

In Situ ^1H and ^{13}C MAS NMR Kinetic Study of the Mechanism of H/D Exchange for Propane on Zeolite H–ZSM-5

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The kinetics of hydrogen (H/D) exchange between Brønsted acid sites of zeolite H–ZSM-5 and variously deuterated propanes (propane- d_8 , propane-1,1,1,3,3,3- d_6 , propane-2,2- d_2) have been monitored in situ by ^1H MAS NMR spectroscopy within the temperature range of 503–556 K. The contribution of intramolecular hydrogen transfer to the H/D exchange in the adsorbed propane was estimated by monitoring the kinetics of ^{13}C -labeled carbon scrambling in propane-2- ^{13}C in situ with ^{13}C MAS NMR at 543–573 K. Possible mechanisms of the exchange have been verified on the basis of the analysis of the variation of protium concentration in both the methyl and the methylene groups of propane in dependence of the reaction time. The main route of the exchange consists of a direct exchange of the acidic OH groups of the zeolite with either the methyl groups or the methylene group presumably with a pentacoordinated carbonium ion intermediate. The assumption that the intramolecular H scrambling between the methyl groups and the methylene group of propane via carbenium-ion-type intermediates is the fastest process among the other possible routes (*J. Catal.* **2003**, *215*, 122) does not account for the experimental kinetics of H/D exchange for propanes with different initial contents and locations of deuterium in a propane molecule. The rate constant (k_3) for intramolecular H/D exchange between the methyl and the methylene groups is 4–5 times lower compared to those of the direct exchange of both the methyl (k_1) and the methylene (k_2) groups with Brønsted acid sites of the zeolite, the k_1 being ca. 1.5 times higher than k_2 . At lower temperature (473 K), the exchange is slower, and the expected difference between k_1 and k_2 is more essential, $k_1 = 3k_2$. This accounts for earlier observed regioselectivity of the exchange for propane on H–ZSM-5 at 473 K (*J. Am. Chem. Soc.* **1995**, *117*, 1135). Faster direct exchange with the methyl groups compared to that with the methylene groups was attributed to a possible, more spatial accessibility of the methyl groups for the exchange. Similar activation energies for H and C scramblings with a 2 times more rapid rate of H scrambling was rationalized by the proceeding of these two processes through an isopropyl cation intermediate, as in classical carbenium ion chemistry.

Introduction

Chemical transformations of inert alkanes in the presence of solid acid catalysts,¹ such as cracking, isomerization, alkylation, and aromatization, follow the activation of their C–H bonds by the catalyst.² The hydrogen exchange between the alkane molecule and the Brønsted acid sites of the solid acid catalyst,³ which can be monitored by the use of isotopic labeling, provides valuable information about the mechanism of alkane activation and the involved reaction intermediates. Despite numerous experimental^{13–19} and theoretical^{13,20–23} studies of the hydrogen (H/D) exchange for alkanes, the mechanism of the exchange is still debatable. It seems for small alkanes with one and two carbon atoms (methane, ethane) that the H/D exchange proceeds via a simple proton transfer between alkane and an acidic surface proton in a concerted step with a carbonium ion (pentacoordinated carbon atom) intermediate, where the exchanging hydrogen atoms are halfway between a carbon atom of the alkane and an acidic oxygen atom of the catalyst.^{13,14,16,17,22} For alkanes with three or more carbon atoms, an alternative path for the H/D exchange exists, which includes a trivalent carbenium ion

intermediate. The exchange occurs in this case between the acidic hydroxyl groups of the catalyst and the alkene, which is in equilibrium with the corresponding carbenium ion. As a result, a significant regioselectivity (only methyl hydrogens are exchanged) for the H/D exchange is observed.^{6,7} Regioselectivity was clearly demonstrated for isobutane on different solid acid catalysts.^{4,6,7,15,16}

Regioselectivity of the exchange for propane on sulfated zirconia (SZ) was also demonstrated by Haouas et al.^{18,19} At low temperature (323 K), only the methyl groups of propane are involved in the exchange. At higher temperatures, both the methyl and methylene groups of propane exchange hydrogen atoms. However, the rate of the H/D exchange in the methyl groups is essentially higher compared to that for the methylene group. It has been concluded that the regioselectivity of the exchange is determined by the isopropyl cation and propene intermediates, which are in equilibrium with each other, whereas the exchange in the methylene group occurs via intramolecular H scrambling between the methylene and the methyl group mainly via hydride (deuteride) shifts in the isomeric propylum ions.

The H/D exchange in propane on zeolite ZSM-5 requires higher temperatures (423–573 K) in contrast to that on SZ and

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exhibits no evident regioselectivity.^{11,18} Two controversial rationalizations of the mechanism have been discussed. Stepanov et al.¹¹ have found that the apparent rates of H/D exchange are similar for both groups of propane. Therefore, it was concluded that both methyl and methylene groups independently exchanged with acidic OH groups of the zeolite by pentacoordinated carbonium ion intermediates. Haouas et al.¹⁸ assumed that the mechanism of the exchange of propane on ZSM-5 was similar to that on SZ, but the stage of the intramolecular H/D scrambling in propane on zeolite was faster than the regioselective exchange in the methyl groups. This could account for equal rates for the exchange in the methyl and methylene groups observed in propane on ZSM-5¹¹ without assuming a direct exchange between the methylene group and the acidic hydroxyl group.

In this paper, we have performed a detailed analysis of the kinetics of hydrogen exchange between propane and zeolite H-ZSM-5. The use of propane-*d*₈, propane-1,1,1,3,3,3-*d*₆, propane-2,2-*d*₂, and the in situ ¹H MAS NMR spectroscopy provide three dependent kinetics measurements carried out under similar conditions. The contribution of intramolecular hydrogen transfer to the H/D exchange in the adsorbed propane was also estimated by monitoring the kinetics of ¹³C-labeled carbon scrambling in propane-2-¹³C in situ with ¹³C MAS NMR. These measurements made it possible for us to further clarify the mechanism of the exchange.

Experimental Section

Sample Preparation. The zeolite NH₄-ZSM-5 was kindly provided by Tricat Zeolites. The template free synthesized, and more than 99% of ammonium's exchanged form was transferred into the hydrogen form by the activation procedure described below. ²⁹Si MAS NMR spectrum analysis²⁴ gave the silicon-to-aluminum ratio of the hydrated ammonium form as Si/Al = 13.2. The ²⁷Al MAS NMR spectrum has shown that aluminum atoms exist only on framework positions. The quantity of the acidic AlOHSi groups of 1200 μmol g⁻¹, which was estimated by adsorption of a calibrated amount of benzene, was in good accordance with the expected quantity of 1170 μmol g⁻¹ (6.8 groups per unit cell) which was based on the found Si/Al ratio.

Propane-*d*₈ (99.4% D), propane-1,1,1,3,3,3-*d*₆ (99% D), and propane-2,2-*d*₂ (98% D), purchased from Aldrich Chemical Co. Inc., and propane-2-¹³C (99% ¹³C), purchased from ICON Inc., were used without further purification. The samples for NMR measurements were prepared by heating 60 mg of the zeolite sample in the glass tubes of 5.5-mm outer diameter. The samples were activated by an increase of the temperature from 300 to 673 K at the rate of 10 K h⁻¹ under vacuum. Further, the samples were maintained at 673 K for 24 h under vacuum (less than 10⁻² Pa). The loading was performed at room temperature with four molecules of propane per unit cell (ca. 600 μmol/g), and each sample was then sealed off (length of the glass tube = 12 mm). Before NMR measurement started, the NMR probe with the sample was preheated at 453 K for 20 min. The H/D exchange did not occur at this temperature at any notable rate. Then the temperature was rapidly increased within 3–10 min by 50–120 K to the temperature of the exchange measurement and equilibrated for 1–2 min, and the acquisition of the NMR signal started. It should be noted here that the chemical conversion of propane via cracking or dehydrogenation did not occur to a notable degree under conditions of our experiment,²⁵ so the H/D exchange and ¹³C-labeled carbon scrambling were the main transformations of propane.

