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Regioselective H/D exchange of propane on Zn/H-MFI zeolite

A. G. Stepanov,[a],* S. S. Arzumanov,[a] V. N. Parmon,[a] Yu. G. Kolyagin,[b] I. I. Ivanova,[b] and D. Freude[c],*

[a]*Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Prospekt Akademika Lavrentieva 5, Novosibirsk 630090, Russia*
[b]*Department of Chemistry, Moscow State University, Lenin Hills 1, Bld. 3, Moscow 119992, Russia*
[c]*Abteilung Grenzflächenphysik, Universität Leipzig, Linnéstraße 5, Leipzig 04103, Germany*

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The hydrogen exchange for propane-d_8 adsorbed on zeolite Zn/H-MFI has been studied by ^{1}H MAS NMR spectroscopy *in situ* within the temperature range of 420–490 K. Kinetic measurements of the H/D exchange between the acidic hydroxyl groups of the zeolite and the adsorbed deuterated propane molecules show that only methyl groups of the alkane are involved in the exchange. Two mechanisms are proposed to rationalize the regioselectivity of the exchange: (i) propane dehydrogenation on Zn-sites followed by protonation of propene by acidic OH groups in accordance to the Markovnikov's rule and abstraction of deuteride ion from another propane molecule; (ii) the reversible heterolytic dissociative adsorption of propane to form Zn-propyl species and acidic OH groups.

KEY WORDS: propane; Zn/H-MFI zeolite; H/D exchange; kinetics; mechanism; *in situ* ^{1}H MAS NMR spectroscopy.

1. Introduction

Incorporation of zinc cations into high-silica zeolites enhances the selectivity of zeolite catalysts towards light alkane dehydrogenation and aromatization [1–3]. It seems that the incorporated Zn^{2+} cations act as strong Lewis sites and change the mechanism of the alkane activation and transformation favoring a hydrogen removal step [2, 4–10]. Hydrogen exchange precedes usually the chemical conversion of alkane on solid acid catalysts [11]. A valuable information on the mechanism of the alkane activation and transformation on zinc-containing zeolites is expected to be obtained from the analysis of hydrogen exchange between the residue Brönsted sites of the Zn-modified zeolite and the alkane.

Different mechanisms of the H/D exchange between propane and the catalyst Brønsted sites were justified for different solid acid catalysts. Stepanov *et al.* [12, 13] claimed a direct exchange between either the methyl or methylene groups of propane and the acid sites of zeolite H-MFI. Each of these groups exchange via a concerted step involving a pentacoordinate carbonium ion transition state, in which the exchanging hydrogen atoms are on a half way between the oxygen of the zeolite and the carbon atom of the alkane [14–18]. Haouas *et al.* [19, 20] have provided experimental evidences for regioselective exchange of propane on unpromoted (SZ) and Al_2O_3-promoted sulfated zirconia (ASZ). The regioselectivity of the H/D exchange into the methyl groups was in favor of a carbenium-ion-mechanism, initiated by hydride abstraction from the alkane with the catalyst Lewis sites [20, 21].

In this paper the mechanism of H/D exchange for propane on zinc modified H-MFI catalyst has been investigated by ^{1}H MAS NMR *in situ* spectroscopy.

2. Experimental

2.1. Materials and samples preparation

A starting zeolite Na-MFI (Si/Al = 35) was synthesized using mono-n-propylamine as the template, then calcined at 600 °C for 5 h. Hydrogen form H-MFI was obtained from the sodium form by the triple ion exchange with a 0.1 M aqueous solution of NH_4NO_3 and subsequent calcination at 823 K for 6 h. Preparation of Zn/H-MFI was carried out by the impregnation with an aqueous solution of $Zn(NO_3)_2$, subsequent drying at 393 K for 15 h and calcination at 823 K for 12 h. The content of zinc was of 8.0 wt. The materials were characterized by elemental analysis, XRD, SEM, UV-vis diffuse reflectance spectroscopy, solid-state ^{1}H, ^{27}Al, and ^{29}Si MAS NMR spectroscopy, nitrogen adsorption, and FTIR of adsorbed pyridine and CO. The elemental analysis of zeolites was performed by atomic absorption spectroscopy. The XRD patterns were obtained with the DRON-3M (USSR) diffractometer, using Cu-Kα radiation. SEM images were obtained on the CAMSCAN electron microscope. UV-vis diffuse reflectance spectra were measured on a Specord M-40 equipped with reflectance accessories. ^{1}H, ^{27}Al and ^{29}Si MAS NMR experiments to characterize

