Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Catalysis 235 (2005) 221–228
JOURNAL OF CATALYSIS
www.elsevier.com/locate/jcat

In situ ^{1}H and ^{13}C MAS NMR study of the mechanism of H/D exchange for deuterated propane adsorbed on H-ZSM-5

Alexander G. Stepanov [a,*], Sergei S. Arzumanov [a], Mikhail V. Luzgin [a], Horst Ernst [b], Dieter Freude [b,*], Valentin N. Parmon [a]

[a] *Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Prospekt Akademika Lavrentieva 5, Novosibirsk 630090, Russia*
[b] *Abteilung Grenzflächenphysik, Universität Leipzig, Linnéstraße 5, 04103 Leipzig, Germany*

Received 19 April 2005; revised 20 July 2005; accepted 7 August 2005

Abstract

The kinetics of hydrogen exchange between the molecules of propane-d_8, propane-1,1,1,3,3,3-d_6, propane-2,2-d_2, and Brönsted acid sites of the zeolite H-ZSM-5 have been monitored in situ by ^{1}H MAS NMR spectroscopy in the temperature range of 230–280 °C. The intramolecular hydrogen transfer was estimated by in situ ^{13}C MAS NMR spectroscopy of the kinetics of ^{13}C-label scrambling in adsorbed propane-2-^{13}C. The hydrogen exchange was found to occur directly between methyl or methylene groups of the alkane and the zeolite acid sites via a pentacoordinated carbonium ion. The exchange with the methyl groups is faster than that with the methylene group. This accounts for the earlier observed regioselectivity of the hydrogen exchange for propane on acidic zeolites (J. Am. Chem. Soc. 117 (1995) 1135). The intramolecular hydrogen transfer between methyl and methylene groups is one order of magnitude slower than the hydrogen exchange of the both groups with the zeolite acid sites.

Keywords: Propane; H-ZSM-5 zeolite; H/D exchange; Kinetics; Mechanism; ^{1}H MAS NMR; ^{13}C MAS NMR; In situ spectroscopy

1. Introduction

Alkane conversion on solid acid catalysts like isomerization, cracking, dehydrogenation, or aromatization is preceded by the molecule activation on the active sites of the catalysts. Some reaction intermediates appear and provide further alkane conversion. Initial steps of the alkane activation are usually accompanied by hydrogen exchange with Brönsted acid sites of the catalyst [1]. Valuable information about the reaction intermediates could be obtained by studying the isotopic exchange using ^{1}H-, ^{2}H (D)-, or ^{13}C-labeled molecules and in situ spectroscopic techniques like NMR.

Different mechanisms of the hydrogen (H/D) exchange for alkanes on various solid acid catalysts have been discussed. For small alkanes with one and two carbon atoms, the H/D exchange proceeds at high temperatures. The mechanism seems to have no alternative to the direct proton transfer between the solid surface and the alkane molecule in a concerted step involving a pentacoordinated carbon atom [2–6]. For alkanes with three and four carbon atoms, an alternative mechanism (to the pentacoordinated transition state) has been described that includes a carbenium ion intermediate in equilibrium with an alkene. This mechanism is based on the experimentally observed regioselectivity for the H/D exchange [7–9], similar to regioselectivity of the exchange for isobutane in concentrated sulfuric acid [10].

For isobutane, the H/D exchange is regioselective on zeolites [8,9], sulfated zirconia (SZ) [9,11], and amorphous silica–alumina [7]. Regioselectivity of the exchange for isobutane has been also confirmed by in situ ^{1}H MAS NMR [12]. A reported suppression of the exchange by CO also favors carbenium ions in equilibrium with olefin as the key intermediates of the exchange [12]. Haouas et al. [11,13] offered arguments for regioselective exchange of propane on SZ as well as the possible formation of propene in equilibrium with isopropyl cation providing the regioselective exchange on SZ. Supporting ar-

---

* Corresponding authors. Fax: +49-341-97-39349.
E-mail addresses: stepanov@catalysis.ru (A.G. Stepanov), freude@uni-leipzig.de (D. Freude).

0021-9517/$ – see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2005.08.002

guments included that only methyl groups are involved in the exchange at moderate temperature; that at higher temperatures, the rate of the exchange for the methyl groups is notably higher than that for the methylene group; that an induction period for the exchange exists; that essentially different activation energies of the exchange for methyl and methylene groups can be found; and that similar activation energies for carbon-13 and D scrambling exist for the adsorbed propane.

On the basis of the results obtained for SZ, Haouas et al. [11,13] claimed that the mechanism should be similar for the exchange of propane on other solid acids, proceeding at higher temperatures. However, the experimental data [9,11,13] do not provide a reliable evidence of the similarity of the mechanism for propane on H-ZSM-5. The regioselectivity is not as evident as it is for isobutene, and the degree of exchange is too low at low temperature to allow reliable identification of the regioselectivity. It should be noted that the statistical distribution of ^{1}H isotope in propane favors protium in the methyl groups for the exchange between deuterated propane and acidic OH groups of the zeolite. This implies that at a low degree of exchange, the ^{1}H intensity of methyl groups is always three times higher than that of the methylene group. This may be why the observable amount of exchange into the methyl group is apparently higher and gives the impression that regioselectivity occurs at a low degree of exchange [9]. At higher temperatures, where the degree of exchange is notable, the regioselectivity vanishes [13].

