H/D exchange of molecular hydrogen with Brønsted acid sites of Zn- and Ga-modified zeolite BEA

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Kinetics of hydrogen H/D exchange between Brønsted acid sites of pure acid-form and Zn- or Ga-modified zeolites beta (BEA) and deuterated hydrogen (D_2) has been studied by ^1H MAS NMR spectroscopy *in situ* within the temperature range of 383–548 K. A remarkable increase of the rate of the H/D exchange has been found for Zn- and Ga-modified zeolites compared to the pure acid-form zeolite. The rate of exchange for Zn-modified zeolite is one order of magnitude higher compared to the rate for Ga-modified zeolite and two orders of magnitude larger compared to the pure acid-form zeolite. This promoting effect of metal on the rate of H/D exchange was rationalized by a preliminary dissociative adsorption of molecular hydrogen on metal oxide species or metal cations. The adsorbed hydrogen is further involved in the exchange with the acid OH groups located in vicinity of metal species. The role of different metal species in the possible mechanisms of the exchange with involvement of zeolite Brønsted acid sites and metal species is discussed.

1. Introduction

Zn- and Ga-modified high-silica zeolites are efficient catalysts for the light alkanes aromatization.[1–4] The mechanism of the enhanced conversion of alkane to aromatics upon modification of zeolite by Zn or Ga is still controversial.[5–7] Derouane *et al.*[8] claimed a concurrent action of both metal sites and Brønsted acid sites (BAS) in a bifunctional mechanism of alkane activation. Another hypothesis implied that alkane C–H bond activation occurred on BAS, the activation being independent of the addition of metal cations.[2] Recombinative desorption of hydrogen H-atoms as H_2, which occurs on Zn or Ga species, was assumed to be the limiting step of the reaction.[2,9,10]

Based on H/D exchange studies of alkanes with Zn-modified high-silica zeolites ZSM-5 and BEA, we have recently demonstrated that the activation of an alkane C–H bond by Brønsted acid sites can be strongly influenced by Zn species, which increase the rate of the exchange by one–two orders of magnitude, whereas the activation energy is decreased.[11–13]

Recombinative desorption of hydrogen is assumed to occur only with involvement of metal species; Brønsted acid sites of metal-modified zeolite are not involved in molecular hydrogen desorption.[14–17] Since the recombination of hydrogen atoms has been proposed as the rate-limiting step in the dehydrocyclodimerization of C_{3+} alkanes over Ga/H-ZSM-5,[2] and both metal and Brønsted acid sites are indeed involved in alkane activation,[8,11] it is of considerable interest to understand the concurrent influence of both metal species

and acidic OH groups on the molecular hydrogen activation by these catalysts. The hypothesis that hydrogen recombinative desorption can also occur with involvement of acidic OH groups requires verification. This could be done by analysis of the H/D hydrogen exchange between molecular hydrogen and Brønsted acid sites of metal-modified zeolites.

In this paper we present an analysis of the kinetics of H/D hydrogen exchange for acid-form and Zn- and Ga-modified zeolite BEA by ^1H MAS NMR *in situ*, in order to shed some light on peculiarities of molecular hydrogen activation by the metal-modified zeolite BEA in comparison with the pure acid-form zeolite.

2. Experimental

2.1 Materials characterization and samples preparation

The acidic form of the zeolite beta (H-BEA-73) (Si/Al = 17, average crystal size 0.1–0.2 μm) was synthesized using tetraethylammonium hydroxide as template with subsequent calcination at 823 K in an air flow for 6 h.[18]

Zn- and Ga-modified zeolites beta were prepared by incipient wetness impregnation of the parent samples of dry zeolite H-BEA-73 with saturated aqueous solution of zinc formate or gallium nitrate. 5.7 g of H-BEA-73 was impregnated with 0.36 g of $Zn(HCOO)_2 \times 2H_2O$ in 6.2 ml of hot water and 5.4 g of H-BEA-73 were impregnated with 0.635 g of $Ga(NO_3)_3 \times 8H_2O$ in 7 ml of water to obtain Zn- and Ga-form zeolites. The prepared samples were dried at 373 K overnight with the following calcination in air flow at 670–800 K. The Zn-modified sample of zeolite beta contained 2.07 wt% of zinc (Zn/H-BEA-73). Ga-modified zeolite sample contained 1.72 wt% of gallium (Ga/H-BEA-73). The composition of the zeolite unit cell (Table 1) was determined by chemical