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*To whom correspondence should be addressed.
E-mails: stepanov@catalysis.ru; freude@uni-leipzig.de

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the zeolite were performed on a Bruker MSL 400 spectrometer. Sorption-desorption isotherms of nitrogen were measured at 77 K using an automated porosimeter (Micromeritics ASAP 2000). Analysis of the results on characterization of zinc species suggested that Zn/H-MFI involves three types of Zn species: small and large ZnO clusters and zinc cations. The simple estimations derived from chemical analysis, XRD and FTIR data pointed that most part of the embedded Zn exists in the form of subnanomeric ZnO clusters inside the zeolitic pores (68 of the total amount of Zn introduced). The content of large ZnO crystals determined from XRD amounted to 5. Assuming that each Al atom generated a Brønsted site in H-MFI and supposing that the protons are replaced by monopositive ZnOH+ cations, the maximum content of Zn in cationic positions was estimated to be 33%.

For Zn/H-MFI sample used in this study with high Zn content, (OZ)–$(Zn–O–Zn)^{2+}$(OZ)– or (ZO)–Zn^{+}–O–Si cations should preferably form based on the literature data [2, 22]. However, the presence of Zn^{2+} or $ZnOH^{+}$ cannot be excluded. A detailed characteristics of the Zn/H-MFI catalytst used is provided elsewhere [23].

Propane-d_8 (99.4% D) purchased from Aldrich Chemical Company Inc. was used without further purification. Samples for the NMR measurements were prepared by heating 80 mg of a zeolite sample in the glass tubes of the 5.5 mm outer diameter. The temperature was increased with the rate of 10 K h^{-1} under vacuum. The samples were further maintained at 400 °C for 24 h under vacuum (less than 10^{-2} Pa). The adsorption of propane was performed at ambient temperature, propane loading being 4 molecules per unit cell of the zeolite (ca. 680 μmol/g). After the adsorption, the sample was sealed off to give a 10 mm length glass tube, which could be tightly inserted in a 7 mm zirconia rotor.

2.1.1. NMR measurements

In situ ^{1}H MAS NMR kinetics measurements were performed on a Bruker AVANCE 400 spectrometer (Larmor frequency of 400.13 MHz) at 420–490 K, using a high temperature probe produced by Bruker Biospin GMBH. The rotation frequency of the 7 mm zirconia rotor with an inserted sealed glass tube was 3 kHz. For ^{1}H NMR free induction decay's (FID) were recorded with the 45° flip angle preparation pulses of 3.6μs duration, 25μs ring down delay, 4 s recycle delay and 24 scans for accumulation. The interval between two successive steps in the time scale of the kinetic measurements ranged from 1.8 to 10 min in dependence of temperature and corresponding apparent rate of the ^{1}H isotope transfer. The temperature of the samples was controlled by a Bruker BVT-1000 variable-temperature unit. The calibration of temperature inside the sample was made with a ^{207}Pb MAS NMR chemical shift thermometer [24], with an accuracy of ±2 K.

2.2. Analysis of the reaction rates

The rate constant k for the H/D exchange between deuterated propane and an acidic OH group of the zeolite, which is further identified as the rate of the H/D exchange [11], has been determined by the exponential fit:

$$I_t = I_\infty[1 - \exp(-kt)] \qquad (1)$$

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 $t = \infty$ (equilibrium of the system). Time $t = 0$ corresponds to the experiment start, when the temperature was increased from ambient to the desired temperature of the reaction.

3. Results and discussion

Propane adsorbed on H-MFI zeolite exhibits in the ^{1}H MAS NMR spectrum two distinct signals at 1.0 and 1.5 ppm from the methyl and the methylene groups, respectively (see figure 1 in Ref. [12]). This allows selective monitoring of hydrogen exchange in either the methyl or methylene groups of propane by following the increase of the intensity of corresponding signals of propane upon adsorption of deuterated propane-d_8 on Zn/H-MFI zeolite.