We previously demonstrated that both methyl and methylene groups of propane on H-ZSM-5 are equally involved in the exchange, with similar rates and similar high activation energies [14], in contrast to propane on SZ, where the exchange occurs with different rates and activation energies for CH_3 and CH_2 groups [11]. Moreover, carbon monoxide did not suppress the exchange of propane on H-ZSM-5 [14]. This implies another mechanism of hydrogen exchange for propane—namely, that the methyl and methylene groups exchange without formation of a common carbenium ion intermediate, and each of these groups exchanges via a concerted mechanism through a pentacoordinated carbonium ion transition state, in which the exchanging hydrogen atoms are allocated between the oxygen atom of the zeolite and the carbon atom of either the methyl or methylene group of propane [6].

In this paper we provide further arguments that the hydrogen exchange of propane on H-ZSM-5 zeolite occurs mainly by a direct interaction between the zeolite acid sites and either methyl or methylene groups, probably in concert with the formation of the intermediate pentacoordinated transition state. Our arguments are based on the analysis of the kinetics of the exchange obtained with in situ ^{1}H MAS NMR monitoring the protium isotope transfer from the zeolite acid sites into deuterated propane. Propane was labeled with deuterium isotope in either methyl or methylene groups or entirely deuterated. In situ monitoring of the kinetics of the ^{13}C-label scrambling in adsorbed propane was also performed to show a negligible contribution of the accompanying intramolecular H scrambling to the observed kinetics of the H/D exchange.

2. Experimental

2.1. Materials and sample preparation

Zeolite ZSM-5 ($Si/Al = 13.2$) was kindly provided by Tricat Zeolites. The template-free synthesized ammonium form was transferred into the H form by the activation procedure. The ^{27}Al MAS NMR spectrum showed the absence of extra-framework aluminum species, because only one narrow signal at 54 ppm could be observed. The quantity of the acidic AlOHSi groups of 1200 μmol g^{-1}, which was estimated by the adsorption of a calibrated quantity of benzene and the comparison of the intensities of the OH and benzene signals, was in a good concordance with the expected quantity of 1170 μmol g^{-1}, corresponding to 6.8 groups per unit cell, which was derived from the framework Si/Al ratio. The latter was determined by deconvoluting the ^{29}Si MAS NMR spectrum [15] and comparing the intensity with that of ^{27}Al MAS NMR using a well-characterized reference sample. Thus, the ^{1}H MAS NMR intensity measurement of the bridging AlOHSi groups in the activated fused sample was in good agreement with the concentration of the framework aluminum atoms of the hydrated sample determined by ^{29}Si MAS NMR.

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), all purchased from Aldrich Chemical Company, and propane-2-^{13}C (99% ^{13}C), purchased from ICON, were used without further purification. The samples for the NMR measurements were activated by heating 60 mg of the zeolite sample in 5.5-mm-o.d. glass tubes under vacuum. The temperature was increased from 298 K to 673 K at a rate of 10 K h^{-1}. The samples were further maintained at 673 K for 24 h under vacuum ($<10^{-2}$ Pa), then cooled to room temperature. The loading of the zeolite with propane was performed at room temperature with 4 propane molecules per unit cell (ca. 600 μmol g^{-1}). Then the glass tube (12-mm long) was sealed off. The NMR probe including the sample was preheated at 180 °C for 20 min before the start of NMR measurements. H/D exchange does not occur at this temperature. The temperature was rapidly increased over 3–10 min by 50–120 K to the temperature of the exchange measurement, equilibrated for 1–2 min, after which signal acquisition was started. Note that the chemical conversion of propane via cracking or dehydrogenation did not occur to a notable degree under the conditions of our experiment, so H/D exchange and ^{13}C-label scrambling were the main transformations of the propane.

2.2. NMR measurements

In situ ^{1}H and ^{13}C MAS NMR measurements were performed on a Bruker Avance 400 spectrometer at 230–280 °C using a Bruker high-temperature probe. Larmor frequencies were 400.13 MHz for ^{1}H nuclei and 100.619 MHz for ^{13}C nuclei. The rotation frequency of a 7-mm rotor with the inserted sealed glass tube was 3–4 kHz. For ^{1}H NMR, free induction decays (FIDs) were recorded with the 45° preparation pulses of 3.6 μs duration, 25 μs ring-down delay, 4 s recycle delay, and 24 scans for signal accumulation. For ^{13}C NMR, FIDs 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 accuracy of the determination of the relative line position with respect to TMS was 0.05 ppm. The sample temperature was controlled by a Bruker BVT-1000 variable-temperature unit. Calibration of the temperature inside the rotor was performed with an accuracy of ±2 K by means of a lead nitrate sample as a ^{207}Pb MAS NMR chemical shift thermometer [16].

2.3. Analysis of reaction rates

The apparent rate constant, k, for the H/D exchange between deuterated propane and acidic OH groups of the zeolite, which is usually identified with the rate for H/D exchange [1], has been determined by simple exponential fits:

$$I_t = I_\infty\left[1 - \exp(-kt)\right], \quad I_t = I_0\left[\exp(-kt)\right], \tag{1}$$

where I_t, I_∞, and I_0 denote the integral intensities of signals from CH_n groups ($n = 2$ or 3) in the ^{1}H MAS NMR spectra at the observation time t, $t = \infty$ (equilibrium), or $t = 0$, respectively. The time $t = 0$ corresponds to the start of the experiment, when the temperature is rapidly increased from room temperature to the desired temperature. Similar expressions were used to estimate the rate constants for ^{13}C-label scrambling in the adsorbed propane-2-^{13}C.

