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In situ ^{1}H MAS NMR studies of the H/D exchange of deuterated propane adsorbed on zeolite H-ZSM-5

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The hydrogen exchange in the propane-d_8 loaded zeolite H-ZSM-5 was monitored by *in situ* ^{1}H MAS NMR spectroscopy within the temperature range 457–543 K. Measurements of the H/D exchange between the acidic hydroxyl groups of the zeolite and the adsorbed deuterated propane molecules show that both methyl and methylene groups of alkane are involved in the exchange. The comparison of the experimentally obtained apparent activation energies for the exchange in methyl groups (108 ± 7 kJ mol^{-1}) and methylene groups (117 ± 7 kJ mol^{-1}) with theoretical values for methane and ethane supports the assumption that the H/D exchange for methyl and methylene groups takes place via a pentavalent transition state.

Keywords: hydrogen exchange, zeolite H-ZSM-5, propane, *in situ* ^{1}H MAS NMR

1. Introduction

Hydrogen exchange between alkanes and acidic OH groups of zeolites involves steps in which a cleavage and formation of C–H bonds in a hydrocarbon and of O–H bonds in acidic hydroxyl groups occur. An H/D exchange in the deuterated alkane implies the activation of the molecule. Various experimental [1–13] and theoretical [1,6–8,14] studies were carried out, in order to clarify both the mechanism of hydrogen exchange itself and its relation to the cracking and dehydrogenation of alkanes. Usually H/D exchange proceeds on zeolites at 620–770 K in parallel with cracking or dehydrogenation. However, the rate of hydrogen exchange is essentially higher compared to those of cracking or dehydrogenation [1,6,7,12].

Recently, the hydrogen exchange in small alkanes adsorbed on acidic zeolites could be observed even at lower temperature (370–470 K), while cracking and dehydrogenation were not observed [4,5,9–11]. This is in agreement with the more earlier finding for hydrogen exchange in small alkanes adsorbed on silica–alumina [14]. It could be shown that this exchange is regiospecific, e.g., for isobutane on zeolite H-ZSM-5 only methyl groups are involved in the H/D exchange [9–11,14]. Regiospecificity of hydrogen exchange implies that the exchange cannot be considered as proceeding via a simple transfer of the zeolitic proton to alkane and the symmetrical return of the hydrogen atom from alkane to the zeolite [7,13]. Other mechanisms may be involved in regiospecific H/D exchange, e.g., via formation of intermediate carbenium ions [9,14].

In this paper we present *in situ* ^{1}H MAS NMR studies of the kinetics of the H/D exchange between propane molecules and acidic OH groups (SiOHAl) in zeolite H-ZSM-5. ^{1}H MAS NMR allows selective monitoring of the hydrogen exchange for CH_3 and CH_2 groups of small alkanes, in contrary to the IR spectroscopy [4,12]. The simultaneous observation of the H/D exchange in the methyl and in the methylene groups of the propane molecules should give additional information on both the mechanism of H/D exchange in particular and on alkane activation in common.

2. Experimental

Zeolite H-ZSM-5 ($Si/Al = 35$) was synthesized by Schwieger [15] using mono-n-propylamine as template, then calcined at 600 °C for 5 h and finally exchanged with 0.5 M HCl. Samples for NMR measurements were prepared by heating 80 mg zeolite in glass tubes with 5 mm outer diameter. The temperature was increased at a rate of 10 K h^{-1} under vacuum. Samples were maintained at 400 °C at less than 10^{-2} Pa for 24 h, loaded at room temperature with 4 molecules of deuterated propane-d_8 (C_3D_8, 98% ^{2}H isotope enrichment) per unit cell and sealed off (10 mm length of the glass tube). This corresponds to a loading of 700 μmol propane per gram of dehydrated zeolite. Some samples were loaded in addition with an equal concentration of water or CO or with 70 μmol g^{-1} propene.

