The activation of CD_4 for H/D exchange over H-zeolites

J. Valyon*, J. Engelhardt, D. Kalló, and M. Hegedüs

Institute of Chemistry, Chemical Research Center, Hungarian Academy of Sciences, P.O. Box 17, H-1525 Budapest, Hungary

Received 18 July 2001; accepted 2 April 2002

The H/D exchange was studied between CD_4 and H-zeolites using pulsed a microcatalytic reactor and MS analysis. Methane-d_3 was the only exchange product, while a large fraction of the reactant was retained by the zeolite. The apparent activation energies (E_a) were determined for CHD_3 production assuming first-order reaction kinetics. The E_a was close to $80\,kJ\,mol^{-1}$ over the H-ZSM-5 and H-mordenite, and about $50\,kJ\,mol^{-1}$ over H-beta. Results suggested that, at the low methane loading applied, the H/D exchange was initiated predominantly by heterolytic dissociation of CD_4 to $CD_3^{\delta-}$ and $D^{\delta+}$ over Lewis acid–Lewis base pair sites.

KEY WORDS: H/D exchange; deuteromethane; H-zeolites; Lewis acid–Lewis base pair sites.

1. Introduction

Numerous studies have been devoted to the H/D exchange reactions of alkanes and Brønsted acids to learn more about the transition states and active intermediates of catalytic alkane transformations [1–23]. Liquid superacids were shown to protonate alkanes and form carbonium ions [1–4]. The dynamic exchange between the hydrogen atoms of alkanes and the acid was considered to proceed through these carbonium ions. However, studies concerning the interaction of small alkanes and strong solid acid catalysts, such as H-zeolites, failed to verify carbonium ion formation. The H/D exchange was shown to proceed successively *via* carbenium ions and alkenes as intermediates [3–11]. Since the formation of C_1 alkene is impossible, the H/D exchange between methane and acidic zeolites was considered to be evidence of the formation of a carbonium ion-like (CH_5^+) transition state complex [12–14]. Results of quantum chemical calculations supported this notion [15–19]. The exchange was suggested to proceed through a positively charged hydrocarbon fragment coordinated to two oxide ions of the zeolite framework [19]. The true activation energy (E_t) was calculated to be $122–150\,kJ\,mol^{-1}$ [15–19]. The apparent activation energy (E_a), obtained experimentally, was in the same range [12–14].

Goeppert *et al.* [20] concluded that the H/D exchange between methane and a solid Brønsted acid is a suitable reaction to probe superacidity. Over SO_4^{2-}/ZrO_2 and its iron-promoted version, the E_t of the exchange reaction was estimated as $93–96\,kJ\,mol^{-1}$ [21]. This E_t value, which is lower than that determined for H-zeolites but quite close to the value ($88\,kJ\,mol^{-1}$) calculated by Esteves *et al.* [2] for the exchange reaction with superacid HF/SbF_5, was considered to be evidence of the superacid character of iron-promoted and -unpromoted SO_4^{2-}/ZrO_2. Jentoft and Gates [22], however, found that SO_4^{2-}/ZrO_2 is significantly less active in the H/D exchange than the iron-, manganese-promoted catalyst and zeolite ZSM-5.

In a recent work [23] the H/D exchange was studied between CD_4 and H-zeolites of different acidity, as well as γ-Al_2O_3 at low conversions of the perdeuteromethane and the hydroxyl groups. The results suggested that a fraction of the CD_4 was adsorbed dissociatively over Lewis acid–Lewis base pair sites. The theoretical calculations of Fărcaşiu and Lukinskas [24] showed that the surface species formed are possible intermediates of the H/D exchange. This notion is supported by the results of the present study.

2. Experimental

Characterization data of the zeolite samples studied, such as mordenite (LZ-M6, UOP), ZSM-5 (T-3ZIPC, VEB Chem. Komb., Bitterfeld-Wolfen, Germany), beta (Valfor CP, PQ Corp.), Y (LZY-62, UOP) and USY (LZY-82, UOP) were taken from refs. [25–27] and are given in table 1. The original zeolite powders were ion-exchanged with 2 M NH_4NO_3 solution, filtered, dried at 393 K, and pressed into pellets without binder. The pellets were crushed; the 0.25–0.50 mm particle size fraction was separated by sieving and used in the experiments.