Kinetic data were simulated in accordance with either consecutive or parallel schemes of the exchange (vide infra, Schemes 3 and 4). The first-order kinetic equations were used for the modeling. The solution of the system of kinetic equations within each of the kinetic schemes contained four variable parameters: rate constants k_1 and k_3 and equilibrium constants K_{eq1} and K_{eq2}. The equilibrium constants were assumed to correspond to the expected statistical distribution of protium isotope after the exchange is finished. The rate constants were adjusted to fit the observed kinetic curves.

3. Results and discussion

Adsorbed propane exhibits two distinct signals from the methyl groups (1.0 ppm) and methylene group (1.5 ppm) in the ^{1}H MAS NMR spectrum at the temperature range of 180–300 °C, where hydrogen exchange is observed for propane on zeolite H-ZSM-5 (see Fig. 1 in [14]). These two signals correspond to propane molecules in the NMR time scale in a fast exchange between the locations in the zeolite pores and the gas phase in the intercrystalline space of the zeolite sample. Two separate signals from propane means that a transfer of the hydrogen isotope, protium, from the acidic (bridging) SiOHAl groups to the deuterated propane can be monitored for both methyl and methylene groups in situ with ^{1}H MAS NMR. Selective or preferential exchange to either methyl or methylene groups can be clearly distinguished by monitoring the reaction kinetics, because the selective exchange would imply an essentially faster rate of the protium transfer to one of the two groups.

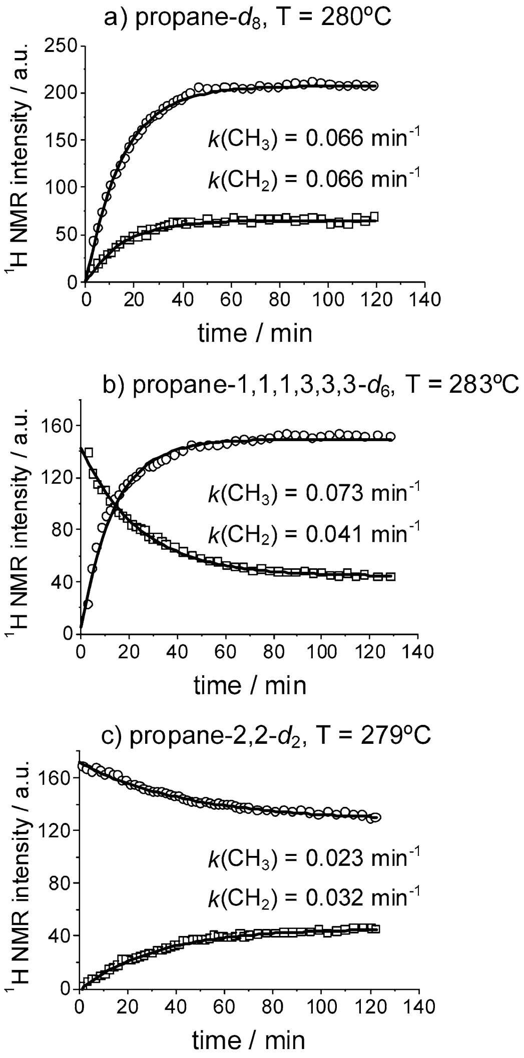
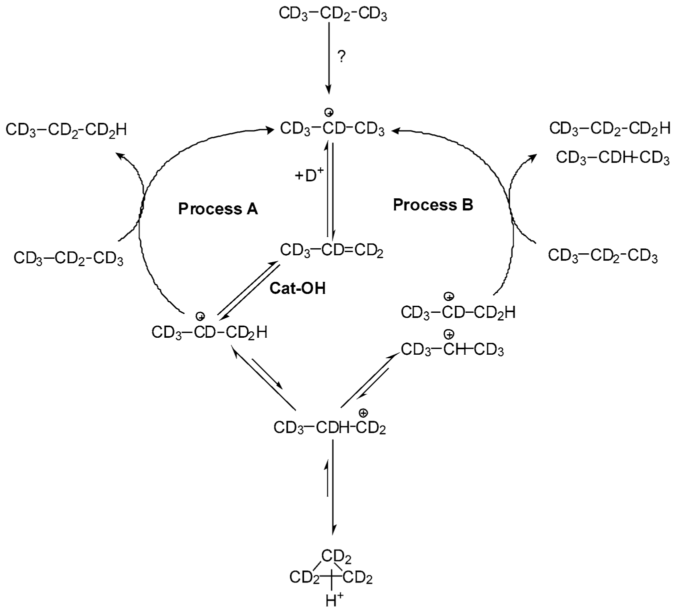


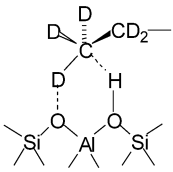
Fig. 1. Kinetics of hydrogen exchange between acidic OH groups of H-ZSM-5 and methyl (○) and methylene (□) groups for deuterated propane. The curves were fitted (solid lines) with apparent rate constants $k(CH_3)$ and $k(CH_2)$ on the basis of Eq. (1).