Figure 1 shows ^{1}H MAS NMR spectra of propane-d_8 adsorbed on Zn/H-MFI. The initial spectrum corresponds to the spectrum of OH groups of the zeolite. A signal at 1.8 ppm belongs to terminal SiOH groups while a signal at 4.7 ppm arises from the bridging

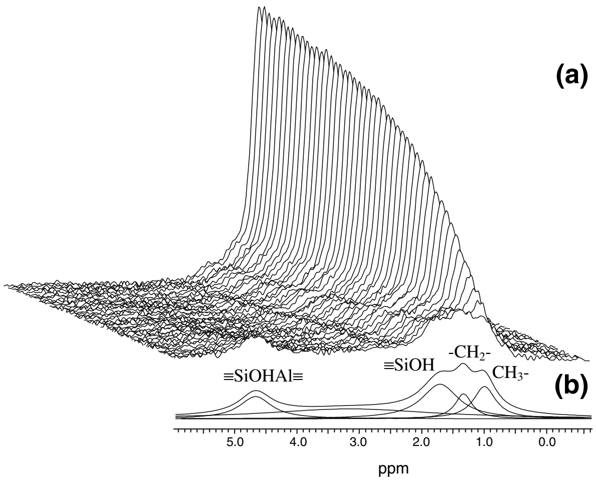
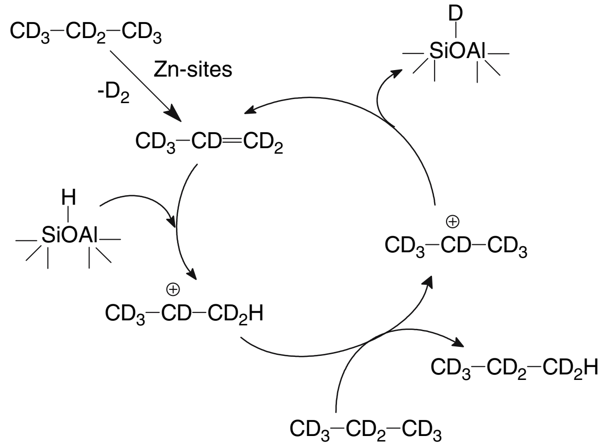


Figure 1. (a) Variation of ^{1}H MAS NMR spectra with time at 471 K for propane-d_8 adsorbed on Zn/H-MFI. The time interval between the recording successive spectra was 3 min. The first spectrum (bottom), recorded at $t = 3$ min, was simulated (b) to emphasize signals from the acidic bridging hydroxyls and silanol groups and residue protium in the methyl and methylene groups of deuterated propane. A broad signal centered at 3 ppm, which is clearly visible under simulation of the first spectrum in (a), could be assigned to ZnOH groups.

SiOHAl groups. Heating of the sample above 400 K results in a growth of the intensity of the signal from the methyl groups. Simultaneously, the intensity of the signal at 4.7 ppm from the SiOHAl decreases. However, no noticeable changes in the intensity of the signal at 1.5 ppm from the methylene group of propane is detected at 420–490 K (see figure 1). An increase of the intensity of the signal exclusively at 1.0 ppm points to the transfer of protium from the bridging OH groups of the zeolite into the methyl groups of deuterated propane. The methylene group of propane is not involved in H/D exchange. These data show the regioselective hydrogen exchange on Zn/H-MFI in contrast to H-MFI, for which both the methyl and methylene groups of propane are involved into the exchange with the acidic OH groups [12, 13, 25]. It should be noted here that H/D exchange is the basic route for propane conversion within the temperature range used in this study as follows from ^{13}C MAS NMR analysis of the products of propane-*2*-^{13}C conversion at 420–490 K., very small intensity signals from Zn-n-propyl species [23] or propene oligomers (1–2 conversion of propane) being detected at 490 K.

Regioselectivity of the exchange for Zn/H-MFI implies that the mechanism of the exchange changes, when the zeolite is modified with Zn. Similar to the results obtained for sulfated zirconia [20], the regioselectivity of the exchange could be rationalized by involvement of propylene and isopropyl cation intermediates in the exchange in accordance to scheme 1. In this scheme, propylene formed by dehydrogenation on Zn-sites is further protonated by SiOHAl group in accordance to Markovnikov's rule, offering the isopropyl cation with the selective protium label in the methyl group. The cation abstracts further deuterium from propane–d_8 and gives deuterated propane selectively enriched by protium in the methyl group, regenerating isopropyl cation. Haouas *et al.* have suggested that the mechanism presented in scheme 1 is initialized by hydride abstraction from propane with strong Lewis sites of sulfated zirconia [20]. For the case with Zn-containing H-MFI, the dehydrogenation of propane molecule to form carbenium ion can occur either on zinc cations or Lewis sites of subnanomeric custers of ZnO due to prevalence of these two Zn species in the zeolite [1, 23, 26–29].