An RXM-100 Multifunctional Catalyst Testing and Characterization Machine (Advanced Scientific Designs, Inc.) was used to study the H/D exchange reaction between CD_4 and H-zeolites. The experiments were carried out with 1% CD_4/99% He mixture. The mixture was prepared by increasing the pressure in a cylinder containing pure CD_4 (Cambridge Isotope Laboratories, Inc.) with

---

* To whom correspondence should be addressed.
E-mail: valyon@chemres.hu

Table 1
Characterization of the zeolites[a]

Zeolite	Si/Al	Al_T [b] (mmol/g)	Al_F (mmol/g)	B [e] (mmol/g)	L [f] (mmol/g)
H-mordenite	6.8	2.06	2.05 [c]	2.08	0.023
H-ZSM-5	15.6	0.99	0.95 [c]	0.90	0.080
H-beta	12.5	1.21	0.77 [c]	0.51	0.103 (0.28)
H-Y	2.68	5.15	4.65 [d]	–	–
H-USY	8.35	4.32	2.66 [d]	–	–

[a] Data were taken from ref. [25] for H-mordenite, H-ZSM-5 and H-beta and from refs. [26,27] for H-Y and H-USY.

[b] Total Al content from chemical analysis.

[c] Framework Al content of the original zeolite calculated from the ion-exchange capacity.

[d] Framework Al content of the sample dehydrated at 673 K averaged from data determined by XRD, ^{29}Si NMR and ^{27}Al NMR.

[e] Concentration of Brønsted acid sites calculated from NH_3-TPD results, before the TPD measurement sample was dehydrated at 773 K.

[f] Concentration of strong Lewis acid sites calculated from NH_3-TPD results. The concentration of the weak Lewis acid sites present in zeolite H-beta is given in parentheses.

ultrapure He. The MS fragmentation of three methane isotopomers is given in table 2. According to our MS analysis the CD_4/He mixture contained 0.03% CHD_3.

The NH_4-zeolite sample was placed into a quartz U-tube microreactor of 10 mm internal diameter in an amount to contain 3×10^{20} Al atom. The sample was converted into H-form *in situ* in a pure O_2 flow of 25 ml/min by increasing the temperature at a rate of 1 K/min to 773 K. The treatment in O_2 flow was continued at this temperature for 1 h and followed by a 1 h He flush. The activated zeolite sample was cooled in a flow of 20 ml/min He to the temperature of the H/D exchange test. Using a sampling valve, three successive doses of 1.13 cm^3 CD_4/He gas mixture were introduced into the He flow. Each dose contained 2.7×10^{17} CD_4 molecules. The reactor effluent was bled *via* a leak into the MS unit. The pressure in the MS chamber was 1.1×10^{-3} Pa. Signals were detected at $m/z = 20$, 19 and 18. No MS signal appeared at $m/z = 17$. The absence of the $m/z = 17$ signal suggested that CH_2D_2 ($m/z = 18$) was not formed as exchange product. The intensity of the $m/z = 20$ and $m/z = 19$ signals were continuously recorded and the integrated areas of the elution peaks, thus obtained, were determined using a computer program (a_{20} and a_{19}). Doses were fully eluted in about 3 min. Conversion was calculated by relating the areas of the peaks to those obtained from doses by-passing the reactor (a_{20}^0 and a_{19}^0). Since no multiply-exchanged product was detected, the CHD_3 impurity of the reactant was assumed to appear together with the product CHD_3. Therefore, the a_{19} area was corrected with the area of a_{19}^0. The experiment was repeated at five temperatures in the 523–723 K range. The results obtained were virtually independent of the temperature sequence of the experiments.

3. Results

The reaction occurring in a reactant pulse passing through a catalyst bed can be described by kinetic equations analogous to those used for the reaction in a steady-state flow reactor, providing that reaction is first-order in the reactant pressure. The first-order condition is fulfilled if the adsorption isotherm is linear, i.e., the amount of adsorbed intermediate formed from the reactant is proportional to the reactant pressure [28,29]. In other words, the apparent order of H/D isotopic exchange processes must follow first-order kinetics, if all the hydrogen (deuterium) atoms held by the solid are energetically and geometrically equivalent [30]. For the Brønsted acid sites of high-silica zeolites, the equivalency criterion is most probably satisfied. Although the partial pressure of the reactant varies from point to point through the reactant pulse, for first-order reaction the fractional conversion of the reactant is independent of pressure [29]. Therefore, the pulsed microcatalytic method used in our study was deemed as rapid, simple, and suitable for studying the H/D exchange between CD_4 and H-zeolites. The

Table 2
Fragmentation of methane isotopomers in MS[a]

	$m/z = 14$	15	16	17	18	19	20	$\sum$
CD_4	0 (7)	0 (0)	13 (11)	3 (0)	89 (84)	3 (0)	100 (100)	208 (202)
CHD_3	0 (7)	7 (7)	14 (13)	56 (48)	34 (28)	100 (100)	–	211 (203)
CH_2D_2	6 (0)	10 (8)	34 (30)	65 (64)	100 (100)	–	–	215 (202)

[a] The intensity values in parentheses were taken from the Registry of Mass Spectral Data.

