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Low-Temperature Alkane C–H Bond Activation by Zeolites: An In Situ Solid-State NMR H/D Exchange Study for a Carbenium Concerto

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Abstract: Isotopic H/D exchange has been monitored by in situ MAS NMR spectroscopy of 2-[D_{14}]methylpentane with H-USY to probe the controversy over the alkane conversion mechanism. The probe molecule has distinct exchangeable sites with different accessibility to the zeolite surface. In the early stages of the process, the regioselectivity of exchange demonstrates that the slow step of the mechanism is controlled by a carbenium ion intermediate. At a later stage of exchange, intramolecular hydride migrations, typical of carbenium chemistry, replace D by H also on other carbon atoms, resulting in a loss of regioselectivity. Therefore, the first and the subsequent steps of the H/D exchange proceed at this temperature through a carbenium intermediate species.

Keywords: activation energy · C–H activation · kinetics · NMR spectroscopy · regioselectivity

Introduction

For the twenty-first century, high efficiency oil conversion and petrochemical processes will be a central issue together with the control and distribution of other energy sources. To reach high conversion performances, zeolites are key materials because their properties can be tuned either by selecting their pore size and their internal shape or by modifying their Brønsted and Lewis acidity essential for the chemical reactivity.[1] C–H bond activation over zeolites is the primary chemical process of the catalytic isomerization and cracking of alkanes.[2,3] Only liquid superacids[4] are known to activate saturated hydrocarbons at room temperature and well below in relation to the σ-basicity of C–H and C–C bonds.[5,6] If carbocations are generally accepted as reaction intermediates in acid-catalyzed hydrocarbon reactions, their mode of formation and their true nature are still a matter of controversy.[7] Whereas the number of Brønsted acid sites of a catalyst can be measured with a good accuracy by various techniques,[8] the heterogeneity of their environment and strength have been demonstrated by experiment and theory.[9] The carbocation intermediates are generally present at very low concentration[10] and thus are difficult to directly detect and observe. We have recently shown[11] that these intermediates are active even at room temperature with zeolites, which substantially facilitates their study. One of the most efficient methods to investigate the reactivity of the alkanes with solid acid catalysts is the isotopic H/D exchange.[12–15] Time-resolved in situ spectroscopic studies provide a complete picture of the overall operative system, and operates in realistic experimental conditions.[14,16–18] In the case of isobutane, in contact with various solid acids at 150 °C, various authors proposed a mechanism based on carbenium ion intermediates,[19–23] similar to that occurring in concentrated sulfuric acid.[24,25] Recently, an alternative mechanism, for the same reaction but at room temperature, based on a carbonium ion type complex at the surface of the zeolite was published.[26] The authors explained the regioselectivity of the exchange as being due to steric hindrance and site accessibility in a confined environment and further supported their conclusion by a theoretical study.[27] Additional theoretical studies have appeared since then[28,29,39,40] and have evaluated both approaches, showing that if the carbonium mechanism is the simplest to model, the carbenium one exhibits probably the lowest activation energy. To gauge in more detail the conversion mechanism of alkanes on zeolites, we carried out an in situ solid-state NMR spectroscopic investigation of the H/D exchange be-

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tween H-USY zeolite and 2-[D_{14}]methylpentane ([D_{14}]2MP) containing various exchangeable sites with different degrees of accessibility.