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Table 1 Characteristics of the zeolite BEA samples

Zeolite sample	Si/Al[a]	Concentration of OH groups,[b] $\mu mol\ g^{-1}$				Zeolite unit cell
		SiOHAl/4.0, 5.1 ppm	AlOH/2.2–2.7 ppm	SiOH/2.1 ppm	SiOH/1.8 ppm	
H-BEA-73	17	645	100	240	210	$Al^{oct}_{0.747}\ [Na^+]_{0.002}\ H_{2.472}\ Al^{tetr}_{2.474}\ Si_{60.779}\ O_{128}$
Zn/H-BEA-73 (2.07 wt% Zn)	17	610	120	270	280	$[ZnO]_{0.768}\ Al^{oct}_{0.080}\ [Na^+]_{0.002}\ [Zn^{2+}]_{0.372}\ H_{2.395}\ Al^{tetr}_{3.141}\ Si_{60.779}\ O_{128}$
Ga/H-BEA-73 (1.72 wt% Ga)	17	690	100	215	195	$[Ga_2O_3]_{0.413}\ Al^{oct}_{0.938}\ [Na^+]_{0.002}\ H_{2.737}\ Ga^{tetr}_{0.456}\ Al^{tetr}_{2.283}\ Si_{60.779}\ O_{128}$

[a] Estimated based on ^{29}Si MAS NMR spectra with accuracy *ca.*6%. [b] Error in estimation of concentration is 10–17%.

analysis, quantitative analysis of acidic groups with ^{1}H MAS NMR, and a qualitative analysis of the states of Zn and Ga in these materials based on XRD, ^{1}H{^{27}Al} spin-echo double resonance (TRAPDOR[19,20]), ^{27}Al, ^{29}Si, ^{71}Ga MAS NMR, UV-vis diffuse reflectance and IR spectroscopy.

The ^{27}Al MAS NMR spectra of the samples H-BEA-73 and Ga/H-BEA-73 show a few signals from octahedrally coordinated extra-framework aluminium species (23% and 30% of signal intensity, correspondingly) in vicinity of 0 ppm and the signal at 54 ppm due to tetrahedrally coordinated framework aluminium atoms. Concentrations of the acidic OH groups were obtained from their signal intensities in the ^{1}H MAS NMR spectra by comparison with the signal of methane as internal standard.

X-Ray powder diffraction analysis (XRD) of Zn/H-BEA-73 revealed exclusively the crystalline phase of zeolite beta. It could be excluded that the Zn/H-BEA-73 sample contains a bulk ZnO phase larger than 0.5 wt%. The UV–vis diffuse reflectance spectrum of Zn/H-BEA-73 exhibits the 270-nm-band due to sub-nanometric ZnO clusters inside zeolite pores.[21]

We could not detect a gallium oxide bulk phase in the zeolite Ga/H-BEA-73 by XRD analysis. ^{71}Ga MAS NMR has shown the main signal at 159 ppm from the Ga sites tetrahedrally coordinated by oxygen (Ga^{IV}) and less intense signal at 0 ppm from the Ga sites octahedrally coordinated by oxygen (Ga^{VI}). These data indicate that the signal at 0 ppm may arise from the Ga^{VI} in Ga_2O_3 species, which is however not detected by XRD due to the small dimension of Ga_2O_3 species, while the signal at 159 ppm belongs to a notable extent to tetrahedrally coordinated Ga species in the zeolite framework.[22,23]

