shown in Scheme 2.[33,24,40–42]

Much experimental work, often associated with theoretical calculations, has been published[24,41–44] in relation to



Scheme 2. The direct H/D exchange mechanism.

linear alkanes with the observation that H/D exchange between these alkanes (which are much less reactive than branched alkanes) and zeolites occurred at higher temperatures (150–500 °C, depending on the alkane and the zeolite). For linear alkanes, which exchange hydrons at temperatures above 150 °C, most probably both mechanisms are involved.

In comparison with isobutane, other alkanes, such as 2-methylpentane, 3-methylpentane, *n*-butane, and *n*-hexane, are better models for studying the regioselectivity of the exchange as the accessibility of the various protons to the acid sites of the surface is quite different. A comparison of ^{1}H,^{1}H-decoupled ^{2}H and ^{13}C NMR spectra, recorded before and after contact of these alkanes with various deuteriated zeolites, provides specific information on the regioselectivity of the exchange process.

For comparison, we have also reinvestigated the exchange that occurs between deuteriated zeolites and isobutane. Our results are collected in Table 1.

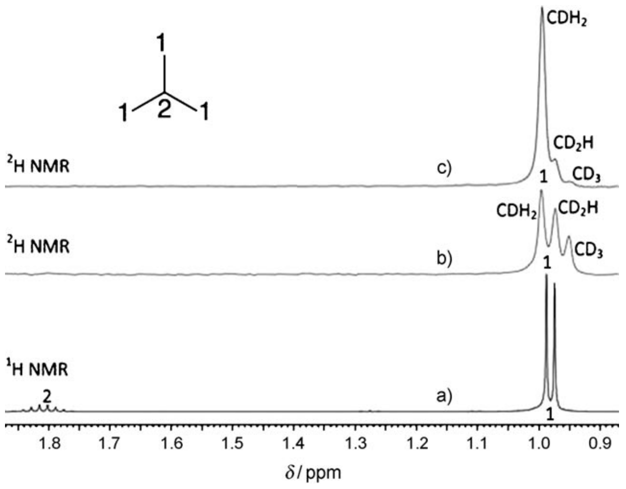
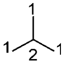
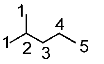
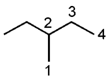
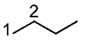
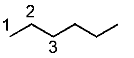
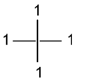


Figure 1. ^{1}H NMR spectrum of isobutane (a) and ^{1}H-decoupled ^{2}H NMR spectra of isobutane after exchange with D-USY at room temperature after 3 h (b) and after 16 h (c).

Table 1. H/D exchange between alkanes and D-zeolites.

Alkane	Entry	Zeolite	Time [h]	% exchange by positions[a,b]				
				1	2	3	4	5
	1	D-USY	3	1.0[a] (28)[b]	–	/	/	/
	2	D-USY	16	3.4 (94)	–	/	/	/
	3	D-USY	3	1.3 (24)	–	2.8 (52)	–	–
	4	D-USY	16	3.7 (69)	–	4.0 (74)	–	–
	5	D-MOR	3	1.7 (45)	–	2.3 (61)	–	–
	6	D-MOR	16	2.4 (63)	–	3.3 (87)	–	–
	7	D-ZSM5	3	0.08 (5.7)	–	0.1 (7.1)	–	–
	8	D-ZSM5	16	0.17 (12)	–	0.2 (14)	–	–
	9	D-USY	3	1.4 (23)	–	1.6 (26)	–	/
	10	D-USY	16	2.0 (29)	–	1.8 (32)	–	/
	11	D-USY	24	–	–	/	/	/
	12	D-USY	24	–	–	–	/	/
	13	D-USY	24	–	/	/	/	/

[a] Atom % for each position. [b] % of statistical distribution.

Exchange between D-USY and isobutane (iB): The expected statistical distribution of deuterium between 125×10^{-3} g of D-USY (titrated as 4×10^{-3} mol acid sites per g) and 1.5×10^{-3} mol of isobutane (nine exchangeable protons) is 3.6 % deuterium. When isobutane (2-methylpropane) was recirculated over a sample of D_2O-exchanged USY at room temperature over 3 h, the ^{1}H-decoupled ^{2}H NMR spectrum of the alkane (Figure 1b) quenched in the recirculation loop revealed a deuterium content of approximately 1.0 % deuteriation of the methyl hydrons (28 % of the statistical distribution, s.d).