Results and Discussion

The ^{1}H MAS NMR spectrum (not shown) of the zeolite USY after subsequent activation at approximately 250 °C for 2 h under vacuum and prior to adsorption of any hydrocarbon exhibits three poorly resolved broad signals at $\delta = 1.6$, 2.7–2.8, and 4.4–5.0 ppm, respectively, assigned to the silanol group Si**OH** and Brønsted protons SiO**H**Al in large cavities, and SiO**H**Al in hexagonal prism units, respectively.[30,31] After adsorption of 4 μL of [D_{14}]2MP on 50 mg of USY zeolite at 298 K, ^{1}H MAS NMR spectra recorded at various times (Supporting Information) show the broad proton signals of the zeolite, the intensities of which decrease progressively with reaction time, and meanwhile, two narrow signals at $\delta = 0.7$ and 1.0 ppm from protons on methyl and methylene at the C3-position, respectively, continuously increase in intensity, as a direct consequence of H/D exchange between the zeolite and the alkane. The regioselectivity of the H/D exchange in 2MP was further checked by means of ^{13}C NMR spectroscopy offering a much better spectral resolution than ^{1}H NMR spectroscopy especially for the methyl signals C1/C5 (Figure 1). Indeed, from ^{1}H NMR alone it was not possible to conclude firmly whether besides the methylene group at the C3-position ($\delta = 1.0$ ppm), only methyl groups at position C1 and not those in position C5 ($\delta = 0.7$ ppm) were involved in the H/D exchange. Nevertheless, it was clear from the ^{1}H NMR spectra that no exchange occurred either in the methylene group C4 ($\delta = 1.2$ ppm), nor in the methine group C2 ($\delta = 1.5$ ppm; see the Supporting Information). A ^{13}C{^{1}H} DEPT-45 (distortionless enhancement by polarization transfer) spectrum, in which the polarization transfer from protons to carbon occurs through scalar coupling $^1J_{C-H}$ allows the assignment of carbon sites and, therefore, their attached protons. The ^{13}C{^{1}H} DEPT-45 spectrum of the nondeuteriated, fully protonated 2MP (Figure 1c) exhibits five singlet resonances at $\delta = 14$, 21, 23, 28, and 42 ppm with a respective relative signal area of (2.8):(2.0):(6.0):(1.1):(2.1). Assignment of these resonances to C5, C4, C1, C2, and C3, respectively, is based upon the correspondence of the relative ratio of protons bound to these carbon atoms, that is, 3:2:6:1:2, with the corresponding signal area proportions. This indicates that the INEPT (insensitive nuclei enhanced by polarization transfer) transfer occurred with similar efficiency on all carbon atoms in the 2MP molecule. The ^{13}C{^{1}H} DEPT-45 spectrum of USY adsorbed with [D_{14}]2MP (Figure 1b) after one month of contact time, displays only resonances of C1 and C3, definitely confirming that the H/D exchange with the zeolite involved only deuterons at the methyl position C1 and methylene position C3. The small but significant shifts of the C1 peak, observed between spectra of neat 2MP and adsorbed 2MP on the USY zeolite is due to differences in local interactions of the hydrocarbon molecule between the liquid bulk state and the solid surface adsorbed state. Finally, the high-power decoupled ^{13}C{^{1}H} spectrum (Figure 1a) of the same sample of Figure 1b shows the five separate resonances with scalar coupling J_{C-D} patterns of carbon with their deuterium attached. From the decomposition of the Figure 1b spectrum (Supporting Information), the H/D isotopomers distribution with at least one H is obtained showing an exact statistical isotopic distribution of exchanged protons on C1 and C3 of 6:2.

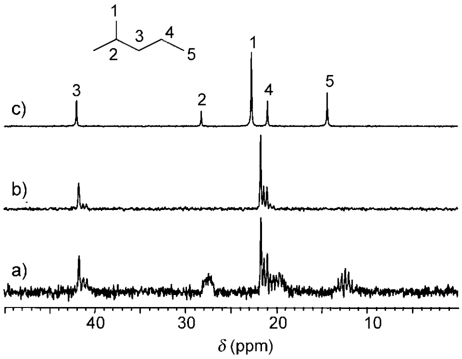


Figure 1. ^{13}C{^{1}H} MAS spectra with a) high-power decoupling and b) DEPT-45 detections of adsorbed [D_{14}]2MP on USY zeolite and equilibrated for approximately one week at 298 K. For comparison, the ^{13}C{^{1}H} DEPT-45 spectrum of neat fully protonated 2MP is shown in c).

At slightly higher temperatures, the previous regioselectivity of the H/D exchange observed at room temperature is preserved only during the early stages of the process (Figure 2). When [D_{14}]2MP was exposed to the surface of H-USY zeolite for 1 h at 318 K, only NMR spectroscopic signals of protons on C1 and C3 carbon atoms were observed, as shown in Figure 2a. For longer contact times, an additional signal at approximately $\delta = 1.2$ ppm corresponding to protons on C4 began to appear, and a significant amount of protons at this position was recorded after 8 h at 318 K (Figure 2b). When the rotor was cooled down and left

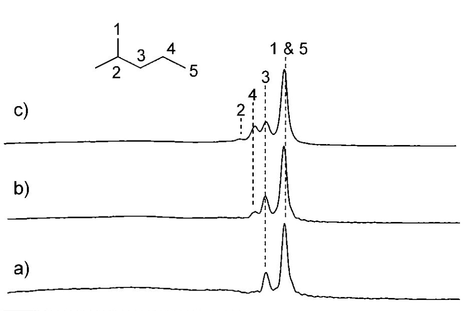


Figure 2. ^{1}H MAS spectra of adsorbed [D_{14}]2MP on USY zeolite recorded a) at 318 K after 1 h, b) after 8 h of contact time at this temperature, and c) after one month equilibrating at room temperature subsequent to heating at 318 K for 8 h.