Fig. 1a shows the kinetics of the protium transfer from the zeolite to the methyl and methylene groups of propane, which initially was fully deuterated (propane-d_8). It is seen that the intensities of the ^{1}H MAS NMR signals for both methyl and methylene group increase with time. The 3:1 ratio of the signal intensities of methyl to methylene groups is retained from the start until the end of the observed time interval. The apparent rate constants for the protium transfer to both methyl $k(CH_3)$ and methylene $k(CH_2)$ groups are also similar (Fig. 1a). These results confirm our previous findings that there is no evident selective or prevailing protium transfer into any fragment of the deuterated propane molecule [14]. Both methyl and methylene groups are equally involved in the exchange.

We can use two mechanisms, 1 and 2, to rationalize the experimental results. Mechanism 1 assumes that hydrogen exchange occurs through the formation of propene and isopropyl carbenium ion as intermediates in a catalytic cycle, proposed by Haouas et al. [13] (see Scheme 1). Mechanism 1 implies a regioselective exchange into the methyl groups (process A in



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. Adopted from Ref. [13].



Scheme 2. Transition state for the direct hydrogen exchange between CD_n ($n = 2, 3$) groups of propane-d_8 and acid sites of H-ZSM-5.

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. This mechanism means a *consecutive* scheme of hydrogen exchange; that is, the exchange occurs first from the zeolite OH groups into the methyl groups and then from the methyl groups into the methylene group. The nonselective exchange observed for propane-d_8 on H-ZSM-5 [14] could imply that process B proceeds at a much higher rate than process A.

For mechanism 2, either the methyl groups or the methylene group exchange with the acidic OH group independently of each other, without the formation of a common intermediate (isopropyl cation in Scheme 1). Each of the groups exchanges directly through the formation of a pentacoordinated transition state, with the exchanging hydrogen atoms at a halfway position between the carbon of the methyl or methylene group and the zeolitic oxygen atoms (see Scheme 2). Mechanism 2 was concluded for methane and ethane in theoretical considerations of the exchange in alkanes [6] and suggested for propane in our previous NMR study [14] and in IR studies by others [4,17]. This mechanism implies a *parallel* scheme of exchange of the SiOHAl group with the methyl and methylene groups.

Next we discuss consecutive and parallel schemes of the exchange to rationalize the experimental kinetics for variously deuterated propane.

$$\mathrm{A} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{B} \underset{k_4}{\overset{k_3}{\rightleftarrows}} \mathrm{C}$$

Scheme 3. The consecutive scheme for hydrogen exchange.

3.1. *The consecutive scheme for hydrogen exchange*

Similar apparent rates for protium transfer from the bridging OH group into methyl and methylene groups of propane-d_8 (see Fig. 1a) should imply that the rate of intramolecular H scrambling from methyl into the methylene group is significantly higher that into methyl groups, if the consecutive scheme of the exchange is considered. The kinetic data were simulated to verify the ratio between the rate constant for the exchange into the methyl groups and the constant for H scrambling between the methyl and methylene groups under the condition of equal apparent rate constants of the exchange into both methyl and methylene groups. A simple reaction scheme (Scheme 3) was chosen to follow the consecutive transfer of protium from the zeolite OH groups first into the deuterated methyl groups and then into the methylene groups.

In Scheme 3, A denotes protons of the acidic (bridging) OH group, and B and C are the protons of the methyl and methylene groups, respectively. The rate constants k_1 and k_3 describe the exchange into methyl and methylene groups, respectively. Equilibrium constants $K_{\mathrm{eq}1} = k_1/k_2$ and $K_{\mathrm{eq}2} = k_3/k_4$ are defined by the statistical distribution of the protium isotope and are equal to 3.0 and 0.33, respectively, under our conditions.

The simulation shows that experimental curves in Fig. 2a with similar apparent rate constants $k(\mathrm{CH_3})$ and $k(\mathrm{CH_2})$ could be well fitted with k_1 and k_3 for mechanism 1, provided that $k_3 \geqslant 5k_1$. This implies that the growth of the signal intensities from the methyl and methylene groups with similar apparent rate constants could be possible via mechanism 1 if the rate constant k_3 for the intramolecular H scrambling is at least five times higher than that for hydrogen exchange with the methyl groups.

For the kinetics of the exchange for propane-1,1,1,3,3,3-d_6 (propane-d_6) and propane-2,2-d_2 (propane-d_2) with $k_3 \geqslant 5k_1$, one can expect a priori a very rapid increase in the intensity of the ^{1}H NMR signal from the formerly deuterated group and a rapid decrease of that from the formerly protonated groups at the beginning of the reaction, if intramolecular H scrambling occurs. A further slow variation in intensity should be caused by the exchange between the methyl groups and the zeolite acid groups. Fig. 1b shows the kinetic curves of protium enrichment in the methyl groups and protium depletion in the methylene group of propane-d_6. It can be seen that the ^{1}H concentration in the methyl groups increases faster than it decreases in the methylene groups, $k(\mathrm{CH_3}) > k(\mathrm{CH_2})$. The rapid increase in the intensity of the methyl groups and rapid decrease in the intensity of the methylene group expected for the condition $k_3 \geqslant 5k_1$, which has been found for propane-d_8, is not observed. This is also valid for propane-d_2 (see Fig. 1c). Therefore, simulations of the experimental kinetics for propane-d_6 and propane-d_2 in accordance with the consecutive scheme of the exchange (Scheme 3), which uses a ratio of k_3 to k_1 similar to that of