Remarkably, as a result of the isotope effect on chemical shifts,[45–47] three isotopologues are observed: Three peaks assigned to CDH_2, CD_2H, and CD_3 can be seen. This nonsequential isotopic enrichment at the initial stage, when the catalyst is still richer in deuterium, has already been described by Hindin et al.[21] and later by Schoofs et al.[34] on the basis of a mass spectral kinetic analysis. This phenomenon probably originates from the slow desorption of adsorbed species relative to the deprotonation/reprotonation process. In contrast, in the case of direct exchange, as with methane or neopentane, the incorporation of deuterium has been shown to be sequential.[33]

When the same experiment was repeated over 16 h, the ^{1}H-decoupled ^{2}H NMR spectrum of the recovered alkane (Figure 1c) showed mostly the monodeuteriated isotopologue with 3.4 % of deuterium in the methyl protons (94 % of the statistical distribution at equilibrium was reached). As a result of the equilibrium associated with such a H/D exchange reaction, the monodeuteriated isotopologue is the major product after a long contact time.

Exchange between D-USY and 2-methylpentane (2MP): The expected statistical distribution (s.d.) of deuterium that results from H/D exchange between 125×10^{-3} g of D-USY and 1.1×10^{-3} mol of 2MP is 5.4 % deuterium in each exchangeable hydron.

When 2-methylpentane was recirculated for 3 h over a sample of D_2O-exchanged USY at room temperature and trapped, the ^{1}H-decoupled ^{2}H NMR spectrum of the alkane (Figure 2b) quenched at the outlet of the reactor revealed

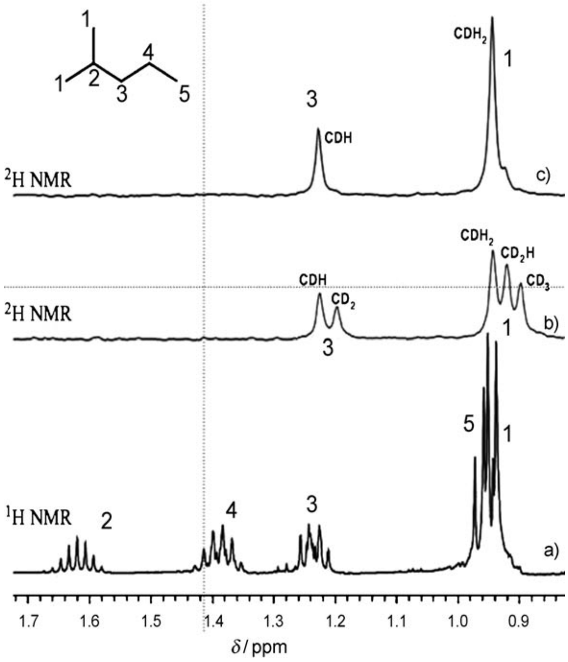


Figure 2. ^{1}H NMR spectrum of 2-methylpentane (a) and ^{1}H-decoupled ^{2}H NMR spectra of 2-methylpentane after exchange with D-USY at room temperature after 3 h (b) and after 16 h (c).

that only hydrons next to the branching carbon were exchanged: 1.3 % of deuterium (24 % of the s.d.) in the methyl groups and 2.8 % of deuterium (52 % of the s.d.) at the α-methylene position (Table 1, entry 3) with a ratio close to 2:6 between the methylene and methyl deuterons. Neither the β-methylene protons nor the more accessible terminal methyl group were involved in the H/D exchange. Again, as a result of the isotope effect on chemical shifts,[47–49] various isotopologues are observed in the early stages of the exchange process: Three peaks assigned to CDH_2, CD_2H, and CD_3 for the methyl group and two peaks assigned to CDH and CD_2 for the α-methylene group (Figure 2b).