NMR Measurements. In situ MAS NMR measurements were performed on a Bruker Avance 400 spectrometer at 503–

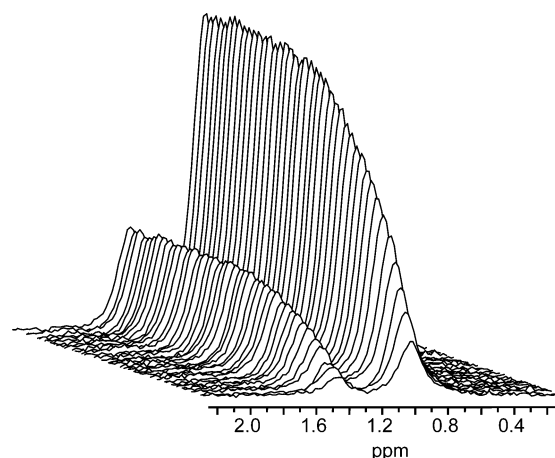


Figure 1. Stack plot of the ¹H MAS NMR spectra at 553 K of propane-*d*₈ adsorbed on H-ZSM-5 in the vicinity of the methyl (1.0 ppm) and the methylene (1.5 ppm) groups. The first spectrum (bottom) was recorded 3 min after the temperature was raised to 553 K. The time between subsequent spectra recording was 1.8 min (spectra 1–22) and 3.6 min (spectra 22–41).

573 K using a high-temperature probe produced by Bruker Biospin GmbH. The rotation frequency of the 7-mm rotor with the inserted sealed glass tube was 3 kHz. ¹H NMR free induction decays (FID) were acquired after 45° preparation pulses of 3.6-μs duration and 25-μs ring down delay. Recycle delays of 4 and 24 scans were used for the accumulation of one spectrum. For ¹³C NMR, free induction decays (FID) were acquired with the 90° flip angle preparation pulses of 3.6-μs duration, 25-μs ring down delay, 6-s recycle delay, and 96 scans for the signal accumulation. Proton high-power decoupling was used during 70 ms of the acquisition time. The interval between two steps in the time scale of the kinetics measurements ranged from 1.8 to 24 min depending on the temperature and the rate of H/D exchange or ¹³C-labeled carbon scrambling. The accuracy of the determination of the relative line position with respect to TMS was 0.05 ppm. The sample temperature was controlled by the Bruker BVT-1000 variable-temperature unit. The temperature calibration in the probe was performed with an accuracy of ±2 K by using lead nitrate, located inside the rotor, as a ²⁰⁷Pb MAS NMR chemical shift thermometer.²⁶

Results and Discussion

H/D Exchange in Deuterated Propane on H-ZSM-5. Figure 1 shows the ¹H MAS NMR spectrum of propane-*d*₈ adsorbed on zeolite H-ZSM-5 in dependence of the reaction time. The intensity of two signals increases in the ¹H MAS NMR spectrum with the reaction time. The signal at 1.0 ppm arises from the protons of the methyl groups, whereas the signal at 1.5 ppm is due to the protons of the methylene group. The growth of these signals is caused by the transfer of protium from the SiOHAl groups to the CD₃ and CD₂ groups of propane-*d*₈. The ratio of the signal intensities (methyl to methylene groups) is close to 3:1 independent of the reaction time. This constant ratio shows that there is no preferential H/D exchange into methyl or methylene groups of propane under the conditions of our experiments.

Figure 2 describes the process of the H/D exchange in propane-2,2-*d*₂. An increase of the signal intensity from the methylene group and a decrease of the signal intensity from the methyl groups are observed. Obviously, an increase of the intensity of protium in the methylene group points to a depletion of deuterium from this group. The deuterium is transferred to

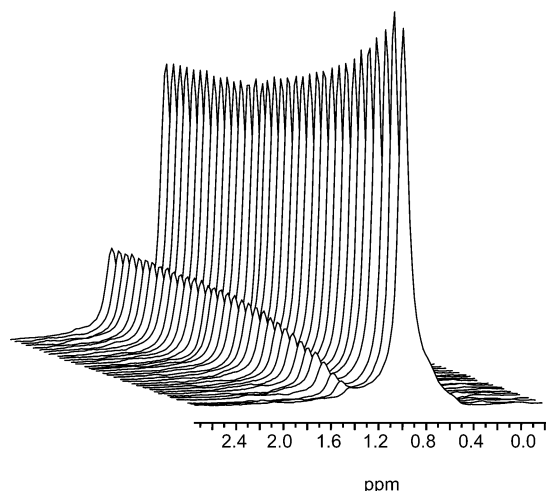


Figure 2. Stack plot of the ^1H MAS NMR spectra at 552 K of propane-2,2- d_2 adsorbed on H-ZSM-5 in the vicinity of methyl (1.0 ppm) and methylene (1.5 ppm) groups. The first spectrum (bottom) was recorded 3.8 min after and the last spectrum (top) 126 min after the temperature was raised to 552 K. The time between subsequent spectra recording was 3.6 min.

the methyl group of propane; this decreases the intensity of the ^1H NMR signal from the methyl groups. In the case of propane-1,1,1,3,3,3- d_6 , the concentration of protium increases in the methyl groups and decreases in the methylene group (see Figure 3). The ratio of the signal intensities in the final spectrum for propane-2,2- d_2 as well as for propane-1,1,1,3,3,3- d_6 is close to 3:1. The observed variation of the intensities of the methyl and methylene groups in propane-2,2- d_2 and propane-1,1,1,3,3,3- d_6 can be rationalized by intramolecular transfer of deuterium inside the propane molecule or by H/D exchange between propane molecules and the acidic SiOHAl groups.

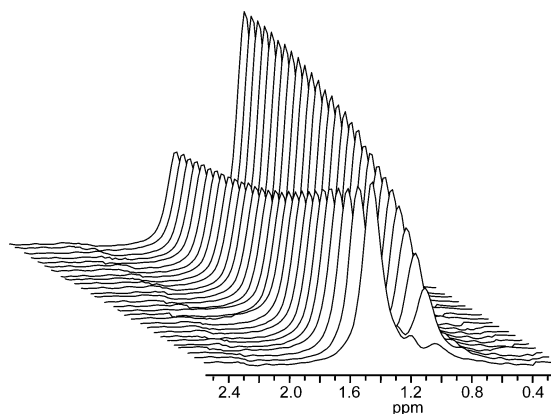
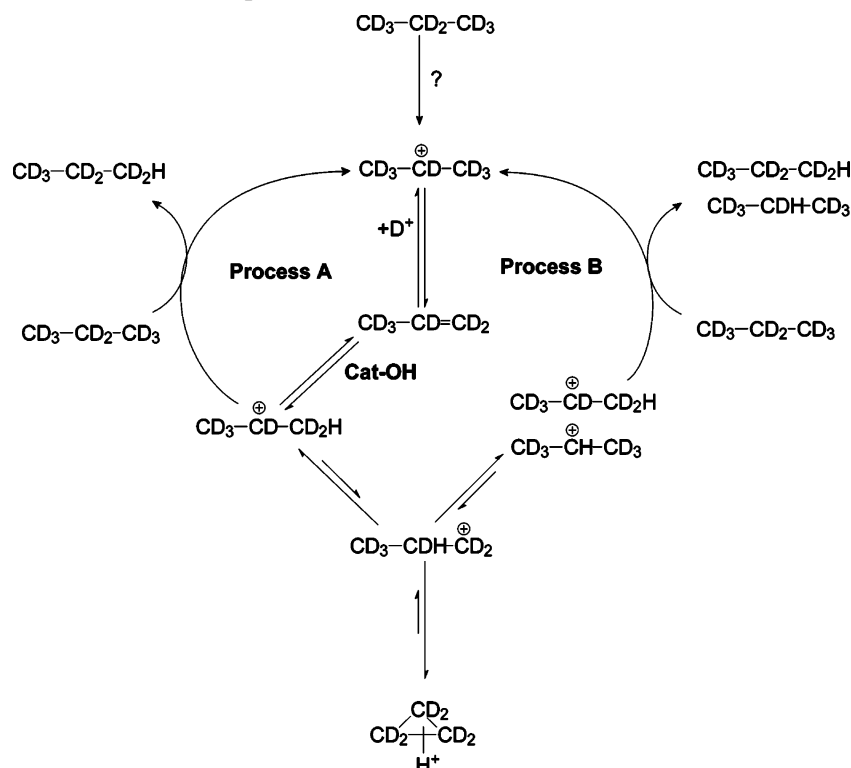