Table 3
The temperature dependence of the total (C_t) and the H/D exchange (C_{ex}) conversion (%) of CD_4 over H-zeolites[a]

T (K)	H-Y		H-USY		H-mordenite		H-ZSM-5		T (K)	H-beta	
	C_{ex}	C_t	C_{ex}	C_t	C_{ex}	C_t	C_{ex}	C_t		C_{ex}	C_t
603	0	4.22	0	3.37	0.71	4.18	0.73	2.65	523	0.56	4.08
633	0	4.89	0	5.16	1.06	11.02	1.43	5.93	543	0.85	5.76
663	0	5.54	0	5.55	2.09	15.08	2.92	7.88	563	1.21	6.73
693	0.04	6.77	0.10	7.29	4.02	20.84	5.13	12.39	583	1.63	8.86
723	0.05	8.73	0.29	7.67	7.85	26.38	9.33	18.94	603	2.11	11.91

[a] The microcatalytic pulse technique was used. The concentration of the reactor effluent was followed continuously by recording the intensity of the $m/z = 20$ and $m/z = 19$ MS signals. $C_{ex}(\%) = 100(a_{19} - a^0_{19})/a^0_{20}$, $C_t(\%) = 100(a^0_{20} - a_{20})/a^0_{20}$. Designations of a_{19} and a_{20} stand for the integrated peak areas obtained from eluted reactant CD_4 and product CHD_3, respectively. Doses bypassing the reactor were analyzed under MS conditions, identical to those used for measuring H/D exchange, to determine a^0_{19} and a^0_{20}.

reaction proceeded far from equilibrium and the conversion was a linear function of the contact time. The conversions obtained at identical flow rate and pulse size over catalysts containing equal amounts of Al atoms, i.e., the conversions at identical contact times, could be used directly to compare the specific activities of the catalysts.

In relation with the CD_4/H-zeolite reaction the pulsed microcatalytic method was not used previously. Kramer *et al.* [12] calculated E_a, the apparent activation energy of the reaction from the temperature dependence of the first-order decay or evolution of the IR bands, corresponding to the OH or OD stretching vibrations. The change could be monitored by IR spectroscopy, since much higher exchange conversion of the OH groups was attained than in our experiment. Another experimental approach is the use of a batch-type recirculation reactor [14,21]. Again, the experiments were designed so that the amount of methane hydrogen atoms should be comparable with the amount of OD groups in the fully deuterated zeolites. Using the pulse reactor method we were able to measure exchange conversion of very small reactant doses hardly influencing the proton-concentration of zeolite. Thus, less than 1% of the zeolitic Brønsted acid sites were converted in the total H/D exchange experiments. The CD_4 conversion was also low. At 723 K, the highest temperature applied, the total conversion (C_t) remained below 30% (table 3). The conversion to CHD_3 (C_{ex}), the only product detected in the gas phase, was always much lower than C_t. It is to be mentioned that no decrease in the conversion was observed when zeolite samples were exposed to about 50 subsequent pulses at the applied reaction temperatures. The converted CD_4, not appearing as CHD_3, was fully retained in some form by the zeolites. However, from larger doses, containing methane in an amount comparable with the amount of acid sites, formation of C_2 hydrocarbons, such as ethane or ethene, could be detected at 623–673 K both over H-ZSM-5 and H-beta [23]. In contrast, no C_2 hydrocarbon was formed over mordenite, but the dark discoloration indicated coke formation on the solid. Results suggested that higher methane coverage of the active sites favors C–C coupling, dehydrogenation and formation of carbonaceous deposits on the surface.