Industrially produced deuterium gas, D_2 (99% D), was used without further purification. The samples for NMR measurements were prepared by heating 80 mg of the zeolite powder in the glass tubes of 5.5 mm outer diameter from 300 to 673 K at the rate of 10 K h^{-1} under vacuum. Finally, the samples were maintained at 673 K for 24 h under vacuum (less than 10^{-2} Pa), loaded with deuterium (D_2) at the temperature of liquid nitrogen with 2 molecules (*ca.* 700 $\mu mol\ g^{-1}$) of D_2 per unit cell and then sealed off. The glass tube of 10 mm length and 5.5 mm diameter could be tightly inserted into a 7 mm zirconia MAS-rotor. For the analysis of the H/D exchange reaction kinetics, the NMR probe with the sample was preheated for 20 min at the temperature at which the exchange did not yet occur to a notable rate. Then the temperature was rapidly increased within 3–10 min by 50–100 K to the reaction temperature and equilibrated for 2–3 min, before acquisition of the NMR signal.

2.2 NMR measurements

NMR spectra were recorded at 9.4 T on a Bruker Avance-400 spectrometer equipped with a high-temperature broad-band double-resonance MAS probe. Zirconia rotors (7 mm outer diameter) with an inserted sealed glass tube were spun at 3–5 kHz by dried compressed air at 300–568 K. ^{1}H MAS spectra were recorded by the Hahn-echo pulse sequence ($\pi/2$–τ–π–τ–acquisition), where τ equals to one rotor period (200–333 μs). The excitation pulse length was 4.5 μs ($\pi/2$), and typically 6–24 scans were accumulated with a 4–60 s delay. In double-resonance ^{1}H{^{27}Al} TRAPDOR experiments[19,20] a Hahn-echo sequence was applied to the ^{1}H channel with irradiation of aluminium during both τ periods. The ^{27}Al nutation frequency of the irradiation field was about 70 kHz. ^{27}Al MAS spectra were acquired with a 0.6-μs-pulse ($\pi/12$), and about 1000 scans were accumulated with a 0.5 s recycle delay. ^{29}Si MAS NMR spectra were recorded with $\pi/2$ excitation pulse of 5.0 μs duration, and 10–15 s repetition time, and 1000 scans for signal accumulation. Both ^{27}Al and ^{29}Si NMR spectra were recorded using 4 mm rotors and a spinning rate of 10 kHz. The chemical shifts were referenced to TMS for ^{1}H and ^{29}Si NMR and to 0.1 M Al(NO$_3$)$_3$ solution for ^{27}Al NMR.

^{71}Ga MAS NMR studies were performed on an Avance 750 spectrometer at resonance frequency of 228.8 MHz with a samples spinning rate of 25 kHz (2 mm MAS NMR rotor). For obtaining the ^{71}Ga MAS NMR spectra, a single-pulse excitation of 0.5 μs, a repetition time of 0.5 s and 18 000 scans were used. The ^{71}Ga MAS NMR signals were referenced to a saturated solution of Ga(NO$_3$)$_3$.

The sample temperature was controlled by the Bruker BVT-2000 variable-temperature unit. The calibration of the temperature inside the rotor for the kinetic measurements was performed with an accuracy of ±2 K by using lead nitrate, located inside the rotor, as a ^{207}Pb MAS NMR chemical shift thermometer.[24]

2.3 IR measurements

IR spectra were recorded on a Shimadzu FTIR-8300 spectrometer within the spectral range of 700–6000 cm^{-1} with 4 cm^{-1} resolution. 50 scans were acquired for each spectrum. Zeolite samples were pressed in self-supporting wafers (diameter: 0.5–1.0 cm, ρ = 8–12 mg cm^{-2}) and activated in the IR cell at 773 K for 1 h in air and further 1 h at 773 K in a vacuum of 10^{-2}–10^{-3} Pa. The adsorption of CO for testing the Brønsted acidity was performed at 77 K with 60–600 Pa of CO pressure. In the recorded spectra, the absorbance was normalized to