In situ ^{1}H MAS NMR measurements were performed on a Bruker MSL 300 spectrometer at 457–543 K at a Larmor frequency of 300 MHz and a rotation frequency of ca. 4 kHz. Free induction decays (FID) were recorded with 45° flip angle preparation pulses of 3.5 μs duration, 25 μs ring down delay, 2–4 s recycle delay and 24–48 scans for accumulation. The interval between two steps in the time scale of the kinetics ranged from 1 min to 1 h in dependence of temperature and corresponding rate of hydrogen transfer. The accuracy of the determination of the relative line position with respect to TMS was 0.05 ppm.

The measuring temperature was controlled by a Bruker BVT-2000 variable-temperature unit. The calibration of the temperature inside the sample could be made with an accuracy of ±2 K by means of a lead nitrate sample as ^{207}Pb MAS NMR chemical shift thermometer [16].

The rate R of the H/D exchange between deuterated propane and acidic OH group of the zeolite was determined by an exponential fit [1]:

$$I_t = I_\infty \left[1 - \exp(-Rt)\right], \qquad (1)$$

where I_t and I_∞ 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 and at $t = \infty$ (equilibrium), respectively. The time $t = 0$ corresponds to the start of the experiment, when the temperature was increased from room temperature to the desired exchange temperature.

3. Results and discussion

Figure 1 shows the stack plot of the ^{1}H MAS NMR spectra of propane (C_3D_8) adsorbed on zeolite H-ZSM-5, which was measured in dependence of the exchange time at 519 K. The increasing intensity of the signals from methyl and methylene groups at 1.0 and 1.45 ppm, respectively, shows the transfer of protons from the acidic hydroxyl groups to the deuterated propane molecules. The ratio between the intensities of the CH_3 and CH_2 groups in the final spectrum is 3 : 1. This finding implies that both methyl and methylene groups are involved in the hydrogen exchange and that no isotope effect can be observed with respect to methyl and methylene groups.

The kinetics of the hydrogen exchange shows that the rates of exchange are significantly different for methyl and methylene groups, see table 1. The apparent activation energies, see table 2, were obtained by Arrhenius plots of the exchange rate vs. temperature, cf. figure 3. The activation energy for methylene groups exceeds the value for the methyl groups by 9 kJ mol^{-1}. The values of apparent activation energies for both methyl and methylene groups are close to the activation energy obtained from theoretical calculations of hydrogen exchange for methane with 122 kJ mol^{-1} [6] or ethane with 118 kJ mol^{-1} [7].

A carbenium ion ($*$) or a pentavalent transition state ($**$) may be considered to account for the experimental observations. ($*$) involves a formation of carbenium ion as intermediate or transition state by means of hydride abstraction from propane, as it has been suggested for isobutane on solid acids [9–11,14]. ($**$) involves the transfer of the zeolitic hydroxyl protons to the propane molecule and the symmetrical return of one of the hydrogen atoms from either methyl or methylene group to the oxygen atom of the zeolite framework via a pentavalent transition state of the carbon atom, as suggested in theoretical considerations of the exchange [6,7,13].