sealed for one month at room temperature, the NMR spectrum showed a further increase of this signal with an appearance of a fourth resonance at approximately $\delta = 1.5$ ppm due to protons present in methine at the C2 position. At this stage of the reaction, the protons were redistributed almost statistically on all possible positions of the hydrocarbon. This result is different from the previous observations reported for the same reaction at room temperature, which showed an exclusive proton exchange even for long contact times (over a period of one month) on carbon atoms C1 and C3. Thus, it is clear that besides the H/D exchange observed at room temperature another process takes place when the temperature increases from 298 to 318 K.

The time dependence of the NMR spectroscopic signal area as a function of temperature in the 298–318 K range, resulting from H/D exchange kinetics, as well as the corresponding Arrhenius plots are shown in Figure 3. The H/D exchange rate constants were obtained by fitting the experimental points by using a zero-order kinetics model. The values obtained for rate constants and activation energies are summarized in Table 1. The kinetics of the H/D exchange process were measured in two distinct ways: from the progressive protonation/dedeuteration of the hydrocarbon represented by Figure 3a through the ^{1}H NMR spectroscopic signal gain and from the continuous deprotonation/deuteration of the solid acid surface represented by Figure 3b through the ^{1}H NMR spectroscopic signal loss. Although this offers two independent kinetics measurements for the same process, the hydrocarbon observation provides higher data reliability with its much narrower signals relative to the broad signals of the solid. The H/D exchange rate constants measured at C1 and C3 positions were found to be always comparable (see Table 1), and an average value could, therefore, be obtained as presented in Figure 3a. The situation is, however, different for the apparent H/D exchange in C4 at 318 K arising from H/D isotopic scrambling, which showed a 2.5 times slower rate relative to what was observed in C1 and C3. When the catalyst signal is used for measurements, by taking the variation of the sum of all broad signals with time as presented in Figure 3b, a good estimation of the exchange rate constants is obtained, of the same order of magnitude to what was obtained when measuring the hydrocarbon signals (see Table 1).

Table 1. Rate constants from calculated kinetics curves of H/D exchange between [D$_{14}$]2MP and H-USY zeolite observed on C1, C3, and C4 positions of the 2MP molecule, overall 2MP molecule, and USY zeolite and their corresponding activation energies.

	$k_{H/D}$ [10^{-3} h^{-1}] 298 K	308 K	318 K	E_a [kJ.mol^{-1}]
C1	77 ± 2[a]	174 ± 2[a]	405 ± 5[a]	66 ± 2
C3	106 ± 5[a]	135 ± 4[a]	390 ± 5[a]	50 ± 17
C4	–[b]	–[b]	156 ± 15[a]	–[c]
2MP (ΣCn)[d]	83 ± 1[a]	164 ± 1[a]	363 ± 4[a]	58 ± 3
USY[d]	78 ± 23[e]	165 ± 15[e]	484 ± 31[e]	76 ± 7

[a] By using the zero-order kinetics model for the rising NMR spectroscopic signal as follows: $I(t) = I\infty(1-\exp(-(t+t_0)k_{H/D})$ for which $I(t)$ is the observed intensity at time t, $I\infty$ the intensity at the equilibrium, t_0 the time compensating the delay between the start of the experiment and the effective start of the H/D exchange, and $k_{H/D}$ the H/D exchange rate constant. [b] H/D exchange not observed. [c] Not enough data points. [d] Results of curves in Figure 3. [e] By using the zero-order kinetics model for the decaying NMR spectroscopic signal as follows: $I(t) = I_0\exp(-(t+t_0)k_{H/D}) + I\infty$ for which $I(t)$ is the observed intensity at time t, $I\infty$ the intensity at the equilibrium, t_0 the time compensating the delay between the start of the experiment and the effective start of the H/D exchange, and I_0 is the intensity at time $t = t_0$.