When the same experiment was repeated over 16 h, the ^{1}H-decoupled ^{2}H NMR spectrum of the alkane (Figure 2c) showed a large excess of the monodeuteriated isotopologue: CDH_2 (3.7 % of deuterium, i.e., 69 % of the s.d.) and CDH (4.0 % of deuterium, i.e., 74 % of the s.d.) lines resulting from deuteriation at the carbon atoms C-1 and C-3, respectively. No deuteriation was observed either in the β-methylene nor in the more accessible terminal methyl group.[50] Although the ratio of the methylene/methyl deuterons was close to 2:6, we observed that, in general, the deuteriation content in the methylene group was nevertheless slightly higher than in the methyl groups.

This also supports the participation of alkene intermediates in the mechanism as the Saytzev rule[27] favors the more branched alkene 2-methyl-2-pentene over 2-methyl-1-pentene.

These experiments were repeated with other deuteriated zeolites such as Mordenite and MFI and the same regioselective exchange was observed.

Similarly to the H/D exchange between isobutane and zeolite D-USY, we observed a nonsequential exchange. Furthermore, by changing the zeolite from D-USY to D-MOR and D-ZSM5, we have shown that the nonsequential exchange is enhanced in the latter. In full agreement with the adsorption data published by Lercher and co-workers,[41,42] higher adsorption (and desorption) energies for D-MOR and D-ZSM5 may lead to a situation in which the statistical distribution of deuterium is essentially not reached because the desorption rate is limited by the high energy required for this step.

Exchange between D-USY and 3-methylpentane (3MP): Under the same conditions, 3MP exchanged its diastereotopic protons located on the C-3 atom and the methyl protons next to the branching. The external methyl groups remained unchanged (Figure 3), in full agreement with the suggested mechanism.

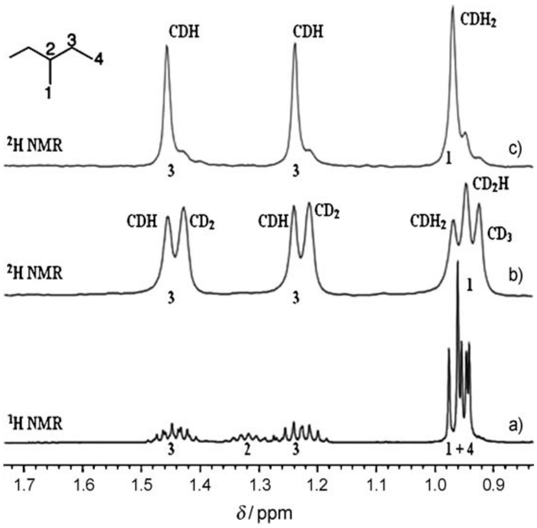
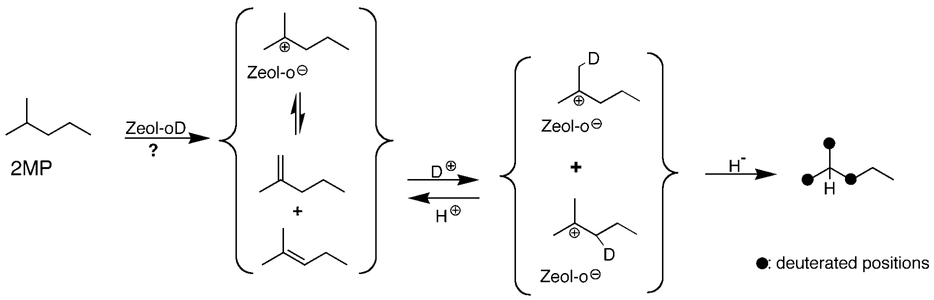


Figure 3. ^{1}H NMR spectrum of 3-methylpentane (a) and ^{1}H-decoupled ^{2}H NMR spectra of 3-methylpentane after exchange with D-USY at room temperature after 3 h (b) and after 16 h (c).