zeolite wafer density ρ. The spectra were recorded at 298 and 77 K. Assessment of Lewis acidity was performed on the base of the absorbance bands at 2190–2233 cm^{-1} belonging to CO coordinated to Lewis site.[25] Among the bands observed for Zn/H-BEA-73 sample, the band at 2213 cm^{-1} was attributed to CO coordinated to isolated Zn^{2+} cations and the band at 2200 cm^{-1} to CO coordinated to small ZnO clusters. The band at 2216 cm^{-1} was assigned to Lewis acid sites of Ga^{3+} cations[26] in small clusters of Ga$_2$O$_3$ in Ga/H-BEA-73 sample. Lewis acid sites caused by extra-framework aluminium species (Al^{3+}) exhibited the bands of adsorbed CO at 2233, 2223 and 2190 cm^{-1}. Quantitative estimations of Lewis sites in accordance with the procedure described in ref. 25 yield 30, 100 and 12 μmol g^{-1} of Lewis acid sites related to Al^{3+} for H-BEA-73, Zn/H-BEA-73 and Ga/H-BEA-73, respectively. The concentration of Lewis acid sites related to Zn species was 15 μmol g^{-1} and that for Ga species was 10 μmol g^{-1}.

2.4 Analysis of the reaction rates

The rate constants k for the H/D exchange between deuterated hydrogen (D$_2$) and acidic OH group of the zeolite has been determined,[12,27] assuming that the exchange is a bimolecular reaction:

$$D_2 + SiOHAl \leftrightarrows SiODAl + HD \qquad (1)$$

$$HD + SiOHAl \leftrightarrows SiODAl + H_2 \qquad (2)$$

The rate constant k is similar for both reactions (1) and (2). Reaction kinetics were obtained in a closed microreactor by measuring *in situ* the increase of the signal intensity of the adsorbed HD and H$_2$ in the ^{1}H MAS NMR spectrum, which corresponded to a transfer of protium from OH groups of zeolite to the deuterated hydrogen.

3. Results and discussions

3.1 Characteristics of acidic hydroxyl groups of the zeolites BEA with IR and NMR

The IR spectra of OH groups of zeolite BEA samples exhibit five clearly distinguishable bands, which are identical to the bands earlier identified for BEA zeolites in ref. 28–38. Similar bands are observed for the acid-form and Zn- and Ga-modified zeolite samples (Fig. 1). The signal at 3745 cm^{-1} belongs to terminal SiOH groups and internal groups at framework defects. The signal at 3610 cm^{-1} is due to strongly acidic bridging hydroxyl groups. The broad band at 3600–3300 cm^{-1} is assigned to bridged hydroxyls which are perturbed by H-bond interactions with the zeolitic framework.[35,37] The signal at 3660 cm^{-1} belongs to the acid OH groups connected to Al partially attached to the framework and located on external surface.[29,30] The band at 3785 cm^{-1} is attributed to low-acidity OH groups bonded to extra-lattice aluminium.[29,31] The band from the silanol OH groups at 3740 cm^{-1}, which is observed as left-hand shoulder to the band 3745 cm^{-1} exhibits a strong acidity, similar to the groups with the band 3610 cm^{-1}.[39] This silanol OH group could also be involved in the reaction of H/D exchange with small alkane molecules.[12]
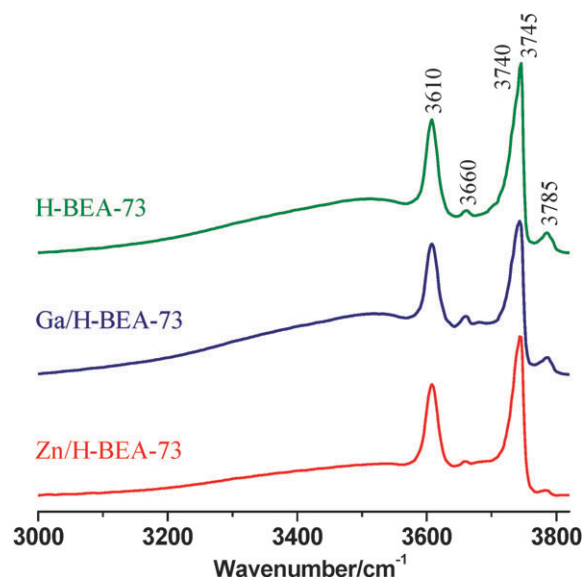

Fig. 1 IR spectrum of zeolite BEA samples.