The data in table 3 are the averages obtained from three successive pulses. The total CD_4 conversions, obtained as small difference of comparable peak areas, $(a^0_{20} - a_{20})/a^0_{20}$, were less accurate than the conversion to CHD_3, $(a_{19} - a^0_{19})/a^0_{20}$. Under the applied reaction conditions the intracrystalline methane transport was estimated to be four orders of magnitude faster than that which could effect catalyst performance. Thus, results were treated as significant regarding the kinetics of the H/D exchange. Not the averages, but the conversions derived from each pulse were used to construct the Arrhenius plots, shown in figure 1, assuming first-order

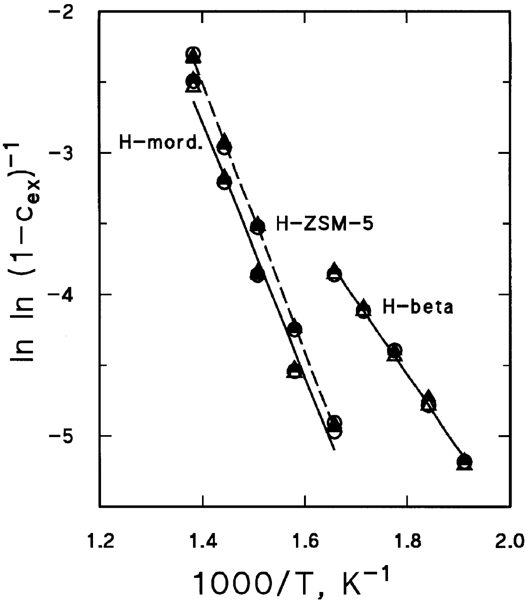


Figure 1. Arrhenius plots for conversion in the H/D exchange between CD_4 and H-zeolites (C_{ex}, molar fraction). Results from the first, second and third doses are indicated with symbols △, ○ and ▲, respectively. The plots were derived from results of pulsed microcatalytic experiments assuming first-order kinetics [28].

Table 4
Acidity of H-zeolites and E_a apparent activation energies for the conversion of CD_4 in H/D exchange

Zeolite	L/B [a]	E_a ($kJ\,mol^{-1}$) [b]
H-mordenite	0.011	74
H-ZSM-5	0.089	77
H-beta	0.202 (0.55)	43

[a] From ref. [25]. L/B represents the relative amount of the strong Lewis and Brønsted acid sites. The amount of the weak Lewis acid sites relative to the Brønsted acid sites is given in parentheses.

[b] Calculated from the temperature dependence of the exchange (C_{ex}) conversions of the CD_4 pulses assuming first-order kinetics.

formation of CHD_3 [28]. The values of E_a apparent activation energies determined from the slope (E_a/R) of the best-fit lines in figure 1 are given in table 4.

Under the experimental conditions where the exchange activity of zeolite H-ZSM-5, H-mordenite and H-beta was significant, the zeolite Y catalysts were inactive or showed low activity. Nevertheless, the H-USY catalyst was more active than the H-Y sample. Under steady-state reaction conditions, the rate of CD_4 consumption ($-r_{CD_4}$) must be equal with the rate of CHD_3 formation (r_{CHD_3}). In such a case, similar E_a values are expected to be obtained from the two kinds of conversions. The large difference of C_{ex} and C_t shows that this is not the case in our pulse experiment. The CD_4 seems to be consumed in two reactions: one giving the CHD_3 product, and the other resulting in a product fully retained by the catalyst.

4. Discussion

The H/D exchange between CD_4 and surface-bound hydrogen atoms is the most simple hydrocarbon reaction over a solid. If no multiple exchange has to be considered the reaction can be given as

$$CD_4 + HOZ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [I] \xrightarrow{k_2} CHD_3 + DOZ \qquad (1)$$

with Z representing the zeolite framework, k_i denoting rate constant and [I] an activated intermediate. Provided that the reactant and the intermediate are in thermodynamic equilibrium and the reaction is first-order in the methane concentration and zeroth-order in the hydrogen concentration of the zeolite, the reaction rate can be given as

$$r = k_2 K_1 [CD_4] = k[CD_4] \qquad (2)$$

where K_1 is the equilibrium constant of adsorption ($K_1 = k_1/k_{-1}$) and k is an apparent reaction-rate constant. The Arrhenius equation describes the temperature dependence of the rate constant as

$$\ln k = \ln A_a - E_a/RT \qquad (3)$$

where A_a and E_a represent the apparent pre-exponential constant and the apparent energy of activation, respectively. With the expressions giving the temperature dependence of k_2 and K_1, equation (3) can be written also as

$$\ln k = \ln k_2 K_1 = \ln A_2 + C - (E_t + \Delta H)/RT \qquad (4)$$

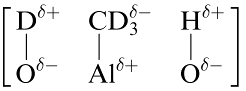
Thus, $\ln A_a$ equals ($\ln A_2 + C$), where A_2 is the true Arrhenius pre-exponential of the reaction and C is integration constant of the van't Hoff equation. Obviously, if adsorption is exothermic the true activation energy of the reaction, E_t, can be obtained as the sum of E_a and ΔH [31].