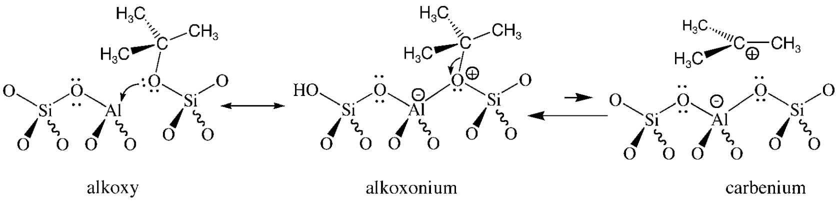
Exchange between D-USY and *n*-butane (*n*B) or *n*-hexane (*n*H): Recently, Stepanov[44] showed that in the presence of H-ZSM5, deuteriated *n*-butane starts exchanging its hydrons at 150 °C. However, as expected as a result of the absence of reactive tertiary hydrogen atoms, neither *n*B nor *n*H showed any reactivity at room temperature even after 24 h of contact with D-USY.

These data are in accordance with the suggestion that at room temperature the mechanism for the H/D exchange between isoalkanes and zeolites is the same as the mechanistic interpretation published earlier for this reaction at 100–150 °C.[10,32,37,49] The exchange takes place exclusively with the hydrons next to the tertiary center, as suggested in Scheme 3.

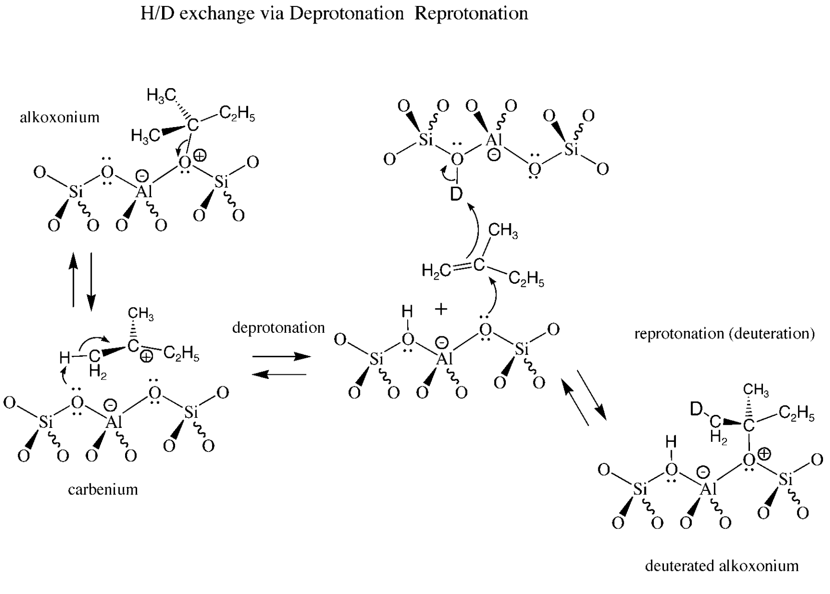


Scheme 3. H/D exchange scheme for 2MP.

The exact nature of the intermediates (carbenium or oxonium ions) is difficult to determine experimentally (Scheme 4). As in any solvent, carbenium ions are not free but solvated. In zeolites, the most stable species is the so-called alkoxy species, which is a resonance form of the oxonium ion. In the zeolitic-confined environment, concerted steps are most probably involved, as suggested in Scheme 5. Tertiary hydride transfer from another alkane to the deuteriated cation occurs before desorption of the regioselectively deuteriated alkane.



Scheme 4. Equilibrium between alkoxy species and carbenium ions.



Scheme 5. H/D exchange by deprotonation/reprotonation.

Conclusion

The results reported herein show that H/D exchange at room temperature between isobutane (or any other isoalkane) and zeolites is better related to the reactivity of the isoalkane than to the accessibility of the protons at the surface of the solid acid. Although the observation of the initial formation of a weak hydrogen bond between the alkane and the zeolite is supported by various techniques, the exchange process between isoalkanes and acidic zeolites is best rationalized by the involvement of adsorbed carbenium ions, in equilibrium with the corresponding olefin, in a fast protonation/deprotonation process before desorption by hydride transfer. However, those alkanes that cannot give an olefin by deprotonation, for example, methane, ethane, and neopentane, undergo direct H/D exchange with solid acids, albeit at much higher temperatures, by a concerted mechanism in which the transition state resembles that of a two-electron–three-center carbonium ion.