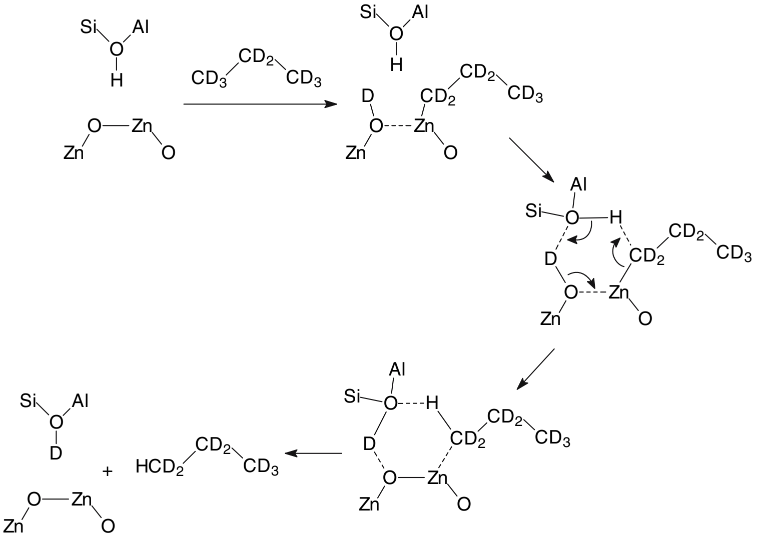


Scheme 1. Mechanism of regioselective H/D exchange for propane-d_8 on Zn/H-MFI with involvement of equilibrated propene and isopropyl cation.

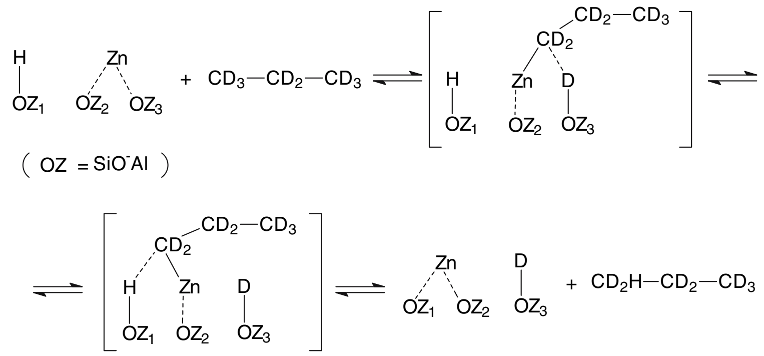
Another hypothesis, which can also account for the regioselective H/D exchange, is based on recent mechanistic studies of the initial stages of propane conversion over Zn/H-MFI by in situ ^{13}C MAS NMR and IR spectroscopy [22]. It has been concluded in ref. 22 on propane dissociative adsorption on zinc oxide sites leading to Zn-propyl species and Zn-OH groups at the very early stages of the reaction over Zn/H-MFI catalyst, containing most part of Zn in the form of subnanomeric ZnO clusters. It is important to mention that NMR data pointed to selective formation n-propylzinc species upon propane dissociative adsorption, while isopropylzinc species were not detected. Protonation of n-propylzinc species by the nearest acidic OH group, followed by recombination of propane should also lead to the regioselective H/D exchange (Scheme 2), thus, providing for an alternative mechanism of H/D exchange.

Kazansky *et al.* [7–9] claimed the dissociative adsorption of methane and ethane on acid-base pairs with distantly separated Zn^{2+} cations and basic oxygen atoms of the zeolite framework of Zn/MFI catalysts with high content of Zn^{2+} cations. In those studies, the simultaneous formation of acidic bridging hydroxyls SiOHAl and zinc ethyl or zinc methyl fragments was confirmed by DRIFT spectroscopy. This implies that dissociative adsorption may also occur on Zn^{2+} cations in the case of propane.