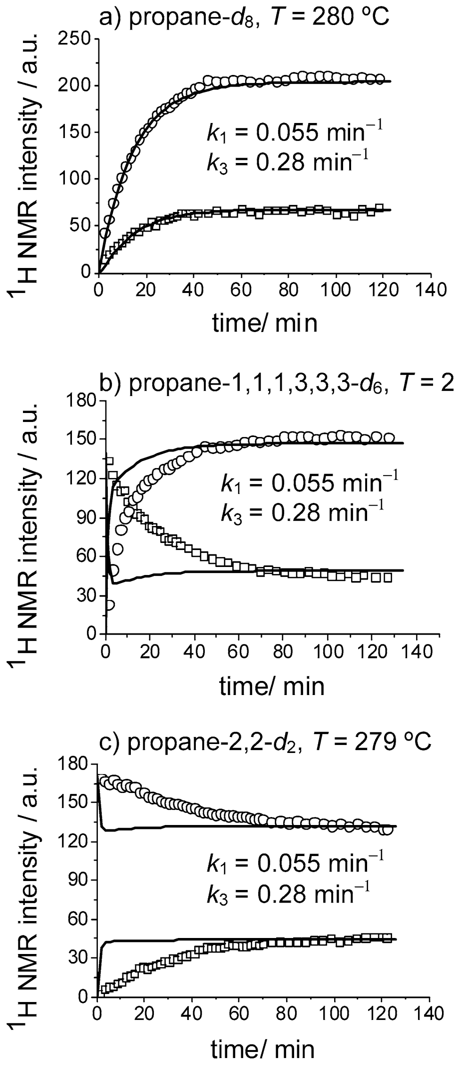


Fig. 2. Simulation of the kinetics of the hydrogen exchange between acidic OH groups of H-ZSM-5 and methyl (○) and methylene (□) groups for differently deuterated propane in accordance to consecutive scheme of hydrogen exchange and $k_1 = 0.055$ min^{-1} and $k_3 = 0.28$ min^{-1}. The solid curves are the kinetics, which are expected for the exchange in accordance with the Scheme 3, provided that $k_3 \geqslant 5k_1$.

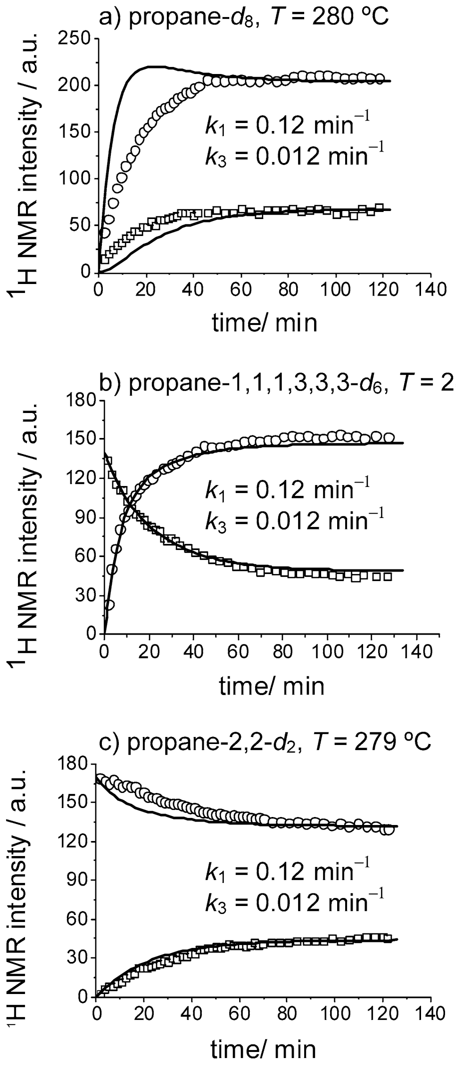


Fig. 3. Simulation of the kinetics of the hydrogen exchange between acidic OH groups of H-ZSM-5 and methyl (○) and methylene (□) groups for differently deuterated propane in accordance to the consecutive scheme of hydrogen exchange and $k_1 = 0.12$ min^{-1} and $k_3 = 0.012$ min^{-1}. The solid curves are the kinetics, which are expected for the exchange in accordance with the Scheme 3, provided that $k_1 = 10k_3$.

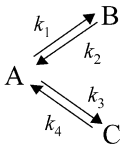
propane-d_8, clearly demonstrate that the simulated curves do not fit experimental kinetics (see Figs. 2b and 2c). To meet condition $k_3 \geqslant 5k_1$ and the consecutive scheme, a depletion of protons of the methylene group for propane-d_6 and the methyl groups for propane-d_2 should occur much faster than the experimentally observed rate (see the solid curves in Figs. 2b and 2c).

Experimental curves for propane-d_6 were well fitted with $k_1 = 0.12$ min^{-1} and $k_3 = 0.012$ min^{-1} (see Fig. 3b). This could imply faster enrichment of the methyl group with protium compared with the protium depletion in the methylene group. This $k_1/k_3 = 10$ ratio would imply a regioselective exchange for propane-d_8. Almost exclusive growth in the intensity of the methyl groups would be observed within the first 10 min of the exchange reaction (see the simulated solid curve in Fig. 3a). For propane-d_2, protium depletion in the methyl groups would also occur faster (see the solid curve for the methyl groups in Fig. 3c). So it follows from the experimental kinetics for propane-d_8 and propane-d_2 that the condition $k_1 = 10k_3$ does not describe the consecutive scheme of the exchange.