Figure 3. Stack plot of the ^1H MAS NMR spectra at 508 K of propane-1,1,1,3,3,3- d_6 adsorbed on H-ZSM-5 in the vicinity of methyl (1.0 ppm) and methylene (1.5 ppm) groups. The first spectrum (bottom) was recorded 2 min after and the last spectrum (top) 11 h after the temperature was raised to 508 K. The time between subsequent spectra recording was 23.5 min.

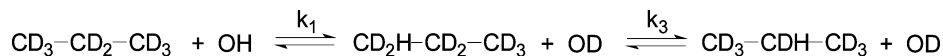
Haouas et al.¹⁸ suggested that the hydrogen exchange in propane occurs through the formation of propene and an isopropyl carbenium ion as intermediates in a catalytic cycle depicted in Scheme 1. This mechanism (mechanism 1) implies a regioselective exchange into the methyl groups (process A in Scheme 1) and the loss of regioselectivity by intramolecular H scrambling (skeletal rearrangement) (process B in Scheme 1) with involvement of the protonated cyclopropane intermediate. It means a *consecutive* scheme (Scheme 2) of hydrogen exchange; i.e., first the exchange occurs from the zeolite OH groups into the methyl group and then further into the methylene group. The observed nonselective exchange for propane- d_8 on H-ZSM-5 (see Figure 1) could imply that process B proceeds at a much higher rate than process A does. Therefore, the second

SCHEME 1: Catalytic Cycle Providing Regioselective H/D Exchange (Process A) and the Loss of Regioselectivity by Skeletal Rearrangement (Process B) for Propane- d_8 on Solid Acids^a

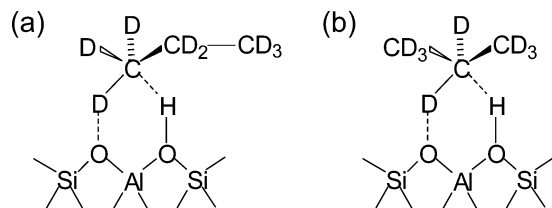


^a Adapted from Haouas et al.¹⁸

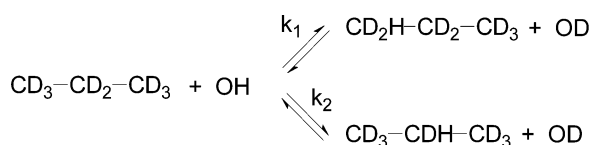
SCHEME 2: Consecutive Scheme Representing the Mechanism of the H/D Exchange in Propane on H-ZSM-5 in the Catalytic Cycle of Scheme 1 with a Carbenium Ion and an Olefin Intermediate



SCHEME 3: Transition States for the Direct H/D Exchange between CD₃ Group (a) and CD₂ Group (b) of Propane-*d*₈ and Acidic AlOHSi Sites of H-ZSM-5



SCHEME 4: Parallel Scheme Representing the Mechanism of the H/D Exchange in Propane via the Carbonium Ion Transition State



stage (rate constant k_3) in the consecutive scheme should be much faster compared to the first stage (rate constant k_1).

Either the methyl groups or the methylene group exchanges with the acidic OH group, independently of each other, without the formation of a common intermediate (isopropyl cation in Scheme 1).¹¹ Each of them exchanges directly through the formation of carbonium ion transition state (pentacoordinated carbon atom) with the hydrogen atoms exchanging at a halfway position between the carbon of the methyl or methylene group and the zeolitic oxygen atoms (Scheme 3). This mechanism (mechanism 2) implies a *parallel* scheme (Scheme 4) of the exchange of the SiOHAl groups with the methyl and methylene groups.

In situ ¹H MAS NMR spectra with resolved signals of protium in the methyl and methylene groups of propanes with different initial deuterium contents (propane-*d*₈, propane-1,1,1,3,3,3-*d*₆, and propane-2,2-*d*₂) enable the clarification of the mechanism of the hydrogen exchange by the consideration of possible mechanisms of the exchange (consecutive, parallel, and cyclic schemes) to rationalize the experimental kinetics for variously deuterated propanes.

Kinetics Model. The two basic mechanisms with either carbenium ions¹⁸ or carbonium ions¹¹ as intermediates are the basis for our discussion of the H/D exchange in propane on HZSM-5 zeolite. Both mechanisms are described by the same conservation equations, if we do not consider the intrinsic dissimilarities in the intermediates or transition states. For all intrinsic reaction paths, we have CD_{*n*} groups ($n = 3$ or 2) in propane, which retain 3 or 2 hydrogen atoms (protium or deuterium) after the H/D exchange reaction with the acidic OH groups. To describe all possible stages involved in both reaction mechanisms, namely, the exchange between acidic groups and the methyl (methylene) groups of propane as well as intramolecular exchange between the methyl and methylene groups, one needs to consider 11 exchange reactions (Table 1). Methyl groups contain three exchangeable hydrogen atoms. Therefore, a successive H/D exchange in deuterated methyl groups can be described by reactions 1–3 (see Table 1). Reactions 4–5 in Table 1 depict the exchange in the methylene groups. Reactions 6–11 describe the intramolecular exchange of protium (deute-

TABLE 1: Exchange Reactions Used for Modeling the Kinetics of the H/D Exchange in Propane on H-ZSM-5

reaction number	exchange reaction	equilibrium constant K_{eq}	rate constant k
1	$\text{CD}_3 + \text{OH} \leftrightarrow \text{CD}_2\text{H} + \text{OD}$	3	k_1
2	$\text{CD}_2\text{H} + \text{OH} \leftrightarrow \text{CDH}_2 + \text{OD}$	1	k_1
3	$\text{CDH}_2 + \text{OH} \leftrightarrow \text{CH}_3 + \text{OD}$	1/3	k_1
4	$\text{CD}_2 + \text{OH} \leftrightarrow \text{CDH} + \text{OD}$	2	k_2
5	$\text{CDH} + \text{OH} \leftrightarrow \text{CH}_2 + \text{OD}$	1/2	k_2
6	$\text{CD}_2\text{H} + \text{CD}_2 \leftrightarrow \text{CDH} + \text{CD}_3$	2/3	k_3
7	$\text{CDH}_2 + \text{CD}_2 \leftrightarrow \text{CH}_2 + \text{CD}_3$	1/3	k_3
8	$\text{CH}_3 + \text{CD}_2 \leftrightarrow \text{CH}_2 + \text{CD}_2\text{H}$	3	k_3
9	$\text{CD}_2\text{H} + \text{CDH} \leftrightarrow \text{CH}_2 + \text{CD}_3$	1/6	k_3
10	$\text{CDH}_2 + \text{CDH} \leftrightarrow \text{CH}_2 + \text{CD}_2\text{H}$	1/2	k_3
11	$\text{CH}_3 + \text{CDH} \leftrightarrow \text{CH}_2 + \text{CDH}_2$	3/2	k_3

rium) between the methyl and the methylene groups. The equilibrium constant K_{eq} for the reaction of isotopic substitution with a general form

$$\text{CD}_k\text{H}_{a-k} + \text{RD}_l\text{H}_{b-l} \leftrightarrow \text{CD}_{k1}\text{H}_{a-k1} + \text{RD}_{l1}\text{H}_{b-l1} \quad (1)$$

where a and b are the total contents of hydrogen isotopes in the methyl, methylene, or hydroxyl groups of the zeolite; k , l , $k1$, and $l1$ are the contents of deuterium in the groups; $R = \text{C}$ or O , can be calculated by the following manner, assuming binomial distribution of isotopes under the exchange:²⁷

$$K_{\text{eq}} = \frac{\binom{a}{k1} \binom{b}{l1}}{\binom{a}{k} \binom{b}{l}} \quad (2)$$