^{1}H MAS NMR spectra of all zeolite samples show three main signals (Fig. 2a and d). The signals at 4.0 and 5.1 ppm are due to the free bridged and weakly hydrogen-bonded bridged hydroxyls (SiOHAl), respectively. The most intense signal at 1.8 ppm arises from SiOH groups at framework defects and external SiOH groups.[32,33,36,37] The intense signal of SiOH groups is a result of the faulted structure of the zeolite beta (BEA).[40,41] ^{1}H{^{27}Al} spin-echo double resonance experiments (TRAPDOR[19,20]) show the suppression of signals of protons, which are in vicinity to aluminium atoms of the SiOHAl or AlOH groups, whereas the signals of protons which are far from aluminium atoms are unaffected (Fig. 2b and c). On-resonance ^{27}Al irradiation for one rotor period results in a loss of intensity of three main resonances in the ^{1}H{^{27}Al} MAS NMR spectrum of all zeolite samples (Fig. 2b). The difference spectra (Fig. 2c) show four clearly distinguishable resonances at 5.1, 4.0, 2.7–2.2 and 0.6 ppm for H-BEA-73 and Ga/H-BEA-73. Zn-modified zeolite samples does not show the signal at 0.6 ppm. The TRAPDOR difference spectrum strongly supports the IR data on the presence of two types of the OH groups associated with non-framework aluminium species for H-BEA-73 and Ga/H-BEA-73 zeolites and one type of non-framework aluminium species for Zn/H-BEA-73 sample. The signal at 2.7–2.2 ppm corresponds to the band at 3660 cm^{-1} and the signal at 0.6 ppm to the band at 3785 cm^{-1}.

The ^{27}Al MAS NMR spectra of hydrated H-BEA-73 and Ga/H-BEA-73 zeolite samples exhibited the signals of the framework aluminium atoms at 54 ppm and at 0 ppm from extra-framework aluminium species. For Zn/H-BEA-73 sample, the intensity of the signal from extra-framework octahedral aluminium atoms was 2.5% with respect to total aluminium signal intensity. The observation of the signal 2.7–2.2 ppm from AlOH groups in TRAPDOR difference spectra for all dehydrated zeolite samples can be explained by tetrahedrally coordinated Al, which is three-fold directly attached to the framework *via* oxygen atoms,
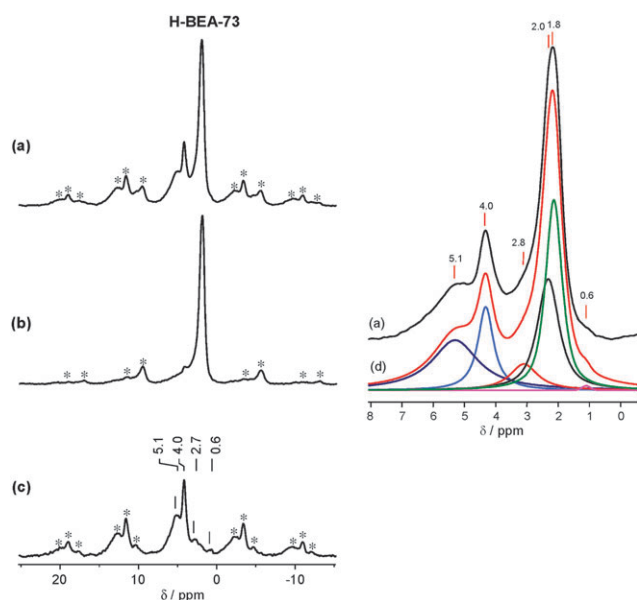
Fig. 2 ^1H MAS NMR room temperature Hahn-echo spectra of zeolite H-BEA-73 sample activated under vacuum at 670 K: (a) without ^{27}Al irradiation, (b) with ^{27}Al irradiation (on resonance). The difference spectrum of (a) and (b) is shown in (c); (d) is decomposition of the experimental spectrum (a) into 6 separate lines. The spinning speed was set to 3 kHz, and τ was equal to one rotor period (333 μs). The spectra for the rest zeolite samples from Table 1 are similar to H-BEA-73. Asterisks * mark spinning sidebands.