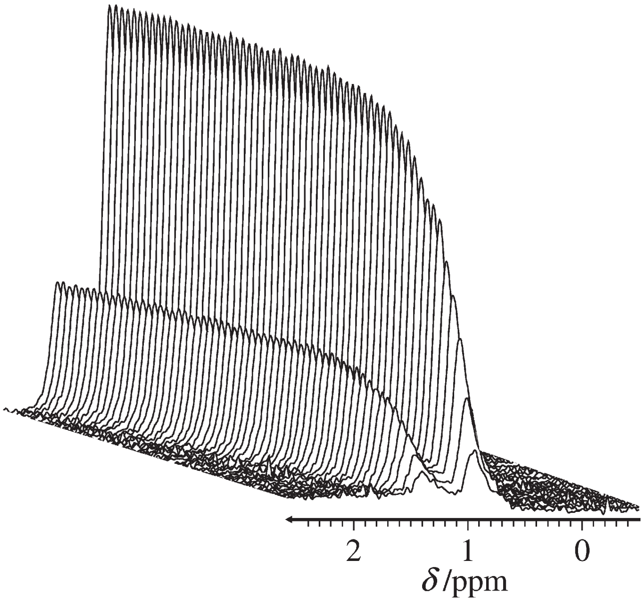

Figure 1. Stack plot of the ^{1}H MAS NMR spectra of the methyl groups (1.0 ppm) and methylene groups (1.45 ppm) of propane-d_8 at 519 K. The first spectrum (bottom) was recorded at $t = 3$ min, the last spectrum (top) at $t = 5$ h. The time between subsequent spectra was 5 min.

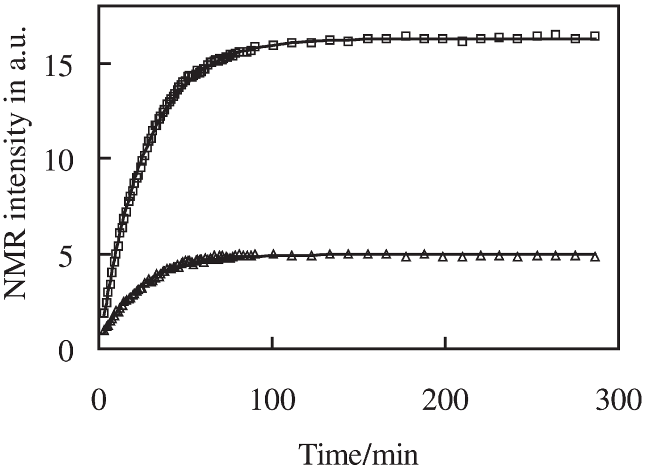

Figure 2. Kinetics of the proton transfer from the acidic OH groups of the zeolite to the methyl groups (□) and methylene groups (△) of the adsorbed propane-d_8 at 519 K. Solid lines represent the fits using $R(CH_3) = 0.03816$ min^{-1} and $R(CH_2) = 0.0436$ min^{-1} for equation (1).

The formation of a propenium cation intermediate, which is in equilibrium with propene, should lead to a regiospecific H/D exchange with a protium enrichment in the methyl group, as it is often observed for propene [1] and isobutane [9–11,14], where only methyl groups were involved in the hydrogen exchange. Therefore, an absence of preferential enrichment of protium in methyl groups indicates that the carbenium ion mechanism, which would involve a formation of a CH_3–CH^+–CH_3 carbenium ion, which is extremely unstable in zeolites [17,18], via hydride abstraction from propane, does not contribute to the hydrogen exchange. Since the C–H bonds of both methyl and methylene groups are exchanged independently without in-

Table 1
Hydrogen exchange rates for the methyl and methylene groups of propane and propane plus additives (propene, water and CO) obtained from the intensities of the ^{1}H MAS NMR spectra. The experimental error of the exchange rates is ±5%.

T (K)	Exchange rate R (1000 min^{-1})									
	Propane		Propane + propene		Propane + H_2O		Propane + CO		Propane + CO + H_2O	
	CH_3	CH_2	CH_3	CH_2	CH_3	CH_2	CH_3	CH_2	CH_3	CH_2
457	1.31	1.05	1.37	1.25	0.95	0.80			0.945	1.28
473	3.10	3.50	3.20	3.11	2.00	1.75	1.43	1.43	1.95	2.63
481							1.99	2.33		
509							7.23	11.7		
519	38.2	43.6	34.2	35.0	28.0	29.0	12.3	20.6	22.4	59.8
543							43.9	49.9		

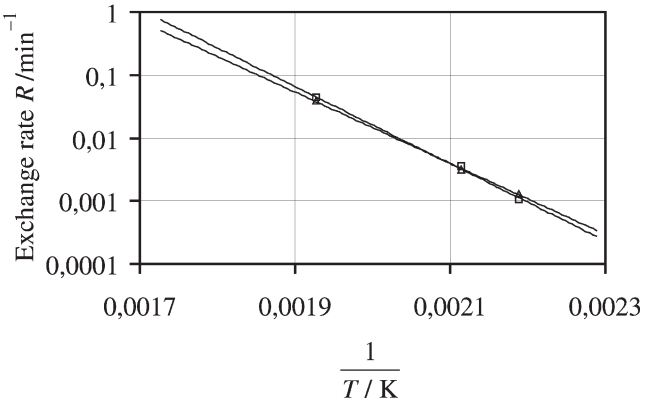

Figure 3. Arrhenius plot of the hydrogen exchange rate for methyl groups (△) and methylene groups (□) of propane.