Here

$$\binom{a}{k} = \frac{a!}{k!(a-k)!}$$

are binomial coefficients. For example, for the reaction 1 in Table 1 we have

$$K_{\text{eq}} = \frac{\binom{a}{k1} \binom{b}{l1}}{\binom{a}{k} \binom{b}{l}} = \frac{\binom{3}{2} \binom{1}{1}}{\binom{3}{3} \binom{1}{0}} = \frac{3 \times 1}{1 \times 1} = 3 \quad (3)$$

The reactions (1–11) from Table 1 allow for the analysis of the kinetics of H/D exchange with either carbenium or carbonium ions as intermediates. The mechanism via a carbenium ion intermediate¹⁸ postulates that exchange with the zeolitic acidic groups is possible only for the CD₃ groups of propane. At the same time, the CD₂ group is able to draw protium from the methyl groups that have already exchanged some deuterium for protium. Consequently, this mechanism can be simulated by taking into account all of the exchange reactions from Table 1 except for the direct H/D exchange between the CD₂ groups and the acidic groups of the zeolite (reactions 4 and 5). Similarly, the mechanism of exchange via the carbonium ions¹¹ can be simulated by considering reactions 1–5 from Table 1. It is also assumed that the exchange reactions of the same type have equal rate constants, and so all 11 stages in Table 1 are characterized by the rate constants k_1 , k_2 , and k_3 .

For the simulation of the experimental data, the following mathematical model for the reaction under static conditions was used:²⁸

$$\frac{dN_i}{dt} = \sum_{j=1}^{11} \nu_{ji} R_j \quad (4)$$

where the index i denotes different participants in the exchange reaction, i.e., the AlOHSi groups of the zeolite (OH and OD), the methyl groups CD_kH_{3-k} ($k = 0-3$), and the methylene groups of propane CD_lH_{2-l} ($l = 0-2$). N_i is the concentration of the corresponding component i ($\mu\text{mol g}^{-1}$); ν_{ji} denotes the stoichiometric coefficient of the component i in the reaction j . R_j is the rate of the reaction j , which is determined as

$$R_j = k_j N_{i1} N_{i2} \left(1 - \frac{N_{k1} N_{k2}}{K_{eq} N_{i1} N_{i2}} \right) \quad (5)$$

where k_j is the rate constant, K_{eq} is the equilibrium constant, N_{i1} , N_{i2} are the concentrations of reagents, and N_{k1} , N_{k2} denote the concentrations of products in the reaction j .

To solve the system of equations (eq 4), the normalization conditions and the initial conditions should be used. The initial conditions are

$$N_i(t=0) = N_i^0 \quad (6)$$

Note that the initial conditions are different for propane with different initial deuterium contents. The normalization conditions are

$$\begin{aligned} [\text{OH}] + [\text{OD}] &= N_{\text{OH}}^0 \\ \sum_{k=0}^3 [\text{CD}_k\text{H}_{3-k}] &= N_{\text{CH}_3}^0 \\ \sum_{l=0}^2 [\text{CD}_l\text{H}_{2-l}] &= N_{\text{CH}_2}^0 \end{aligned} \quad (7)$$

The semi-implicit Runge–Kutta method²⁹ for the integration of sets of stiff equations with an integration step adaptation was used to solve the system of differential equations (eq 4). Thus, the concentrations of all components N_i in dependence of the reaction time could be determined. The concentrations of protium in the methyl and the methylene groups of propane are proportional to the intensities of the corresponding signals in the ^1H NMR spectrum. They were calculated by the equations

$$\begin{aligned} \sum_{k=0}^3 (3-k) [\text{CD}_k\text{H}_{3-k}] &= [\text{H}]_{\text{CH}_3} \propto I_{\text{CH}_3} \\ \sum_{l=0}^2 (2-l) [\text{CD}_l\text{H}_{2-l}] &= [\text{H}]_{\text{CH}_2} \propto I_{\text{CH}_2} \end{aligned} \quad (8)$$

The calculated concentration of protium in the methyl groups $[\text{H}]_{\text{CH}_3}$ and methylene group $[\text{H}]_{\text{CH}_2}$ in dependence of reaction time have to be compared with the experimental kinetic curves. The rate constants k_1 , k_2 , and k_3 were determined in such a way that simulated kinetic curves were fitted to the experimental data in the best way. The determination of the rate constants for different kinetic curves was performed with an accuracy of 10–20%. This accuracy was defined by a spread of the experimental points on the kinetic curves.

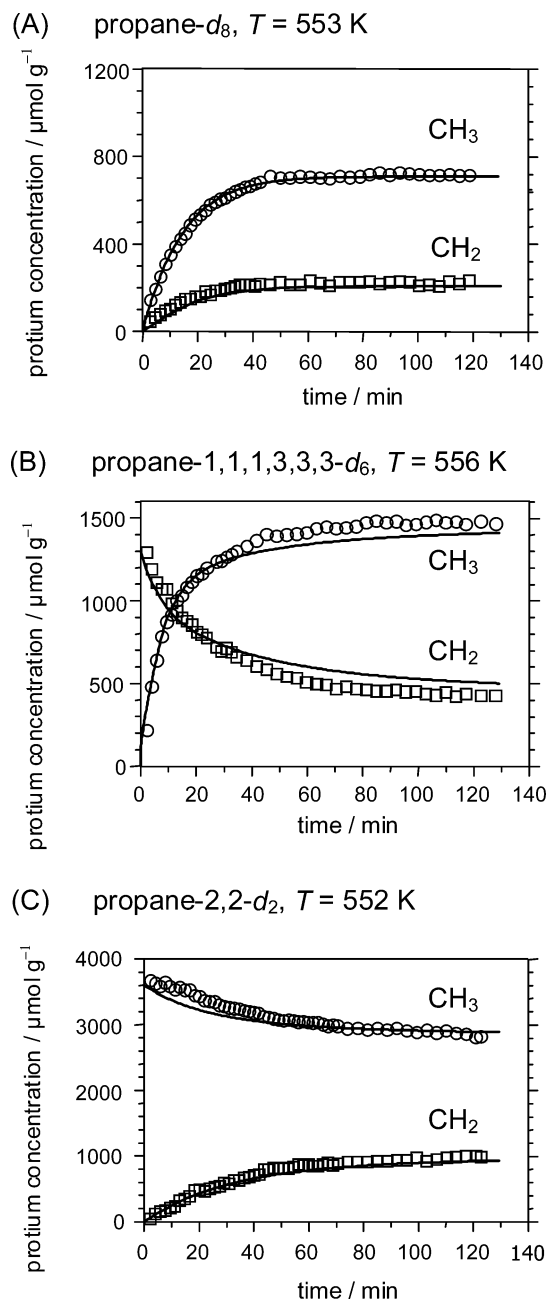


Figure 4. Simulation (solid curves) of the experimental kinetics of the H/D exchange for the methyl (○) and the methylene (□) groups of deuterated propane (propane- d_8 , propane-1,1,1,3,3,3- d_6 , and propane-2,2- d_2) on H-ZSM-5 in accordance to the consecutive kinetic scheme. The rate constants k_1 and k_3 , which correspond to the solid curves, are given in Table 2.