the fourth coordination site is occupied by hydroxyl group. The signal at 0.6 ppm in the spectra of Fig. 2 for the dehydrated samples H-BEA-73 and Ga/H-BEA-73 corresponds to the signal of extra-framework Al species at 0 ppm in ^{27}Al NMR spectra of the hydrated samples. The AlOH group with the signal at 2.7–2.2 ppm is slightly less acidic than the SiOHAl group in agreement with the shift of the band at CO coordination, $\Delta\nu_{OH/CO} = 270\ cm^{-1}$.[42,43] AlOH groups are also involved in the H/D exchange with alkanes.[39] The band of SiOHAl group perturbed by CO shifts by $\Delta\nu_{OH/CO} = 340\ cm^{-1}$ for each of the zeolite samples studied. This implies that the strength of the bridged hydroxyl groups of unmodified and metal-modified zeolite samples are similar.[39,42,43]

The analysis of the concentration of acidic SiOHAl groups by using methane as internal reference has shown that the modification of the zeolite H-BEA-73 with zinc decreases the concentration of bridged hydroxyl groups (Table 1). This indicates a substitution of protons of SiOHAl groups for Zn^{2+} cations. About 24% of SiOHAl groups in Zn/H-BEA-73 are substituted by Zn^{2+} cations. For the Ga-modified zeolite sample, a variation of the quantity of SiOHAl groups confirms ^{71}Ga MAS NMR data on incorporation of Ga in the zeolite framework. Gallium produces the additional acidic GaOHSi groups, exhibiting the signals at 4.0 and 5.1 ppm in ^1H MAS NMR spectra, which are similar to the signals from SiOHAl groups. A total increase of bridged OH groups by 17% corresponding to acidic GaOHSi groups was obtained for Ga/H-BEA-73 compared to the parent H-BEA-73 (Table 1).

3.2 Analysis of the H/D exchange kinetics on Zn/H-BEA and Ga/H-BEA zeolites

H/D exchange between deuterated molecular hydrogen (D_2) and Brønsted acid sites of zeolite H-BEA implies a transfer of protium from bridged groups to the molecule of D_2 with simultaneous deuteration of the Brønsted acid site to form a SiODAl group, according to the reactions (1) and (2). Fig. 3 shows the time dependent variation of the ^1H MAS NMR spectrum of D_2 adsorbed on H-BEA-73 at 483 K. The first spectrum recorded within 5 min of the reaction proceeding corresponds to the spectrum of OH groups of the zeolite and adsorbed hydrogen. The line of adsorbed hydrogen consists of a triplet from HD ($J_{H-D} = 41$ Hz);[44] H_2 seems to be formed only in a very small amount. A signal at 1.8 ppm belongs to the terminal SiOH groups. The signals of the bridged OH groups are not clearly visible in Fig. 3. On further occurrence of the reaction the intensity of HD signal increases with time due to transfer of protium from SiOHAl groups to deuterated hydrogen to form HD.

The kinetics of the reactions were monitored in the temperature range 383–548 K, where the H/D exchange reaction occured with a notable rate. Fig. 4 and 5 show that the rate of H/D exchange for D_2 is increased significantly when H-BEA-73 was replaced with Ga/H-BEA-73 and increased even more when replaced with Zn/H-BEA-73. Arrhenius plots for H/D rate constants yield activation energies of 89–102 kJ mol^{-1} (Fig. 6). For H-BEA-73, the activation energy is close to the theoretically estimated activation energy of 84 kJmol^{-1} [14] for a simple exchange reaction with synchronous transfer of protium of acidic OH group to the molecule of D_2 and symmetrical return of one of deuterium atoms of D_2 to the oxygen of the zeolite framework (Fig. 7).