For linear alkanes, which exchange hydrons at temperatures above 150 °C, both mechanisms most probably are involved.

The fundamental question that still needs to be answered is “How can tertiary alkanes (so-called isoparaffins), which are known to be quite unreactive, be activated by solid acids at such low temperatures?”. Certainly more experimental and theoretical work will be necessary to solve this conundrum.

Experimental Section

Materials and sample preparation: Zeolites: FAU (USY, Si/Al = 2.8; CBV500), MFI (Si/Al = 15; CBV3024E), and MOR (Si/Al = 10.3; CBV20A) were obtained from Zeolyst International in the NH_4^+ form and activated at 550 °C over 4 h. The number of exchangeable hydrons was determined by using a method based on H/D exchange between D_2O and catalysts.[49,50] *n*-Butane (99.95 %, Alphagaz), isobutane (99.95 %, Air Products), 2-methylpentane (99 % +, Alfa

Aesar), 3-methylpentane (99 % +, Acros), and *n*-hexane (99 % +, Aldrich) were checked by GC and used without further purification.

General experimental procedures: Catalytic reactions were performed in an all-glass grease-free batch recirculation reactor at atmospheric pressure. About 125 mg of USY, MOR, and MFI zeolites were first activated at 550 °C under air for 4 h. Then the temperature was lowered to 200 °C and a flow of dry N_2 (40 $mL\,min^{-1}$) containing 3 mol % D_2O was passed for 1 h over the samples followed by a N_2 purge for 30 min. The reactor was then cooled to room temperature and the alkane (ca. 150 μL, 1.1 mmol in the case of 2MP, 145 μL, 1.1 mmol of 3MP, 143 μL, 1.1 mmol of *n*-hexane, 34 mL (gas), 1.5 mmol of isobutene, and 6 % butane in N_2) was introduced into the recirculation loop. The amount of protons provided by the hydrocarbon was in large excess compared with the acid deuterons because the concentrations of the D_2O-exchanged acid sites at 200 °C, as determined by the NMR method,[49,50] were found to be 4.4, 1.9, and 1.0 $mmol\,H^+\,g^{-1}$ for USY, MOR, and ZSM5, respectively. The gas-phase mixture (hydrocarbon and nitrogen) was circulated by a membrane pump at a recirculation rate of 20 $mL\,min^{-1}$. After a given amount of time the alkane was collected in a precooled U-tube (ethanol/liquid nitrogen) and transferred to an NMR tube using $CF_2ClCFCl_2$ as the solvent containing a known mixture of $CDCl_3$ and $CHCl_3$ used as an internal quantitative standard.

NMR analyses: ^1H, ^2H, (^1H-decoupled) ^2H, and ^{13}C NMR spectra were recorded on an AV 500 Bruker spectrometer with a 5 mm $^2H/^1H$ probe and fluorine lock. Spectra were recorded with 32 scans and a 90° pulse over a range of 8.5 ppm. Spectra were acquired with 4K real data and a 3.1 s acquisition time. Proton broad-band decoupling was achieved by using a WALTZ64 sequence. The temperature was controlled at 298 K for all the samples and the data was processed with line-broadening of 0.25 Hz. Free induction decays (FID) were recorded in quantitative mode with a 30° flip angle preparation pulse and around 4 and 3 s recycle delays for ^1H and ^2H NMR spectroscopy, respectively. The ^{13}C NMR spectra were recorded over a bandwidth of 100 ppm and were proton-decoupled using a WALTZ64 sequence. 64K real data points were acquired with a 30° pulse, a 2.6 s acquisition time, and 0.5 s relaxation delay. $CDCl_3$ was used as the internal reference.

Acknowledgements

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[47] The ^{1}H-decoupled ^{13}C NMR spectrum of this sample also indicates that only the partially deuteriated C-1 and C-3 show the α-deuterium isotope effect, whereas C-2 and C-4 experience a β-deuterium isotope effect with there being no observable effect on C-5 (see the Supporting Information).

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