Kinetics Modeling Based on the Consecutive Scheme of the Exchange. Figure 4 shows kinetic curves that were simulated on the basis of the consecutive scheme of the exchange (Scheme 2). This scheme reflects main features of the mechanism of H/D exchange with carbenium ion and olefin intermediates. Reactions 1–3 and 6–11 from Table 1 were taken into account in this simulation. It is seen from Figure 4A that simulated curves are in good correspondence with the experimental kinetics in the case of propane- d_8 . However, simulated curves do not describe all features of the experimental kinetics in two other cases. In the case of propane-1,1,1,3,3,3- d_6 (Figure 4B), both simulated curves seem to achieve equilibrium values for a longer time than the experimental curves. In the case of propane-2,2- d_2 (Figure 4C), unsatisfactory fitting

TABLE 2: Rate Constants for the Consecutive Scheme of the H/D Exchange

	T/K	$k_1 \times 10^5$ ^a	$k_3 \times 10^5$ ^a
propane- <i>d</i> ₈	553	4	>18
propane-1,1,1,3,3,3- <i>d</i> ₆	556	8	0.55
propane-2,2- <i>d</i> ₂	552	0 ÷ 100	2.0

^a g μmol⁻¹ min⁻¹

is observed for the starting region of the decreasing curve that describes the depletion of protium from the methyl groups.

The rate constants used to fit the experimental curves in Figure 4 are given in Table 2. It has been found that a good fitting is observed in the case of propane-*d*₈, when the rate constant of the intramolecular exchange (k_3) is at least 4.5 times higher than that of the exchange between acidic SiOHAl groups and the methyl groups of propane (k_1). A further increase of the k_3 value does not change the simulated curve.

The obtained ratio between constants k_1 and k_3 for propane-*d*₈ (Table 2) is in accordance with the mechanism suggested by Haouas et al.,¹⁸ if we presume a fast intramolecular H/D scrambling in propane and a relatively slow H/D exchange between the methyl groups and acidic OH groups. However, then we should expect the rate constant k_3 to be higher than the rate constant k_1 in the cases of propane-1,1,1,3,3,3-*d*₆ and propane-2,2-*d*₂ as well. In fact, in the case of propane-1,1,1,3,3,3-*d*₆, k_1 is substantially higher than k_3 . To rationalize the observed exchange in propane-1,1,1,3,3,3-*d*₆, one should suppose the rate of intramolecular exchange to be slower than the rate of H/D exchange between the methyl groups and the zeolite acidic groups. This is not in agreement with the ratio between k_1 and k_3 for the exchange in propane-*d*₈.

The difference in the rate constants k_1 and k_3 (Table 2) for propanes with different initial deuterium contents cannot be rationalized by a possible kinetic isotope effect. Obviously, the kinetic isotope effect should have an influence on the magnitudes of rate constants k_1 and k_3 since the direction of protium (deuterium) transfer is changed for propane with different initial amounts and locations of deuterium. The magnitude of the possible isotope effect for H/D exchange with a carbenium ion intermediate was reported to be about 1.4.^{15,16} This kinetic isotope effect is not sufficient to provide some notable differences in the rate constants k_1 and k_3 , which were estimated for exchange with propane-*d*₈ and propane-1,1,1,3,3,3-*d*₆. Thus, the results of the H/D exchange in propane-*d*₈ and propane-1,1,1,3,3,3-*d*₆ lead to a contradictory rationalization of the exchange in the frame of the consecutive scheme.

It has been found for propane-2,2-*d*₂ that the simulated kinetic curve for the methyl groups, which is calculated based on the consecutive scheme, does not fit to the initial part of the experimental data (Figure 4C). At any value of $k_1 = 0$ –100 (see Table 2), the decreasing curve (methyl groups) goes far below the experimental kinetics in the starting region, provided that the increasing curve (methylene group) is fitted well to the experimental points. The simulated kinetic curves insignificantly change their positions for the k_1 values from the range pointed out in Table 2. The consecutive scheme does not account for a slower depletion of protium from the methyl groups in propane-2,2-*d*₂, which is observed in the experimental kinetics. Thus, there is no consistency among the kinetics of the exchange (different values of k_1 or k_3) for the three differently deuterated propanes in the frame of the consecutive scheme of the exchange.

The analysis of the kinetics of H/D exchange in propanes with different initial deuterium contents, based on the consecu-

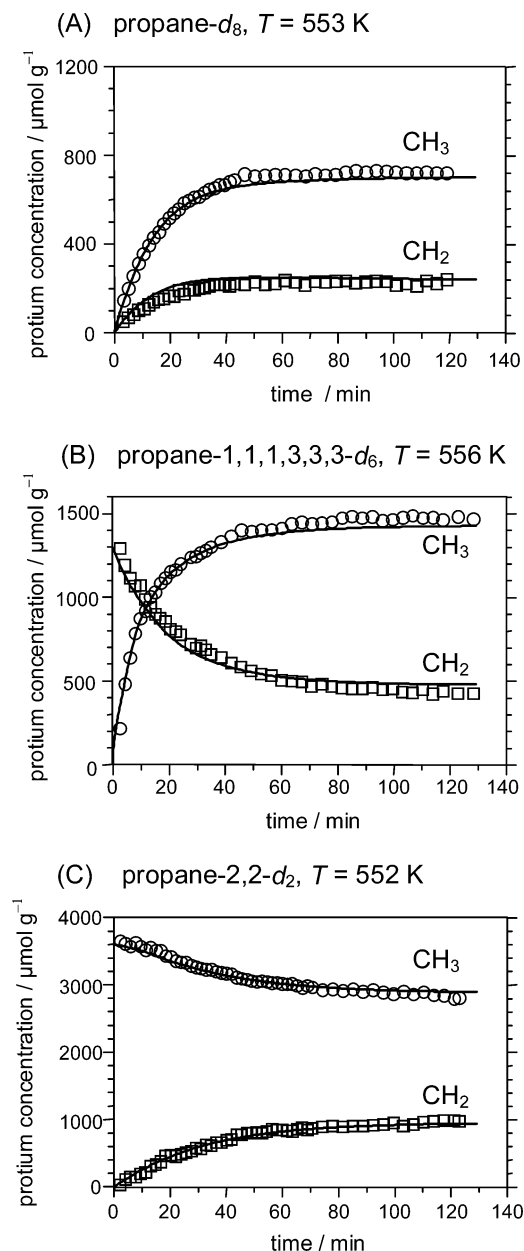


Figure 5. Simulation (solid curves) of the experimental kinetics of the H/D exchange for the methyl (○) and the methylene (□) groups of deuterated propane (propane-*d*₈, propane-1,1,1,3,3,3-*d*₆, and propane-2,2-*d*₂) on H-ZSM-5 in accordance to parallel kinetic scheme. The rate constants k_1 and k_2 , which correspond to the solid curves, are shown in Table 3.

tive scheme (Scheme 2), allows us to conclude that the nonselective exchange in deuterated propane-*d*₈ on H-ZSM-5 cannot be rationalized by a fast intramolecular exchange between the methyl and the methylene groups. Therefore, the mechanism of the exchange via the consecutive scheme with carbenium ion and olefin intermediates cannot govern the H/D exchange for propane on H-ZSM-5. We further considered the alternative mechanism of exchange with a carbonium ion intermediate, which can be represented with a parallel scheme (Scheme 4).