So, the modification of the zeolite with Zn or Ga species causes a dramatic increase of the rate of hydrogen exchange. The temperature threshold of the H/D exchange reaction decreases by about 100 K for Zn/H-BEA-73. The extrapolated exchange rate becomes two orders of magnitude higher at 473–548 K, where the kinetics of the exchange was studied for H-BEA-73. For Ga/H-BEA-73 the effect of metal on H/D exchange is less pronounced. The rate of exchange is one order of magnitude higher compared to that for H-BEA-73.
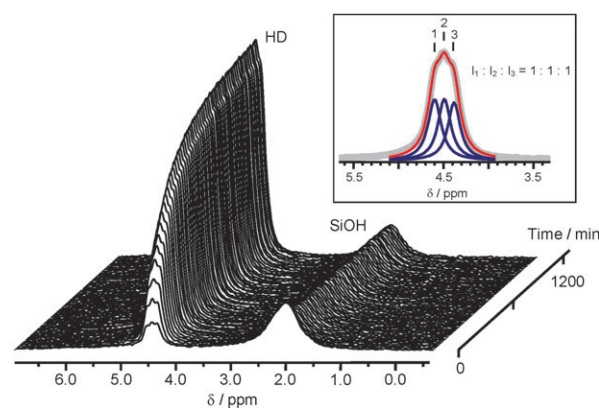

Fig. 3 Stack plot of ^1H MAS NMR spectra at 483 K of molecular deuterium (D_2) adsorbed on zeolite H-BEA-73.
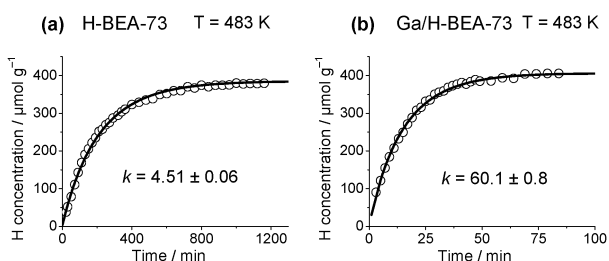
Fig. 4 Kinetics of H/D exchange of D_2 with Brønsted acid sites of zeolites H-BEA-73 (a) and Ga/H-BEA-73 (b) at 483 K. Rate constants k are given in $\times 10^6$ g μmol^{-1} min^{-1} units in Fig. 4 and 5.
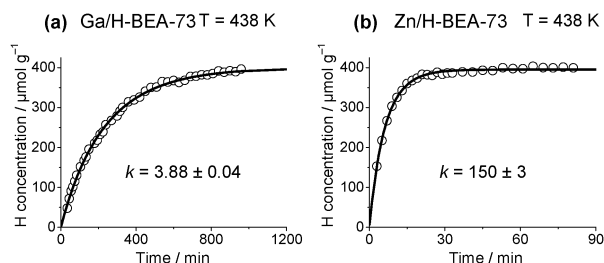
Fig. 5 Kinetics of H/D exchange of D_2 with Brønsted acid sites of zeolites Ga/H-BEA-73 (a) and Zn/H-BEA-73 (b) at 438 K.
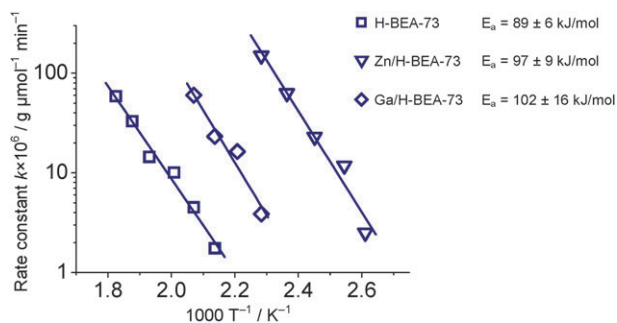
Fig. 6 Arrhenius plots for the rate constants of H/D exchange reaction between molecular deuterium (D_2) and Brønsted acid site of zeolites. (□) H-BEA-73; (◇) Ga/H-BEA-73; (▽) Zn/H-BEA-73.
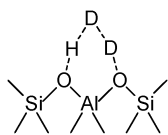
Fig. 7 Transition state for H/D exchange for molecular hydrogen (D_2) with Brønsted acid site of acid-form zeolite in accordance with data of ref. 14.