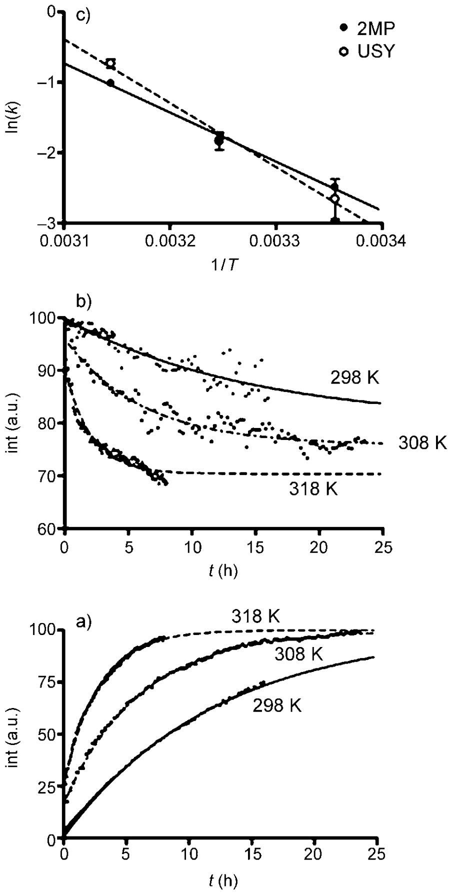
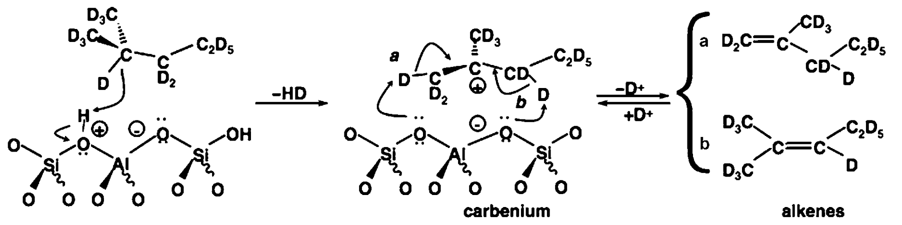


Figure 3. Time-dependence ^{1}H NMR spectroscopic signal area of a) the 2MP molecule and b) the USY zeolite as a function of temperature after adsorption of [D$_{14}$]2MP on USY zeolite. The corresponding Arrhenius plots obtained with the 2MP molecule and USY zeolite signals, respectively, are shown in c).

The H/D exchange reaction between perdeuterated 2MP and acidic USY zeolite occurs exclusively on carbon atoms C1 and C3 of the hydrocarbon. This regioselectivity proves a carbenium ion driven mechanism, with an elimination–addition process governed by the most stable trivalent carbocation. During the initiation step of this mechanism some carbenium ions need to be generated, by which the H/D exchange reaction is further driven. Scheme 1 shows the most probable mechanism leading to such a surface-stabilized carbocation. In this scheme, a direct protonation approach similar to the nonclassical carbonium chemistry is proposed to protonate the deuteron in the methine position in a concerted way to produce, after departure of molecular HD,[32] the most stable tertiary carbocation adsorbed on the nearest Si–

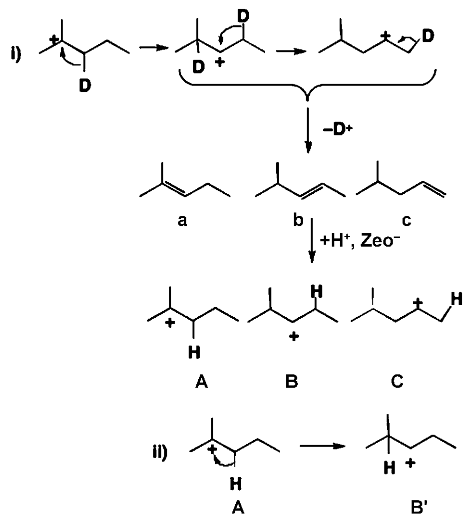


Scheme 1. Proposed mechanism of the initiation step, the formation of surface-adsorbed-alkene intermediates involved in the H/D exchange between $[D_{14}]$2MP and acidic USY zeolite.