Kinetics Modeling Based on the Parallel Scheme of the Exchange. The parallel kinetic scheme describes the mechanism where both the methyl and the methylene groups of propane exchange directly with the acidic groups of the zeolite.¹¹ Figure 5 shows kinetic curves that have been simulated based on Scheme 4. Reactions 1–5 from Table 1 were taken into account in this simulation. Simulated curves are well-fitted to all

TABLE 3: Rate Constants for the Parallel Scheme of the H/D Exchange

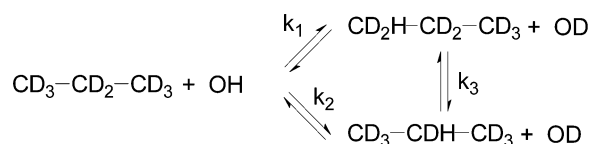
	<i>T</i> /K	<i>k</i> ₁ × 10 ⁵ ^a	<i>k</i> ₂ × 10 ⁵ ^a
propane- <i>d</i> ₈	553	3.6	2.4
propane-1,1,1,3,3,3- <i>d</i> ₆	556	11.9	5.8
propane-2,2- <i>d</i> ₂	552	3.6	4.0

^a g μmol⁻¹ min⁻¹

experimental kinetics. This was not observed for simulated curves in Figure 4 for the consecutive scheme. The rate constants *k*₁ or *k*₂ used to calculate the simulated curves in Figure 5 do not exhibit a profound discrepancy for propanes with different initial deuterium contents (Table 3). Discrepancy among *k*₁ values or *k*₃ values for three differently labeled propanes in the consecutive scheme of the exchange was more profound. Thus, there is a consistency among the kinetics of the exchange for the three differently deuterated propanes in the frame of a parallel scheme. It can be concluded that the H/D exchange in deuterated propane on the zeolite follows mainly the mechanism with the direct exchange of both the methyl and the methylene groups with the zeolite acidic OH groups with a carbonium ion intermediate.

The rate constant *k*₁ for propane-1,1,1,3,3,3-*d*₆ significantly exceeds its values obtained for propane-*d*₈ and propane-2,2-*d*₂ (Table 3). The small difference in reaction temperature can provide only a 20% difference in the rate constants *k*₁ or *k*₂, since the activation energy of the exchange is about 125 kJ mol⁻¹ (vide infra). The kinetic isotope effect cannot explain the difference in *k*₁ values either. This isotope effect for the H/D exchange with a carbonium ion intermediate has been found to be *k*_H/*k*_D = 1.7, where *k*_H is the rate constant for the exchange between CD₄ and the OH group of the zeolite and *k*_D is the rate constant for the exchange between CH₄ and the OD group of the zeolite.¹⁴ The replacement of propane-*d*₈ by propane-1,1,1,3,3,3-*d*₆ (or propane-2,2-*d*₂) should decrease the rate constants *k*₁ and *k*₂. However, the values of *k*₁ and *k*₂ increase. The higher values of rate constants obtained for propane-1,1,1,3,3,3-*d*₆ and propane-2,2-*d*₂ could imply that some additional steps are not taken into consideration in this scheme of the exchange. Such steps may represent an intramolecular hydrogen exchange between the methyl and the methylene groups, which occurs in addition to the direct H/D exchange of the methyl or methylene groups with the zeolite acidic OH groups.

Kinetics Modeling Based on the Cyclic Scheme of the Exchange. It was reported that the ¹³C-labeled carbon scrambling occurred in propane on H-ZSM-5 at a temperature of 573 K.³⁰ The ¹³C scrambling in the adsorbed propane hints to the isopropyl cation formation³¹ on the zeolite, providing this scrambling. It has been demonstrated for a superacidic solution that the ¹³C-labeled carbon scrambling in isopropyl cation is accompanied by H scrambling.^{31–33} Both H and ¹³C scramblings have a common intermediate, namely, isopropyl cation. H scrambling occurs mainly by hydride shift reaction through the 1-propyl cation intermediate, whereas ¹³C scrambling involves a protonated cyclopropane intermediate or transition state. The activation energies are similar, but the H scrambling occurs several times more rapidly than the ¹³C scrambling.³³ We have recently demonstrated that the rate of ¹³C scrambling in propane is indeed slower than the rate of H/D exchange in propane.³⁴ Therefore, the intramolecular H/D exchange between the methyl and the methylene groups of propane, presumably by a hydride shift reaction, may take place simultaneously with both ¹³C scrambling and the direct exchange between the methyl or methylene groups of the alkane and the zeolite OH groups. Thus,

SCHEME 5: Cyclic (Parallel-Consecutive) Scheme of the H/D Exchange

there is one more kinetic scheme (Scheme 5) to be discussed besides consecutive and parallel schemes of the exchange, which have been discussed above. In fact, this is the parallel scheme, where the additional intramolecular H/D exchange (H scrambling) between the methyl and the methylene groups is included. This cyclic scheme takes into account a direct exchange of both the methyl and the methylene groups with the zeolite with a carbonium ion intermediate and intramolecular H scrambling between the methyl and methylene groups with an isopropyl cation intermediate.

Figure 6 shows kinetic curves that were simulated on the basis of the cyclic scheme of exchange (Scheme 5). Reactions 1–11 from Table 1 were taken into account in this simulation. Simulated curves are well-fitted to all experimental kinetics. The rate constants *k*₁, *k*₂, and *k*₃ used to calculate the simulated curves were found to have very close values for propanes with different initial deuterium contents (Table 4). Taking into account the third stage with a quite small value of the rate constant *k*₃ allows one to obtain similar values for the rate constants *k*₁ or *k*₂ for three differently labeled propanes. The third stage with *k*₃ in the cyclic scheme depicts the intramolecular H scrambling in propane, which was assumed to be fast in the mechanism with carbenium ion and olefin intermediates¹⁸ (Scheme 1) (the second step in the consecutive kinetic scheme of exchange). The cyclic scheme demonstrates that the rate of intramolecular H scrambling is slower than the rates of the direct exchange of both the methyl and the methylene groups with the zeolite.

In the case of propane-1,1,1,3,3,3-*d*₆, the intramolecular H scrambling has a noticeable influence on the consistency of the *k*₁ or *k*₂ values for three differently labeled propanes when we move from the parallel to the cyclic scheme of the exchange (see data in Tables 3 and 4). In case of propane-*d*₈, the equilibrium concentration of protium in the methyl and the methylene groups is reached mainly by the direct exchange with the zeolite. Therefore, the third reaction which is characterized by the rate constant *k*₃, has a smaller effect on the consistency of the *k*₁ or *k*₂ values for three differently labeled propanes when we introduce the additional stage of intramolecular exchange into the parallel scheme of the exchange (see data in Tables 3 and 4).

The rate constant *k*₁ was found always to be higher than the rate constant *k*₂ for three differently deuterated propanes (Table 4). This finding cannot be rationalized unambiguously. Indeed, the carbonium ion mechanism should favor the exchange into the methylene group according to the concept of the σ -basicity of C–H bonds developed by Olah et al.^{35,36} for alkane reactivity in superacidic liquid media, i.e., primary CH < secondary CH. This would imply *k*₂ > *k*₁ as long as the C–H bond at the secondary carbon possesses a higher basicity. The higher value of *k*₁ may imply that the σ -basicity concept is not applicable to the zeolites, which do not exhibit superacidic properties.³⁷

Sommer and Bukala³⁸ observed the H/D exchange in propane in DF–SbF₅ and found a similar degree of exchange into the methyl and methylene groups despite the expected difference in σ -basicity of the C–H bonds in methyl and methylene groups. This means that the small difference in basicity, which is