The transition state [I] of the exchange was suggested to be the methonium ion CD_4H^+, coordinated to the basic oxide ions of the zeolite lattice [9,13–19]. For various H-zeolites and also for non-zeolite solid Brønsted acids, such as amorphous silica–alumina, calculations and measurements gave activation energies of about 122–150 $kJ\,mol^{-1}$ [12–14,32]. The ΔH enthalpy of the molecular methane adsorption over H-zeolites was estimated to be lower than about 22 $kJ\,mol^{-1}$ [33,34]. If methane activation is preceded by its molecular adsorption on a Brønsted acid site, the difference between E_a and E_t is commensurate with the uncertainty of the experimentally determined or calculated activation energy values.

Our obtained E_a values range from about 80 to 50 $kJ\,mol^{-1}$, i.e., they are much below that given above (table 4). It seems unlikely that, under the experimental conditions that we applied, the exchange proceeds with the mechanism outlined above but with a much lower energy of activation. If reaction was introduced by molecular methane adsorption, it could be expected that the K_1 sorption equilibrium constant and the coverage of the sites decrease as temperature is increased. In contrast to that, we found higher methane retention at higher temperatures (table 3). The activation of the methane for the H/D exchange must occur in a reversible adsorption–desorption process. It cannot be ruled out, however, that the same activation process was introducing the formation of the retained surface species. The low E_a suggests that, besides the reaction route running through the carbonium-ion-like transition state, another route must be also available for H/D exchange.

We believe that earlier studies of reaction between CD_4 and surface hydrogen atoms of alumina and silica–alumina [32,35] give a better scientific background to the interpretation of our results than recent studies concerning H-zeolites. The H/D exchange rate between CD_4 and surface hydrogen atoms was found to be much higher for alumina than for silica—alumina [32]. For alumina, E_a was found to be as low as 17 $kJ\,mol^{-1}$ [35]. Dehydrated alumina shows Lewis acidity, but strong Brønsted acid sites could not be detected on its surface [36]. The activity of alumina in the H/D exchange reaction with propane was found to show correlation with the Lewis acidity [37]. Studies with MgO, Sm_2O_3 [38], Co/Al_2O_3 [39] and Zn,H-ZSM-5 [40,41] showed that the dissociative adsorption of methane over Lewis acid–Lewis base pair sites generates strongly bound surface species. Recently Schoofs *et al.* [11] substantiated that H/D exchange between isobutane and deuterated Y-zeolites was initiated by hydride abstraction on Lewis acid non-framework aluminum species. All these findings inferred that besides the Brønsted sites, Lewis acid sites of the H-zeolites may play a role in the activation of methane for the H/D exchange with the OH groups.

Recent theoretical calculations [24] substantiated that Lewis acid Al^{3+} ions have the ability to affect metal ion catalysis. The aluminum ions in the zeolite framework were shown to retain some Lewis acid character, but these ions are less active than the ions in bulk aluminum oxides. The hydrogen chemisorption was suggested to proceed through the initial interaction of the H_2 molecule with an Al atom, after which one hydrogen migrates to a neighboring oxygen. The calculations predicted that H/D exchange must occur much faster on the extra-framework aluminum species than on the zeolite itself. Considering all these facts, it seemed rational for us to think that, in presence of acid–base pair sites ($Al^{\delta+}O^{\delta-}$), the exchange between CD_4 and H-zeolites can proceed according to equation (1) through intermediate [I], shown in scheme 1, with the unexpectedly low E_a.



$$\left[\begin{array}{ccc} D^{\delta+} & CD_3^{\delta-} & H^{\delta+} \\ | & | & | \\ O^{\delta-} & Al^{\delta+} & O^{\delta-} \end{array}\right]$$

Scheme 1. Intermediate [I] of the H/D exchange of CD_4, activated over a Lewis acid ($Al^{\delta+}$)–Lewis base ($O^{\delta-}$) pair site, and an OH group.

In the intermediate $CD_3^{\delta-}$ can combine with $D^{\delta+}$ or $H^{\delta+}$ with equal probability and appear in the gas phase as unconverted CD_4 or exchange product CHD_3, respectively.