Thus, an analysis of the kinetics of hydrogen exchange shows no consistency among the kinetics of the exchange for the three differently deuterated propanes in the frame of the consecutive scheme. The consecutive scheme, in which the exchange would occur first to the methyl groups of propane and then essentially faster to the methylene group by an H-scrambling mechanism, is not in agreement with the experimental kinetic data.

3.2. *The parallel scheme for hydrogen exchange*

The parallel exchange of the methyl and methylene groups of propane with acidic OH groups can be described by the simple Scheme 4. In this scheme, A denotes protons of the zeolitic bridging OH groups, and B and C are the protons of the methyl



Scheme 4. The parallel scheme for the hydrogen exchange.

$$CH_3\text{-}^{13}CH_2\text{-}CH_3 \underset{k^C_2}{\overset{k^C_1}{\rightleftarrows}} {}^{13}CH_3\text{-}CH_2\text{-}CH_3$$

Scheme 5. ^{13}C-label scrambling in propane adsorbed on H-ZSM-5.

and methylene groups, respectively. The rate constants k_1 and k_3 describe the exchange into methyl and methylene groups, respectively. The equilibrium constants are $K_{eq1} = k_1/k_2 = 3.0$ and $K_{eq2} = k_3/k_4 = 1$.

Similar apparent rates of the exchange for the methyl and methylene groups for propane-d_8 would imply similar rates k_1 and k_3 for the parallel scheme of the exchange. Slower apparent rates of protium depletion in the initially nondeuterated groups in propane-d_6 and propane-d_2 can be explained by the fact that the Scheme 4 does not consider the bimolecular character of the exchange. Indeed, the apparent rate constants of protium depletion in the CH_2 and CH_3 groups are proportional to the concentration of acidic OD groups, which are not initially present in acidic sites but appear there only after exchange with deuterated methyl or methylene groups.

A simulation of the experimental kinetics in accordance with Scheme 4 in Fig. 4 shows that for each of the three differently deuterated propanes, k_1 is larger than k_3, with a k_1/k_3 ratio ≈ 3. This demonstrates the apparent consistency of the kinetics for the three differently deuterated propanes and thus favors the parallel scheme of hydrogen exchange for propane. The difference in the absolute values of k_1 and k_3 for the differently labeled propane molecules can be explained by a simplified model for rate constant estimation. It does not take into account a particular distribution of deuterium and protium isotopes during the exchange and ignores the involvement of acidic OH/OD groups of the zeolite in the considered model of the exchange. Disregarding the intramolecular transfer between the methyl and methylene groups can also contribute to the observed difference of the k_1 and k_3 values. A contribution of the ^{1}H intramolecular transfer can be estimated by analyzing the kinetics of ^{13}C-label scrambling in adsorbed propane, as we discuss next.

3.3. Kinetics of ^{13}C-label scrambling

It has been demonstrated that ^{13}C-label scrambling occurs for propane on H-ZSM-5 at about 300 °C [18]. ^{13}C-label scrambling in the adsorbed propane can provide information on propyl cation formation [19,20]. It has been shown that ^{13}C-label scrambling is accompanied by H scrambling for isopropyl cation in a superacid [19–21]. Both H and C scrambling have a common intermediate, isopropyl cation. Their activation energies are similar, but H scrambling occurs three times faster by a hydride shift reaction than ^{13}C-label scrambling through protonated cyclopropane [19–21]. The rate of the ^{13}C-label scrambling can be used to estimate how intramolecular H scrambling reduces regioselectivity in the second step of the consecutive scheme of hydrogen exchange. Therefore, we performed an in situ ^{13}C MAS NMR monitoring of the kinetics of the ^{13}C-label scrambling in the adsorbed propane.

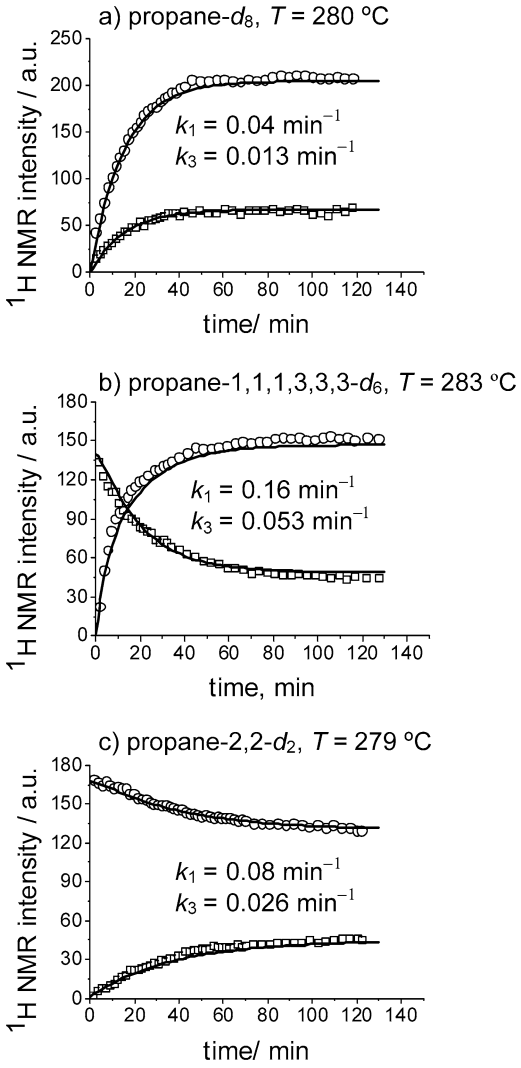


Fig. 4. Simulation of the kinetics of the hydrogen exchange between the acidic OH groups of H-ZSM-5 and the methyl (○) and the methylene (□) groups for differently deuterated propane in accordance to parallel scheme of the exchange. The solid curves are the fits to the kinetics, which are expected for the exchange in accordance with the Scheme 4 and k_1 and k_3, indicated nearby each pair of kinetic curves.