Table 2
Apparent activation energies for hydrogen exchange of the methyl and methylene groups of propane and propane plus additives (propene, water and CO) obtained from the values in table 1 by an Arrhenius fit.

Loading	Activation energy (kJ mol^{-1})	
	CH_3	CH_2
Propane	108 ± 7	117 ± 7
Propane + propene	103 ± 6	106 ± 5
Propane + H_2O	109 ± 10	116 ± 11
Propane + CO	103 ± 9	111 ± 7
Propane + CO + H_2O	102 ± 8	125 ± 18

volvement of a common intermediate, the existence of a pentavalent transition state with the exchanging hydrogen atoms at half-way between carbons of methyl (methylene) groups and zeolitic oxygen atoms becomes more likely. The different exchange rate for methylene groups may be related to the different ability for protonation of the primary and secondary C–H bonds in alkanes, which in accordance with Olah's empirical rule [19] should be higher for the secondary C–H bond in the methylene group of propane. It could be shown by ^{13}C MAS NMR spectroscopy at room temperature that no additional signals appear after the *in situ* ^{1}H MAS NMR measurements at higher temperature. Only a heating of the zeolite sample with adsorbed propane at 523 K for 20 h gives rise to a 1–3% propane conversion via cracking and disproportionation reactions [20]. Therefore, the degree of conversion of propane upon heating even at 519 K for less than 5 h is extremely low and does not affect the observation of the H–D exchange. But it should be noted that an intermolecular hydrogen exchange between adsorbed propane molecules, which was observed for isobutane on H-Y zeolite [10], cannot be observed by means of the applied ^{1}H MAS NMR technique.

Also the coadsorption of other molecules does not support the carbenium ion mechanism: The increase of the exchange rate upon coadsorption of a small amount of propene, which would be expected if a carbenium ion intermediate formed from olefin is involved in alkane activation reaction, was not observed. On the contrary, the rate of exchange for both methyl and methylene groups decreases, see table 1. In the presence of water or CO molecules, which coordinate to the acidic hydroxyl groups and reduce the interaction of propane with these groups, the observed rate of exchange decreases too. A suppression of the H–D exchange would be expected, if the propenium cation intermediate could be involved in the hydrogen exchange, as has been observed for isobutane [21]. But this suppression of the H–D exchange does not occur. It is remarkable that in all cases the rate of exchange and apparent activation energy for the exchange is higher for methylene groups than for methyl groups, see table 2. This implies that the presence of additives such as olefin, CO or water does not influence the mechanism of hydrogen exchange. This confirms that the exchange proceeds via formation of a pentavalent transition state of carbon atoms of the alkane.

4. Conclusions

In situ ^{1}H MAS NMR studies of the kinetics of the H/D exchange between acidic OH groups in zeolite H-ZSM-5 and adsorbed deuterated propane molecules show that both the methyl groups and the methylene groups of propane are involved in the hydrogen exchange. The exchange with methyl groups is different from that with methylene groups due to the different protonation ability of the primary and secondary C–H bonds of alkanes adsorbed on acidic hydroxyl groups in zeolites. Apparent activation energies for both methyl and methylene groups are close to those estimated by theoretical methods [6,7,13]. The exchange is considered as proceeding for both CH_3 and CH_2 independently via a transfer of a hydroxyl proton to an alkane molecule and the symmetrical return of a hydrogen atom from alkane to an oxygen of the zeolite framework.

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