It is to be noticed that the dissociative adsorption can be visualized also as a result of deuteride abstraction. It is known that not only the C–H bond strength is of importance regarding the heterolytic C–H bond dissociation but also the stability of the alkyl ion and its charged H-atom counterpart. The stability of carbenium ions increases with the carbon number and is higher for the branched than for the straight chain isomers. Because of the low stability of the CH_3^+ ion, the hydride abstraction from a methane molecule is energetically much less favorable [16]. Moreover, it does not seem probable that CD_3H could be formed from an intermediate containing $D^{\delta-}$, $CD_3^{\delta+}$ and $H^{\delta+}$.

According to the *ab initio* SCF MO calculations of Capitán *et al.* [42] for the CH_4–$Al(OH)_3$ system the energy barrier of the process resulting in Al-bound methyl group and O-bound hydrogen was as high as $190\,kJ\,mol^{-1}$. The process was endothermic by $40\,kJ\,mol^{-1}$. However, when the calculation simulated the potential created by the infinite solid the process was found clearly exothermic. The results suggested that the electrostatic potential of the lattice can stabilize the methyl–metal compound with a negative charge on the carbon atom. Nevertheless, further theoretical calculations are needed to learn more about the energetics of the methane binding to the possible Lewis acid–Lewis base pair sites of zeolites.

The H/D exchange through the activated intermediate shown in scheme 1 suggests that only a fraction of the $Al^{\delta+}O^{\delta-}$ pair sites can be sites of H/D exchange, which happen to be next to an OH-group. The concentration of the intermediate depends on the OH-concentration, the methane coverage and the mobility of the reacting species at the temperature of the measurement. The slope of the Arrhenius plot and the value of E_a obtained reflect the contribution of all the temperature-dependent factors, influencing the rate of H/D exchange. It is not easy even to estimate the E_t, however; it is probably much higher than E_a and it cannot be excluded that E_t is quite similar for the different zeolites. In this case the different E_a values may reflect the relative stabilities of the methyl–Al intermediates and the different mobility of the reacting surface species within the different zeolites.

Low stability of the $CH_3^{\delta-}H^{\delta+}$ intermediate may facilitate the formation of radicals. The methane dehydrogenation and the coupling reaction of the radicals can give C_2 products, ethane and/or ethene, detected at higher methane loadings. The hydrocarbons formed can undergo further reactions over the Brønsted acid sites, such as oligomerization, cyclization, and polymerization, resulting in the formation of carbonaceous deposits on the catalyst (table 3).

The higher activity of the H-USY sample relative to the virtually inactive zeolite H-Y clearly shows the significance of the extra-framework alumina species in the H/D exchange reaction. The especially low E_a obtained for zeolite H-beta can originate from the defected beta structure. The structure of zeolite beta can be characterized by T-atoms not fully coordinated in the zeolite framework. These T-atoms are Lewis acid sites providing the material with unique catalytic properties [43]. It was suggested that in the H-form some of the Al–O bonds are broken up due to the framework tension forming non-framework aluminum species of Lewis acid character [44,45]. It was reported that the H-beta sample, used in the present work, contains both strong and weak Lewis acid sites [25]. The strong Lewis acid sites were assigned to extra-framework aluminum species formed by partial dehydroxylation of the H-zeolite, while the weak Lewis acid sites were assigned to framework Al-atoms coordinately unsaturated due to framework defects. All the above findings suggest that in H-beta the occurrence of Lewis and Brønsted acid sites in close proximity can be quite probable. Lewis-acid-site extra-framework Al species were detected also in the H-mordenite and the H-ZSM-5 samples, but in much smaller amounts [25] (tables 1 and 4).

At 603 K the specific activity of the H-ZSM-5 and the H-mordenite was nearly the same, whereas the H-beta was about 3–5 times more active (table 3). Surprisingly, both H-Y and H-USY were found to be inactive at this temperature. Structural and compositional effects were shown to determine the H/D exchange rate of CD_4 per Brønsted acid site [14]. Previous studies suggested that H-mordenite is a stronger solid acid than H-ZSM-5, regarding both the strength of the strongest Brønsted acid sites and also the average Brønsted acidity [27,46]. Zeolite H-beta was substantiated to be a weaker Brønsted acid than either the H-mordenite or the H-ZSM-5 [20,27]. Obviously, the specific exchange activities did not follow the Brønsted acid strength of the zeolites. It is to be noticed, however, that for reactions characterized by different activation energies the sequence of the reaction rates may depend on the temperature selected for the comparison. The rate of the reaction over H-beta, characterized with the lowest E_a, must change less with the variation of temperature than the rate over the less-active zeolites. In principle, the specific activities could parallel the acid strengths at higher temperatures, which is out of the range used in this work.