Fig. 5 shows the kinetics of the transfer of the ^{13}C-label from the methylene group of propane into its methyl groups. The rate constant k_1^C for the ^{13}C-label transfer from the CH_3 groups into the CH_2 group is estimated as 0.0036 min^{-1} at 281 °C. If we assume that intramolecular H scrambling occurs with a rate constant three times as high as k_1^C, similar to the ratio of H and C scrambling in superacids [20], then the rate constant k_3 for the consecutive scheme of the exchange should be 0.011 min^{-1}. This is at least one order of magnitude less than the value of intramolecular H scrambling, $k_3 = 0.28$ min^{-1}, expected for propane-d_8 within a frame of the consecutive scheme of the

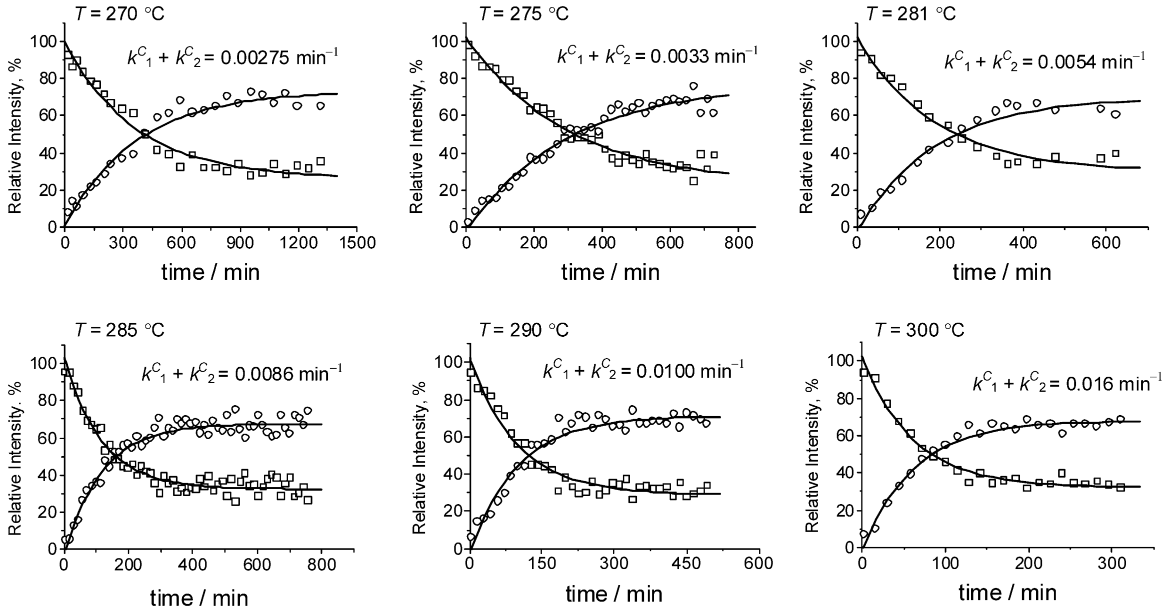


Fig. 5. Kinetics of ^{13}C-label scrambling for propane adsorbed on H-ZSM-5. Propane was initially ^{13}C-labeled in the methylene group, therefore, the intensity of the methylene group signal (□) decreases, whereas that of the methyl groups (○) increases. The solid curves are the fits to the kinetics with the sum $k_1^C + k_2^C$ expected for the exchange in accordance with the Scheme 5.

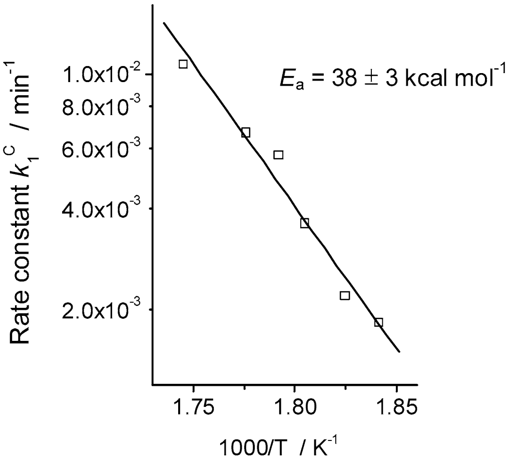


Fig. 6. Arrhenius plot of the rate constant k_1^C for the ^{13}C-label scrambling in propane on zeolite H-ZSM-5.

exchange (Fig. 2a). This implies that intramolecular H scrambling, supplementary to ^{13}C-label scrambling, cannot provide protium transfer from the methyl group into the methylene group at a sufficiently high rate to satisfy the similar apparent rate of exchange for propane-d_8 or the condition $k_3 \geqslant 5k_1$ for the consecutive scheme of the exchange.