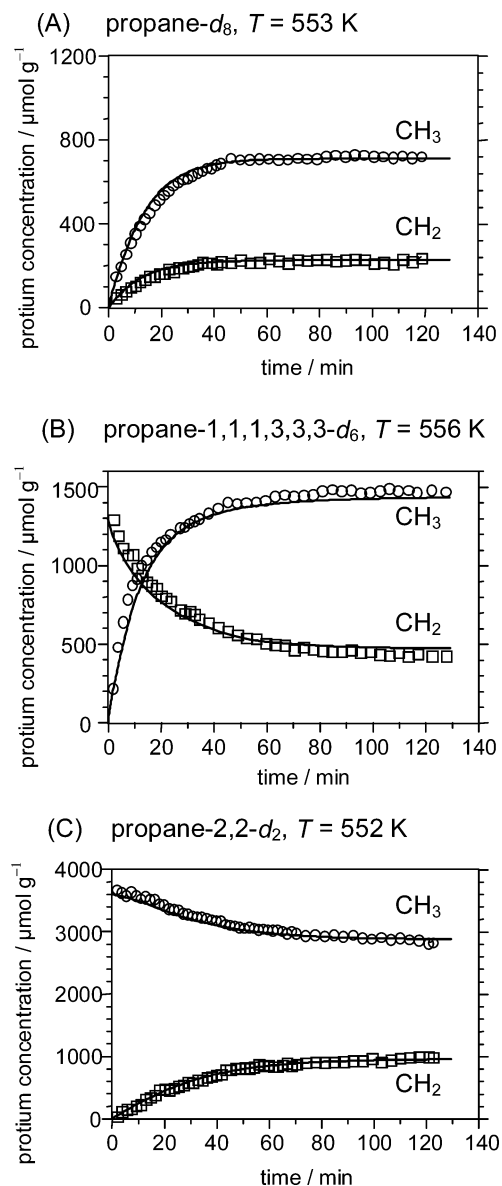


Figure 6. Simulation (solid curves) of the experimental kinetics of the H/D exchange for the methyl (○) and the methylene (□) groups of deuterated propane (propane- d_8 , propane-1,1,1,3,3,3- d_6 , and propane-2,2- d_2) on H-ZSM-5 in accordance to cyclic kinetic scheme. The rate constants k_1 , k_2 , and k_3 , which correspond to the solid curves, are shown in Table 4.

TABLE 4: Rate Constants for the Cyclic Scheme of the H/D Exchange

	T/K	$k_1 \times 10^5^a$	$k_2 \times 10^5^a$	$k_3 \times 10^5^a$
propane- d_8	553	3.4	2.3	0.6
propane-1,1,1,3,3,3- d_6	556	4.5	2.4	0.6
propane-2,2- d_2	552	3.4	2.7	0.6

^a $\mu\text{mol}^{-1} \text{min}^{-1}$

expected for the C–H bonds in the methyl and the methylene groups, can lead to a nonsignificant difference in the protonation exchange rates. This may imply that if the σ -basicity concept were valid for zeolites, k_1 and k_2 would be of similar values, rather than $k_1 > k_2$.

More steric accessibility of the methyl groups compared to that of the methylene group for the simple direct exchange reaction via the transition states depicted in Scheme 3 can indeed account for a higher value of k_1 compared to that of k_2 . However, a possible more steric accessibility of the methyl groups offers

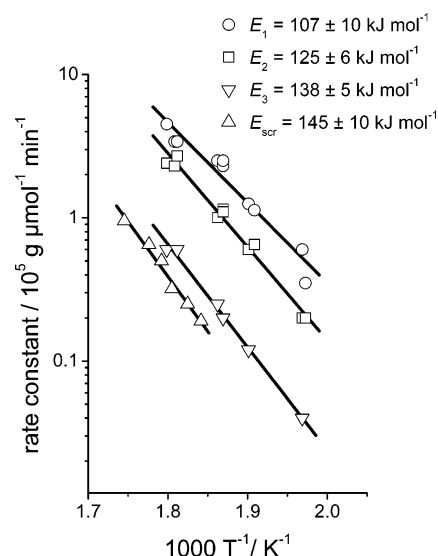


Figure 7. Arrhenius plot and activation energies for the H/D exchange reactions in deuterated propane on H-ZSM-5 and the ^{13}C scrambling in propane-2- ^{13}C on H-ZSM-5. k_1 (○), k_2 (□), k_3 (▽), and k_{scr} (△).

only 1.5 times faster exchange into these groups compared to exchange into the methylene group at 550–560 K; at 473 K, the direct exchange into the methyl group might be 3 times faster, as follows from the energetic of the exchange (vide infra). Other slight differences in the values of the rate constants k_1 or k_2 for the three differently deuterated propanes in Table 4 can arise from small differences in the reaction temperatures, isotope effects, and errors in calculated rate constants.

Table 5 shows the distribution of protium and deuterium over all possible sites of the exchange: hydroxyl groups of the zeolite, the methyl groups $\text{CD}_k\text{H}_{3-k}$, and the methylene groups $\text{CD}_l\text{H}_{2-l}$ of propane. The distribution of the equilibrium condition was calculated from the kinetic curves, simulated on the basis of the cyclic scheme (Scheme 5). Values from Table 5 show that the preferential formation of deuterated forms of methyl (methylene) groups depends on the overall content of deuterium atoms in the initial molecule, as was earlier noticed for the exchange of alkanes with deuterated sulfuric acid.²⁷ In the case of high deuterium content (propane- d_8), the deuterated forms CD_3 and CD_2 are present in higher amounts compared to the other forms of the methyl and methylene groups. In the case of low overall deuterium content (propane-2,2- d_2), concentrations of monodeuterated forms CH_2D and CHD exceed the concentrations of other deuterated forms of the methyl and methylene groups under equilibrium. The case of propane-1,1,1,3,3,3- d_6 is regarded as an intermediate one concerning the overall deuterium content; the deuterated forms CD_3 and CH_2D are not the prevailing species under equilibrium.

We conclude that the cyclic scheme of the exchange (Scheme 5) takes into account all features of the H/D exchange for propane on zeolite H-ZSM-5 in the most precise manner. The main route for the H/D exchange represents a direct exchange between acidic OH groups and methyl and methylene groups presumably with pentacoordinated carbonium ion intermediate. The intramolecular exchange between the methyl and the methylene groups is also performed, but its rate is 4–5 times slower than the rates of the main route.

Activation Energy. The apparent activation energy for the H/D exchange in propane on H-ZSM-5 was estimated on the basis of a cyclic kinetic scheme. The Arrhenius plot (Figure 7) shows three stages which are involved in the cyclic scheme and exhibit the activation energies in the range of 107–138 kJ

TABLE 5: Distribution of Protium and Deuterium ($\mu\text{mol g}^{-1}$) over Acidic Hydroxyl Groups of the Zeolite and the Methyl and the Methylene Groups of Propane Determined by Reaction of 130 min Based on the Simulation of the Kinetics According to the Cyclic Scheme of the Exchange

	T/K	OH	OD	CD_3	CD_2H	CDH_2	CH_3	CD_2	CDH	CH_2
propane- d_8	353	230	940	623	455	113	9	391	186	23
propane-1,1,1,3,3,3- d_6	556	465	605	264	520	342	74	216	288	95
propane-2,2- d_2	552	934	236	8	110	465	617	29	197	374

mol^{-1} . These values are close to earlier estimations¹¹ of $E_a = 109\text{--}125 \text{ kJ mol}^{-1}$ for the H/D exchange in propane on H-ZSM-5. The apparent activation energy for the exchange in methane, where the carbonium ion mechanism has no alternative, was reported^{14,17} to be in the same range of $125\text{--}146 \text{ kJ mol}^{-1}$. The values of activation energy for the H/D exchange in propane on H-ZSM-5 give further evidence that Scheme 1 cannot be the main route for the hydrogen exchange in propane on acidic zeolites. The apparent activation energies for the exchange by mechanism with carbenium ion and olefin intermediates have appreciably smaller values; e.g., the activation energy of the exchange in deuterated propane on sulfated zirconia was reported to be 54 kJ mol^{-1} (regioselective exchange in methyl groups) and 71 kJ mol^{-1} (intramolecular proton scrambling).¹⁹