O–Al site. Some other possibilities for the initiation step may be invoked. Though, as only a small amount of cations is needed to initiate the H/D exchange, it will be very challenging to measure accurately the amount of species involved in the initiation step. The key step for the regioselective H/D exchange on carbon positions directly adjacent to the carbocation center is the formation of alkene intermediates, as often suggested earlier, similar to H/D exchange between isobutane and sulfuric acid.[25] Through the dedeuteration–reprotonation process, the surface-adsorbed carbocation will be in equilibrium with two isomeric alkenes: 2-methyl 1-pentene and 2-methyl 2-pentene. Reprotonation, after subsequent adsorption of the alkene intermediates on available protonic Brønsted acid sites by following the Markovnikov rule, leads to the regioselective introduction of H at positions 1 and 3 of the most stable trivalent carbocation, which is further stabilized in an alkoxy-like form. Desorption takes place through a surface-concerted intermolecular deuteron transfer when an incoming reactant molecule is present in the vicinity leading to a new adsorbed tertiary trivalent cation on a neighboring site, which reinitiates the propagation of the H/D exchange between hydrocarbon and catalyst.[22]

The H/D exchange of 2MP with the USY zeolite involves only protons on the carbon atoms adjacent to the tertiary carbon atom, independent of the accessibility of the sites. The regiospecificity of the H/D exchange at positions C1 and C3 can only be explained with alkene-type intermediates reprotonated according to Markovnikov's rule.[33] Therefore, the room-temperature reactivity of 2MP appears essentially ruled by a carbenium intermediate limiting step. Hydrocarbon activation by a direct protium exchange through the most accessible sites, has been proposed recently.[26,27] This argument cannot capture the present observations on 2MP. Actually, a direct H/D exchange would involve a pentacoordinated carbonium ion, at room temperature, similar to the reaction with methane, obtained at higher temperatures.[34,35] The most accessible sites are not all favored for the H/D exchange, since position C5 is not exchanged at all under these conditions. The contrast between C1 and C5 shows that accessibility is not the dominant factor in the activation energy. Therefore, with almost identical activation energies one can assign safely to protonation of olefins most of the activation energy. Moreover, the exchange rates and activation energy at position C1 compares very well to the sterically less-favorable site C3. Furthermore, the activation energies were found to be in the range of 50–76 $kJ\,mol^{-1}$. These values are close to the H/D exchange reaction between the isobutane molecule on the methyl position and H-ZSM5 (50 $kJ\,mol^{-1}$),[13,36] much closer than to the value for the methane and H-Beta reaction (138 $kJ\,mol^{-1}$).[37] The difference of 88 $kJ\,mol^{-1}$ between methane and isobutane has been imputed to the difference in chemical pathways with these respective molecules for which the former favors carbonium chemistry and the latter carbenium chemistry.

Besides the primary H/D exchange process that takes place at the early stage at room temperature, which is rate limited by a carbenium species, other isotopic exchange routes occur at moderately higher temperatures leading to the progressive H/D isotopic scrambling. As illustrated in Scheme 2, this has been rationalized through successive intramolecular deuteride migration on the vacant cationic site leading to a charge delocalization progressively from the tertiary carbon C2 to the secondary carbon atom C3 and then to carbon C4. The resulting secondary carbocations are known to be less stable than the tertiary one, but the slight increase in temperature could be enough to populate some of the less-stable species. Additionally, with increasing temperature, the activation energy needed for vicinal deuteron shift and stabilization of the adsorbed secondary trivalent cations can be passed, allowing such chemical transformations to occur, which could not be observed at room temperature, even at very long contact times. These secondary per-



Scheme 2. Isotopic H/D scrambling successively on C3, C4, C5, and C2 positions of the $[D_{14}]$2MP molecule.

deuterated cationic intermediates lead each to the corresponding isomeric perdeuterated alkenes, first 2-methyl 2-pentene (**a**) and 2-methyl 3-pentene (**b**), and later to 2-methyl 4-pentene (**c**). Reprotonation of these intermediates by the H-Zeolite by following Markovnikov's rule will generate cations **A**, **B**, and **C** leading to the introduction of hydrogen atoms, first on C3 and C4 and later on C5. This process leads to all C sites of the 2MP molecule being exchanged with the exception of the C2 position. In principle, based on the present carbenium-type mechanism, no H/D exchange between the zeolite and the hydrocarbon at this position should occur. However, cation **A**, once exchanged with the zeolite, can undergo an intramolecular hydride migration from C3 to C2 leading to cation **B′** rationalizing the observed H/D exchange at this position. Because this last exchange needs to have a C3 proton exchanging first, it is therefore expected to be observed that the C2 position is the last "exchanged" site. Though scrambling through protonated cyclopropane could also take into account the hydride transfer, ^{13}C exchange would be revealed if this is or is not the case. In a previous study,[17] it has been shown that the ^{13}C scrambling, and therefore the hydride transfer through protonated cyclopropane, occurs only at a higher temperature, and has not, therefore, been considered at this temperature.