The Arrhenius plot in Fig. 6 yields the activation energy of 38 kcal mol^{-1}. This value is higher than the activation energy of hydrogen exchange for both methyl and methylene groups ($E_a = 28 \pm 3$ kcal mol^{-1}) determined from the temperature dependence of the apparent rate constants of the exchange for propane-d_8 within the temperature range 230–280 °C. The different values of the activation energies for ^{13}C-label scrambling and H/D exchange into the methylene group hint at different transition states for these two processes [20]. Moreover, as we have already noted (vide supra), too low a rate of ^{13}C-label scrambling cannot provide similar apparent rate constants for the methyl and methylene groups of propane-d_8 to satisfy the consecutive scheme of the exchange.

Thus the present study provides evidence that the consecutive scheme of the hydrogen exchange is not realized for propane adsorbed on zeolite H-ZSM-5. The exchange occurs for both methyl and methylene groups via the parallel scheme. Intramolecular H scrambling with the formation of a propyl cation as an intermediate or transition state can contribute to the transfer of the protium atom from the methyl groups into the methylene group, but this contribution is at least one order of magnitude slower than the rate of direct exchange of the methylene group with the zeolite acid sites.

4. Conclusions

Based on in situ by ^{1}H MAS NMR and ^{13}C MAS NMR spectroscopy in the temperature range 230–300 °C, we can draw the following conclusions about the hydrogen exchange between the Brönsted acid sites of zeolite H-ZSM-5 and differently deuterated propane molecules (propane-d_8, propane-1,1,1,3,3,3-d_6, and propane-2,2-d_2), and also about ^{13}C-label scrambling in ^{13}C-labeled propane Both the methyl and methylene groups of propane are involved in the exchange directly with acidic groups of the zeolite. Either the methyl or the methylene group of propane molecule exchanges via a concerted mechanism with a pentacoordinated carbonium ion as the transition state, rather than via the formation of a carbenium ion intermediate. The exchange into the methyl groups occurs faster than the exchange into the methylene groups within the framework of the established carbonium ion mechanism. This accounts for the regioselectivity of the exchange for propane on acidic zeolites as reported by Sommer et al. [9]. Intramolecular H scrambling is one order of magnitude slower than the hydrogen exchange for both methyl and methylene groups with the zeolite acidic OH groups. Intramolecular H scrambling cannot provide a loss of regioselectivity of the exchange into the methyl group of deuterated propane at temperatures $>100\,^\circ\mathrm{C}$ by the fast intramolecular transfer of the protium atom from the methyl groups into the methylene group in the skeletal rearrangement process of carbenium ion intermediate, as was suggested earlier [13].

Acknowledgments

This work was supported by the Russian Foundation for Basic research (grant 04-03-32372), INTAS (grant 03-51-5286) and the Deutsche Forschungsgemeinschaft (project FR 902/15). M.V.L. acknowledges financial support from the Russian Science Support Foundation.

References

[1] A. Ozaki, Isotopic Studies of Heterogeneous Catalysis, Kodansha, Tokyo, 1977.
[2] G.J. Kramer, R.A. van Santen, C.A. Emeis, A.K. Nowak, Nature 363 (1993) 529.
[3] G.L. Kramer, R.A. van Santen, J. Am. Chem. Soc. 117 (1995) 1766.
[4] B. Lee, J.N. Kondo, F. Wakabayashi, K. Domen, Catal. Lett. 59 (1999) 51.
[5] W. Hua, A. Goeppert, J. Sommer, J. Catal. 197 (2001) 406.
[6] S.R. Blaszkowski, M.A.C. Nascimento, R.A. van Santen, J. Phys. Chem. 100 (1996) 3463.
[7] S.G. Hindin, G.A. Mills, A.G. Oblad, J. Am. Chem. Soc. 73 (1951) 278.
[8] J. Engelhardt, W.K. Hall, J. Catal. 151 (1995) 1.
[9] J. Sommer, M. Hachoumy, F. Garin, D. Barthomeuf, J. Vedrine, J. Am. Chem. Soc. 117 (1995) 1135.
[10] J.W. Otvos, D.P. Stevenson, C.D. Wagner, O. Beeck, J. Am. Chem. Soc. 73 (1951) 5741.
[11] M. Haouas, S. Walspurger, F. Taulelle, J. Sommer, J. Am. Chem. Soc. 126 (2004) 599.
[12] J. Sommer, D. Habermacher, R. Jost, A. Sassi, A.G. Stepanov, M.V. Luzgin, D. Freude, H. Ernst, J. Martens, J. Catal. 181 (1999) 265.
[13] M. Haouas, S. Walspurger, J. Sommer, J. Catal. 215 (2003) 122.
[14] A.G. Stepanov, H. Ernst, D. Freude, Catal. Lett. 54 (1998) 1.
[15] G. Engelhardt, D. Michel, High-Resolution Solid-State NMR of Silicalites and Zeolites, Wiley, Chichester, 1987.
[16] D.B. Ferguson, J.F. Haw, Anal. Chem. 67 (1995) 3342.
[17] J.A. Lercher, R.A. van Santen, H. Vinek, Catal. Lett. 27 (1994) 91.
[18] E.G. Derouane, S.B.A. Hamid, I.I. Ivanova, N. Blom, P.E. Hojlundnielsen, J. Mol. Catal. 86 (1994) 371.
[19] M. Saunders, E.L. Hagen, J. Am. Chem. Soc. 90 (1968) 6881.
[20] M. Saunders, A.P. Hewett, O. Kronja, Croat. Chem. Acta 65 (1992) 673.
[21] M. Saunders, P. Vogel, E.L. Hagen, J. Rosenfeld, Acc. Chem. Res. 6 (1973) 53.