The mechanism of H/D exchange for propane involving Zn^{2+} cations is shown on Scheme 3. Zn^{2+} cations located at neighbouring [4] or distanly separated [10] basic oxygens of the Si O$^-$ Al groups in the zeolite framework provide a heterolytic dissociative adsorption of propane and offer Zn-propyl species and acid protons of the SiOHAl group. A reversible formation of Zn-propyl and acidic OH groups from the alkane and Zn^{2+} cations and involvement of the residue SiOHAl groups in this reversible reaction can provide regioselective H/D exchange between the adsorbed alkane and the SiOHAl groups of the zeolite. In scheme 3, OZ_2 and OZ_3 represent basic neighbour or distanly separate oxygens of the Si O$^-$ Al groups in the zeolite framework nearby which Zn^{2+} cations can be located. HOZ_1 is the residue SiOHAl groups that remained in the zeolite after Zn loading. HOZ_1 groups should be in vicinity of Zn^{2+} cations in order the transition state, depicted in Scheme 3 in square brackets, can be formed and the H/D exchange thus occurs. Thus, a heterolytic dissociative adsorption of propane to form intermediate Zn-propyl



Scheme 2. Mechanism of regioselective H/D exchange for propane-d_8 on Zn/H-MFI with involvement of zinc oxide clusters providing the formation of Zn-propyl species.



Scheme 3. Mechanism of regioselective H/D exchange for propane-d_8 on Zn/H-MFI with involvement of Zn^{2+} cations providing the formation of Zn-propyl species.

species (Schemes 2 or 3) provides an alternative to the mechanism of the regioselective H/D exchange for propane on some solid acidic catalysts with involvement of the intermediate propene and isopropyl cation, which is initiated by hydride abstration with the catalyst Lewis sites (Scheme 1).

Carbon monoxide has been demonstrated to exhibit no notable effect on the rate of non-regioselective H/D exchange for propane on H-MFI, which proceeds in a concerted step with involvement of pentacoordinated carbon atom in a transition state [12, 13]. That means that the interaction of CO molecules with the zeolite Brønsted sites has no influence on the exchange. Figure 2 shows that there is an essential suppression of the H/D exchange for propane on Zn/H-MFI carbon. Co-adsorption of CO in amount equal to that of the adsorbed propane results in a decrease of the rate constant by a factor of 43 at 471 K. The suppression of the exchange could be rationalized by the interaction of CO with either isopropyl cation or Zn-sites. Oxocarbenium ion, which could be generated in the former case, loses its ability for deproptonation [30], preventing the exchange via Scheme 1. In the latter case, the interaction

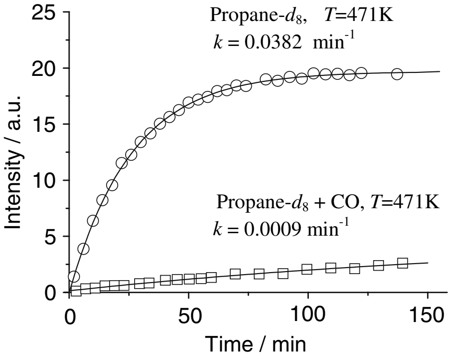


Figure 2. Suppression of hydrogen exchange between the bridged SiOHAl groups of Zn/H-MFI and the methyl groups of propane-d_8 in the presence of carbon monoxide. Kinetics of the exchange in the absence (○) and in the presence (□) of carbon monoxide.