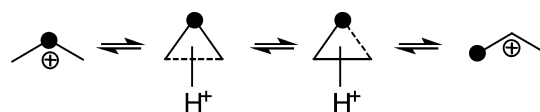
The estimated activation energies allow one to further estimate the k_1 and k_2 values that would be expected for the reaction at 473 K, where the exchange was extremely slow, but regioselective exchange for propane on the zeolites was detected.⁶ Our estimation offers the k_1 value 3 times higher than k_2 at 473 K. A 3 times faster exchange in the methyl group at 473 K can reasonably rationalize the regioselectivity of the H/D exchange observed earlier for propane on H-ZSM-5.⁶

The difference in mechanisms of hydrogen exchange in propane on zeolite H-ZSM-5 and sulfated zirconia could be attributed to the different acidic and other properties of these catalytic materials and might be also due to different reaction temperatures. The present study does not confirm the conclusion by Haouas et al.¹⁹ that, in all acid catalysts, the hydrogen exchange in propane follows the mechanism where the carbenium ion in equilibrium with olefin are the key intermediates without any participation of carbonium ions. As evidenced from the present study, the H/D exchange in propane on acidic

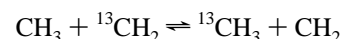
zeolites (contrary to sulfated zirconia) is represented by the complex scheme, where the main route is the mechanism including the direct exchange of both methyl and methylene groups with the zeolite acidic groups via the presumable intermediacy of pentacoordinated carbonium ions.

^{13}C -Labeled Carbon Scrambling. As we have mentioned above, ^{13}C -labeled carbon scrambling is performed in propane on zeolite H-ZSM-5.³⁰ After we have shown the occurrence of intramolecular H scrambling in propane adsorbed on H-ZSM-5, it would be of interest to compare the rates of ^{13}C and H scrambling in relation to confirmation of the formation of isopropyl cation on zeolite, providing both ^{13}C and H scramblings.

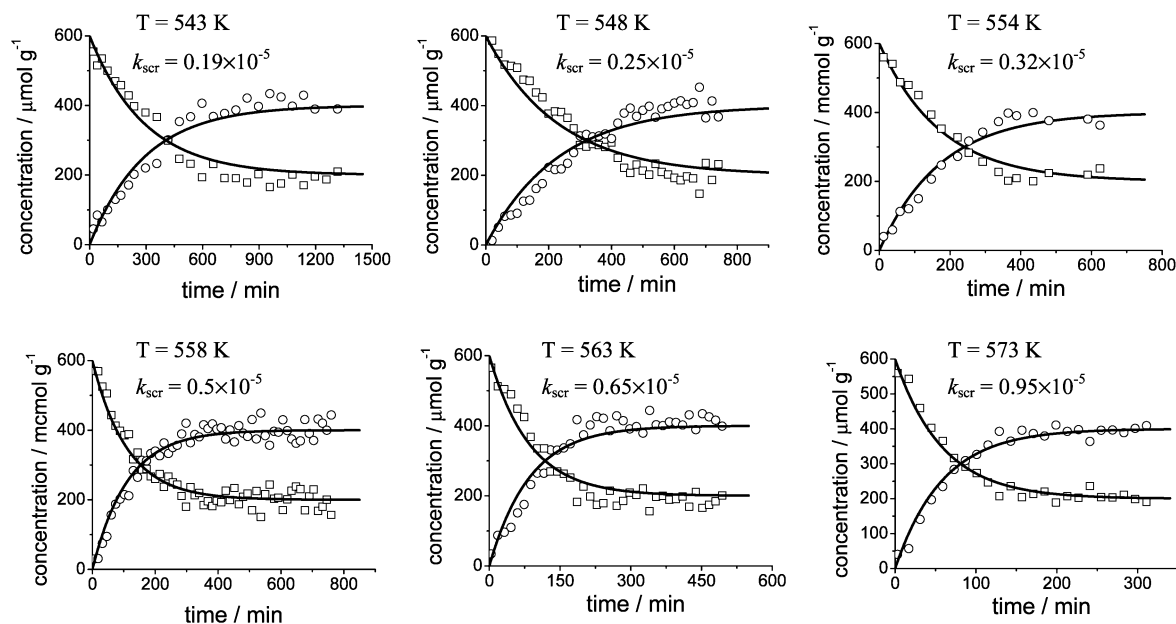
The ^{13}C -labeled carbon (\bullet) scrambling in the adsorbed propane-2- ^{13}C should occur as monomolecular transformation of isopropyl cation:



However, to have the rate constant for ^{13}C -labeled carbon scrambling in the units similar to the rate constants of H scrambling we consider the bimolecular scheme for simulation of the kinetics of ^{13}C -labeled carbon scrambling in adsorbed propane:



In this scheme, the reaction components are the fragments of a molecule of propane. The initial concentration of the unlabeled methyl group is 2 times higher than that of the ^{13}C -labeled

**Figure 8.** Simulation (solid curves) of the experimental kinetics of ^{13}C -labeled carbon scrambling from the methylene (\square) carbon to the methyl (\circ) carbon in propane-2- ^{13}C on H-ZSM-5. Values of k_{scr} are given in $\text{g } \mu\text{mol}^{-1} \text{ min}^{-1}$.

methylene group, and the equilibrium constant is equal to unity in accordance with the general expression (eq 2) for K_{eq} .

Figure 8 shows the experimental and simulated kinetic curves for ^{13}C -labeled carbon scrambling in propane-2- ^{13}C on H-ZSM-5 at temperatures 543–573 K. The rate constants k_{scr} , derived from the simulation of the kinetics of the ^{13}C -labeled carbon scrambling (shown in Figure 8) is about two times lower compared to the rate constant k_3 for H scrambling in the cyclic scheme (cf. k_{scr} and k_3 in Figure 7). The activation energy for ^{13}C scrambling (145 kJ mol $^{-1}$) found from the Arrhenius plot of k_{scr} (see Figure 7) coincides with the activation energy for intramolecular H scrambling.

The ratio of the rate constants k_{scr} and k_3 found for the adsorbed propane and the similarity in activation energies of H and ^{13}C scrambling are in line with previously reported results,^{31–33} where it was shown for isopropyl cation in superacid that the rate constant for ^{13}C scrambling was 3.4 times lower compared to the rate constant for H scrambling by hydride shift reaction, but the activation energies were similar. This is evidence for similarities of the mechanisms of H and ^{13}C scrambling in propane adsorbed on H-ZSM-5 and for isopropyl cation in superacid media. Thus, the obtained data on intramolecular H and ^{13}C scramblings in adsorbed propane find their rationalization in the best way with classical carbenium ion chemistry.

Conclusion

The analyses of the kinetics of the hydrogen exchange between the Brønsted acid sites of zeolite H-ZSM-5 and variously deuterated propanes (propane- d_8 , propane-1,1,1,3,3,3- d_6 , and propane-2,2- d_2) at 503–556 K and intramolecular ^{13}C -labeled carbon scrambling for propane-2- ^{13}C at 534–573 K allowed us to make the following conclusions on the mechanism of hydrogen exchange and ^{13}C isotope interchange. Both the methyl and methylene groups of propane are involved in the direct H/D exchange with acidic groups of the zeolite. The mechanism of the exchange presumably involves a pentacoordinated carbonium ion as the transition state. Intramolecular H scrambling of the protium (deuterium) from the methyl groups into the methylene group is also performed probably via hydride (deuteride) shifts and the skeletal rearrangement process of the carbenium ion intermediate. The rate constant for intramolecular H/D exchange between the methyl and the methylene groups is 4–5 times slower compared to the direct exchange of both the methyl and the methylene groups with Brønsted acid sites of the zeolite. Faster direct exchange with the methyl groups compared to that with the methylene groups might be related to more spatial accessibility of the methyl groups for the exchange. Similar activation energies for H and ^{13}C scramblings with a 2 times more rapid rate of H scrambling in adsorbed propane find their rationalization by proceeding these two processes through the isopropyl cation intermediate, as in classical carbenium ion chemistry.

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