Considering the lower E_a only, a rate of several hundred times faster would be justified over the H-beta sample than over the other zeolites studied. The actual reaction rate is obtained because the lower E_a is associated with a lower A_a pre-exponential constant. Thus, the H/D exchange reactions between CD_4 and the hydrogen atoms of different H-zeolites seem to represent an example for the well-known compensation phenomenon.

The apparent activation energies that we found are seemingly in conflict with those higher values reported in previous studies. The difference cannot be accounted for simply by the presence of active Lewis sites. Schoofs *et al.* [14] obtained higher E_a values, namely 122–130 kJ mol^{-1}, with zeolites H-ZSM-5 and H-Y, also containing Lewis-site extra-framework Al-species [47]. In our opinion, the explanation can be related to the possible chemical and energetic heterogeneity of the active H/D exchange centers. E_a represents the weighted average of the different activation energies of the simultaneously operating centers. The weight of a kind of center corresponds to its contribution to the total reaction rate, i.e., it is related to the number of centers or, more precisely, with the pre-exponential constant and, moreover, with the characteristic activation energy over these centers. At low methane coverage the weight of those very few centers, characterized with higher ΔH and lower E_a, is the highest among all the active sites whereon the H/D exchange proceeds. At the higher methane coverage the few highly active sites are most probably poisoned by carbonaceous deposits, or their contribution to the exchange conversion may simply become subordinate beside the reaction over the less active but more numerous Brønsted acid sites.

5. Conclusions

Both molecular adsorption on Brønsted acid sites and dissociative chemisorption on Lewis acid–Lewis base pair sites can activate methane for exchange reaction with the surface hydrogen atoms. The latter reaction route is characterized by a significantly lower apparent activation energy. This route is also available over H-zeolites containing coordinatively unsaturated Al atoms either in extra-framework species or in the framework of a defected zeolite structure, such as in the framework of zeolite beta. The reaction proceeds predominantly over Lewis acid–Lewis base pair sites, when the amount of reactant CD_4 is less than or commensurate with the number of active Lewis sites. At higher coverage these pair sites are probably poisoned and the reaction on the less active Brønsted acid sites prevails.

Acknowledgment

This work was supported by the Hungarian Scientific Research Fund (OTKA, Project No. T 029735).

References

[1] G. Olah, V. Halpern, J. Shen and Y.K. Mo, J. Am. Chem. Soc. 93 (1971) 1251.

[2] P.M. Esteves, A. Ramirez-Solis and C.J.A. Mota, J. Phys. Chem. B 105 (2001) 4331.

[3] J. Sommer, M. Hachoumy and R. Jost, Catal. Today 38 (1997) 309.

[4] J. Sommer, J. Bukala, M. Hachoumy and R. Jost, J. Am. Chem. Soc. 119 (1997) 3274.

[5] J. Engelhardt and W.K. Hall, J. Catal. 151 (1995) 1.

[6] C.J.A. Mota, S.C. Menezes, L. Nogueira and W.B. Kover, Appl. Catal. A 146 (1996) 181.

[7] J. Sommer, A. Sassi, M. Hachoumy, R. Jost, A. Karlsson and P. Ahlberg, J. Catal. 171 (1997) 391.

[8] C.J.A. Mota, J. Sommer, M. Hachoumy and R. Jost, J. Catal. 172 (1997) 194.

[9] J. Sommer, D. Habermacher, R. Jost, A. Sassi, A.G. Stepanov, M.V. Luzgin, D. Freude, H. Ernst and J. Martens, J. Catal. 181 (1999) 265.

[10] J. Sommer, D. Habermacher, M. Hachoumy, R. Jost and A. Reynaud, Appl. Catal. A General 146 (1996) 193.

[11] B. Schoofs, J. Schuemans and R.A. Schoonheydt, Microporous and Mesoporous Materials 35-36 (2000) 99.

[12] G.J. Kramer, R.A. van Santen, C.A. Emels and A.K. Nowak, Nature 363 (1993) 529.