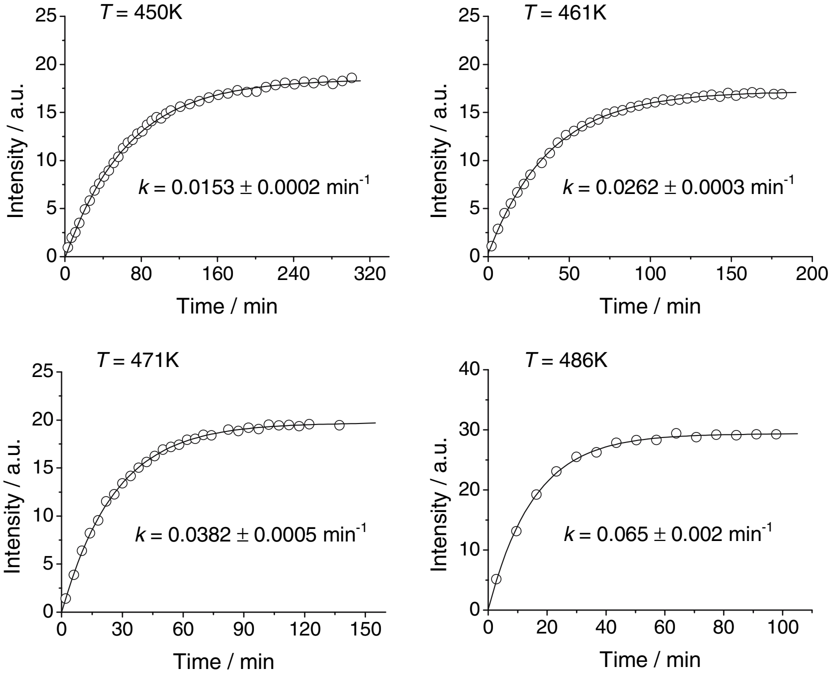


Figure 3. Kinetics of H/D exchange between the bridging SiOHAl groups of Zn/H-MFI and the methyl groups of propane-d_8 at different temperatures. The curves were fitted (solid lines) with apparent rate constants k on the basis of equations(1).

of CO with Zn-sites will prevent the generation of Zn-propyl species and propylene. Thus the results obtained on the exchange in the presence of CO are in favour of both mechanisms and do not allow to distinguish between them.

Measurements of the intensity of the NMR signal of the methyl groups versus the reaction time allowed us to estimate the rate constants for regioselective H/D exchange in the temperature range of 420–490 K (figure 3). Basing on kinetic data of figure 3, the activation energy for this reaction was estimated. Apparent activation energy of 80 kJ mol^{-1} was derived from the Arrhenius plot presented in figure 4.

The activation energy for the direct H/D exchange between the methyl groups of propane and SiOHAl of H-MFI zeolite (Si/Al = 35) via a pentavalent carbonium ion-type transition state was found to be 107 kJ mol^{-1} and the rate constant was one order of magnitude lower within the same temperature range [12, 13]. For regioselective H/D exchange between deuterated propane and sulfated zirconia, the activation energy was reported to be 54 kJ mol^{-1} [20]. The comparison with the literature data shows that kinetic parameters for the H/D exchange in propane-d_8 on Zn/H-MFI are different from those reported for H-MFI [12, 13] and sulfated zirconia [20]. The parameters obtained for Zn/H-MFI cannot be rationalized either by the mechanism with direct H/D exchange of the zeolite acidic OH groups with hydrogens of propane [12, 13] or the mechanism for propane exchange on SZ with carbenium ion involvement [20]. This could be an argument in favour of alternative mechanism of H/D exchange reaction for propane on Zn/H-MFI (Schemes 2 or 3).

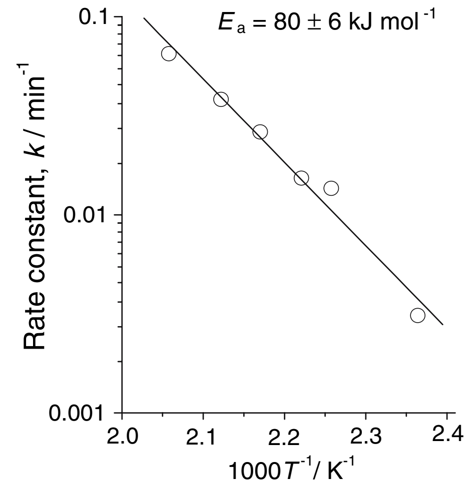


Figure 4. Arrhenius plot for the regioselective H/D exchange in the methyl groups of propane-d_8 on Zn/H-MFI.

4. Conclusions

Analysis of kinetics of the hydrogen exchange between Brönsted acid sites of zeolite Zn/H-MFI and deuterated propane-d_8 by ^{1}H MAS NMR *in situ* in the temperature range of 420–490 K pointed to the regioselective H/D exchange in methyl groups of propane. Two mechanisms are suggested to account for this result. The first one involves propane dehydrogenation on Zn-sites followed by the protonation of propene with acidic OH groups in accordance to the Markovnikov's rule and abstraction of deuterium from the next propane molecule by isopropyl carbenium ion. The alternative mechanism involves a reversible heterolytic dissociative adsorption of propane on ZnO clusters or Zn^{2+} cations to offer Zn-propyl species and acidic sites.

Acknowledgments

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