Conclusion

In this work, in situ ^{1}H and ^{13}C solid-state NMR spectroscopy was used to study the H/D exchange reaction between [D$_{14}$]2MP and H-USY zeolite. Combining the results of previous studies[11,32] and the actual ones we can draw the following conclusions. The first step[32] of the mechanism is most probably controlled by some very acidic sites of the zeolite, probably of superacid strength. These sites are not more than a few fractions of a percent of the total amount of acidic sites and imply the formation of a carbonium and dehydrogenation leading to a subsequent formation of a carbenium species. To reach the conclusion that the critical intermediates are carbenium ions for the subsequent steps, the use of 2MP for the in situ H/D exchange was essential to lift the ambiguity associated to isobutane, which is too symmetrical, as demonstrated recently.[11] It is, therefore, demonstrated that carbenium is the intermediate entity controlling the rate-determining step. The activation energy found in this study is comparable to the isobutane H/D exchange found in Truitt et al. studies[26,38] on H-Beta or HZSM5. It can be certainly inferred from this value, that in the case of isobutane too, for both the zeolites considered, the carbenium ion controls this mechanism. Besides the primary H/D exchange, isotopic H/D scrambling phenomenon through successive intramolecular deuteride (hydride) shifts takes over for the remaining evolution of the H/D exchange, even with a slightly increasing temperature or time of reaction. Regiospecificity of the H/D exchange is, therefore, lost progressively with reaction time, until a statistical redistribution of H/D isotopes on all carbon sites of the molecule is reached. These deuteride/hydride shifts are also typical of carbocation chemistry. The activation energy of the two processes are sufficiently different, to be separated at room temperature, but are much less differentiated at 308 and 318 K. Furthermore, once some scrambling reaction has taken place, it keeps running slowly at room temperature.

The method presented here for studying the H/D exchange, is a decisive episode in a series of movements of opposition and cooperation of different approaches intending to describe the mechanism of alkane conversion. The successive reactions, implying carbenium ions in some form of concerto, acting progressively to rearrange the C–H bonds is the first part of hydrocarbon conversion. The second part has been addressed in a former contribution in which the C–C bonds are at their turn involved, and are well separated from the C–H bond reorganization.[17] With a global picture of the catalytic steps clarified, more efficient hydrocarbon conversion is within reach.

Experimental Section

Samples preparation: USY (Si:Al = 11) sample and [D$_{14}$]2MP (99 % D) were obtained from Zeolyst and CDN Isotopes, respectively. The zeolite sample was prepared by air calcination from the ammonium form in a ceramic reactor body at 550 °C/4 h with a temperature increase rate of 2.5 °C min^{-1}. Brønsted acid site concentration was measured to be equal to 4.33 mmol g^{-1} by using the titration method.[8] Each time, the catalyst was activated directly in the NMR rotor before hydrocarbon adsorption with the help of a homemade experimental setup for NMR sample preparation under a controlled atmosphere.

NMR spectroscopic experiments: All NMR spectroscopic experiments were conducted under MAS by using a 200 MHz NMR spectrometer equipped with a TecMag Apollo console. ^{1}H and ^{13}C NMR spectra were recorded at a Larmor frequency of 200.1 and 50.3 MHz with a spinning rate of 10 and 5 kHz, respectively. For both nuclei, chemical shifts were referenced to tetramethylsilane (TMS) at $\delta = 0.0$ ppm. A Hahn echo sequence was used for ^{1}H NMR spectra with a delay between the 90 and 180° pulses of 100 μs, synchronized to a one rotor period. Typically, a recycle delay of 7.4 s, acquisition time of 0.1 s, and radiofrequency field of 104 kHz were used. Under these experimental conditions all measurements were quantitative, as based on preliminary T_1 relaxation times saturation-recovery experiments. The H/D exchange kinetics experiments were recorded within a temperature range of 298–318 K along a period ranging from ca. 8 to 24 h, depending on the temperature. ^{13}C{^{1}H} MAS spectra were obtained either with a high-power decoupling (hpdec) Bloch decay sequence or through the INEPT method by using a DEPT-45 sequence. In the ^{13}C{^{1}H} hpdec MAS experiments, a pulse duration of 1.4 ms corresponding to a flip angle of 45°, a relaxation delay of 15 s, and a number of scan of 57008 was used. In the ^{13}C{^{1}H} INEPT transfer experiments, a INEPT delay ($1/2\,J_{CH}$) of 3 ms, a relaxation delay of 2.5 s, and a number of scan of 24800 was used.

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