[13] G.J. Kramer and R.A. van Santen, J. Am. Chem. Soc. 117 (1995) 1766.
[14] B. Schoofs, J.A. Martens, P.A. Jacobs and R.A. Schoonheidt, J. Catal. 183 (1999) 355.
[15] E.M. Evleth, E. Kassab and L.R. Sierra, J. Phys Chem. 98 (1994) 1421.
[16] S.R. Blaszkowski, A.P.J. Jansen, M.A.C. Nascimento and R.A. van Santen, J. Phys. Chem. 98 (1994) 12938.
[17] T.N. Truong, J. Phys. Chem. B 101 (1997) 2750.
[18] P.M Esteves, M.A.C. Nascimento and C.J.A. Mota, J. Phys. Chem. B 103 (1999) 10417.
[19] J.M. Vollmer and T.N. Truong, J. Phys. Chem. B 104 (2000) 6308.
[20] A. Goeppert, R. Olindo, J. Sommer and F. Pinna, in: *Recent Reports of the 12th ICC*, *Granada*, *Spain*, *2000*, eds. A. Corma, F.V. Melo, S. Mendioroz and J.L.G. Fierro, R112.
[21] W. Hua, A. Goeppert and J. Sommer, J. Catal. 197 (2001) 406.
[22] R.E. Jentoft and B.C. Gates, Catal. Lett. 72 (2001) 129.
[23] J. Engelhardt and J. Valyon, React. Kinet. Catal. Lett. 74 (2001) 217.
[24] (a) D. Fărcaşiu and P. Lukinskas, Chem. Comm. 2001, 77; (b) P. Lukinskas and D. Fărcaşiu, Appl. Catal. A 209 (2001) 193; (c) D. Fărcaşiu and P. Lukinskas, J. Phys. Chem. A 103 (1999) 8483.
[25] F. Lónyi and J. Valyon, Thermochim. Acta 373 (2001) 53.
[26] P.V. Shertukde, W.K. Hall, J.-M. Dereppe and G. Marcelin, J. Catal. 139 (1993) 468.
[27] B. Umansky, J. Engelhardt and W.K. Hall, J. Catal. 127 (1991) 128.
[28] G.-M. Schwab and A.M. Watson, J. Catal. 4 (1965) 570.
[29] D.W. Bassett and H.W. Habgood, J. Phys. Chem. 64 (1960) 769.
[30] F.J. Cheselske, W.E. Wallace and W.K.H. Hall, J. Phys. Chem. 63 (1959) 505.
[31] G.C. Bond, *Heterogeneous Catalysis—Principles and Applications*, 2nd edition (Oxford University Press, Oxford, 1987).
[32] J.G. Larson and W.K. Hall, J. Phys. Chem. 69 (1965) 3080.
[33] F. Eder, M. Stockenhuber and J.A. Lercher, J. Phys. Chem. B 101 (1997) 5414.
[34] J.F. Denayer, G.V. Baron, J.A. Martens and P.A. Jacobs, J. Phys. Chem. B 102 (1998) 3077.
[35] P.J. Robertson, M.S. Scurrel and C. Kemball, J. Chem. Soc., Faraday Trans. I 71 (1975) 903.
[36] J. Engelhardt, Gy. Onyestyák and W.K. Hall, J. Catal. 157 (1995) 721.
[37] B.D. Flockhardt, S.S. Uppal and R.C. Pink, Trans. Faraday Soc. 67 (1971) 513.
[38] O.V. Buyevskaya, M. Rothaemel, H.W. Zanthoff and M. Baerns, J. Catal. 146 (1994) 346.
[39] L. Guczi, K.V. Sarma and L. Borkó, React. Kinet. Catal. Lett. 68 (1999) 95.
[40] V.B. Kazansky, V.Yu. Borovkov, A.I. Serikh, R.A. van Santen and B.G. Anderson, Catal. Lett. 66 (2000) 39.
[41] L.A.M.M. Barbosa, G.M. Zhidomirov and R.A. van Santen, Phys. Chem. Chem. Phys. 2 (2000) 3909.
[42] M.J. Capitán, J.A. Odriozola, A. Márquez and J.F. Sanz, J. Catal. 156 (1995) 273.
[43] J.C. Jansen, E.J. Creyghton, S.L. Njo, H. van Konigsveld and H. van Bekkum, Catal. Today 38 (1997) 205.
[44] C. Yang and Q. Xu, Zeolites 19 (1997) 404.
[45] A. Vimont, F. Thibault-Starzyk and J.C. Lavalley, J. Phys Chem. B 104 (2000) 286.
[46] N. Katada, H. Igi, J.-H. Kim and M. Niwa, J. Phys. Chem. B 101 (1997) 5969.
[47] M.J. Remy, D. Stanica, G. Poncelet, E.J.P. Feijen, P.J. Grobet, J.A. Martens and P.A. Jacobs, J. Phys. Chem. 100 (1996) 12440.