Arrhenius plots yield activation energies of 97 kJ mol^{-1} for Zn/H-BEA-73 and 102 kJ mol^{-1} for Ga/H-BEA-73, which are similar to the activation energy for H-BEA-73 within the experimental error.

As was indicated above, IR study of adsorbed CO has shown a comparable strength of Brønsted acid sites for all zeolite samples studied. Hence a significant influence of Zn or Ga on the H/D exchange rate cannot arise from a change of the acidity of the hydroxyl groups upon modification of zeolite with Zn or Ga. This implies the involvement of a mechanism

of exchange which is different from that for acid-form zeolite BEA, see Fig. 7. The metal species should be involved in this reaction, and they should be located in the vicinity of Brønsted acid sites of both Zn- and Ga-modified zeolites, in order to affect the H/D exchange reaction.

Gonzales et al.[14] theoretically analyzed the rate of H_2/D_2 exchange on the Brønsted acid center (HZ) of Ga/H-ZSM-5 zeolite and on the active center which involves $ZGa(H)_2$ species. This species was expected to be the active ones in alkane dehydrogenation on Ga/H-ZSM-5 zeolite. It has been found that the rate of exchange is higher for the acidic HZ center compared to the $ZGa(H)_2$ one. This does not agree with our data and the earlier finding by Eglesia et al.[2] on peculiarities of H/D exchange for D_2/H_2, that an exchange is performed easily on Ga-modified zeolite. This may indicate that $ZGa(H)_2$ species are not involved in the exchange or they are not formed under conditions of the H/D exchange reaction. It has been later concluded that GaO^+ species could be more active than Ga^{1+} in H_2/D_2 exchange.[15] Therefore one can assume that metal oxide species promote the H/D exchange reaction.

The metal species in the sample of Zn/H-BEA-73 are mainly subnanometric ZnO species inside the pores of the zeolite and Zn^{2+} cations. Ga species in Ga/H-BEA exist mainly in the form of small Ga_2O_3 particles (invisible by XRD) at the outer surface of zeolite crystallites and inside the zeolite pores. GaO^{+45-48} or $(Ga_2O_2)^{+49}$ species, which could play the role of active sites in dehydrogenation, were not detected. It is known that molecular hydrogen can be dissociatively adsorbed on ZnO[50,51] or Ga_2O_3.[52,53] It could be also dissociatively adsorbed by Zn^{2+} cations[54,55] or ZnO species in a zeolite[56] or probably by GaO^+. Therefore, a strong influence of the metal species on the rate of H/D exchange can be rationalized by preliminary dissociative adsorption of molecular hydrogen on metal oxide species or metal cations to give M–H and OH species. Further, both M–H and OH species formed on metal oxide species or formed with assistance of metal cation are involved in the reaction with the zeolite SiOHAl groups located in the vicinity of metal oxide species or metal cations. Schemes of the possible exchange mechanisms are shown in Fig. 8. These schemes of the mechanisms, with involvement of either metal cations (Fig. 8a) or metal oxide (Fig. 8b), may account for the enhanced rate of the H/D exchange for metal modified zeolites. Notably, the influence of Zn on the rate of H/D exchange is more profound than the influence of Ga. As we already noted, the rate constants for the H/D exchange increase by two orders of magnitude, when Zn is loaded in H-BEA. The rate constants increase only by one order of magnitude, when the zeolite becomes modified with Ga.

In principle, both ZnO and Zn^{2+} cations can accelerate the H/D exchange rate for Zn-modified zeolites. However, taking into account that Zn^{2+} cations should be located on two neighbour[57] or remote SiO^-Al groups[58] and the third SiOHAl group involved in the exchange should also be located in vicinity of the Zn^{2+} cation, the probability of finding three Al atoms in the zeolite framework in a close proximity to one another should be extremely low. This implies that a pathway of H/D exchange with assistance of Zn^{2+} cations (Fig. 8a) is less probable. We believe that small ZnO species, which are
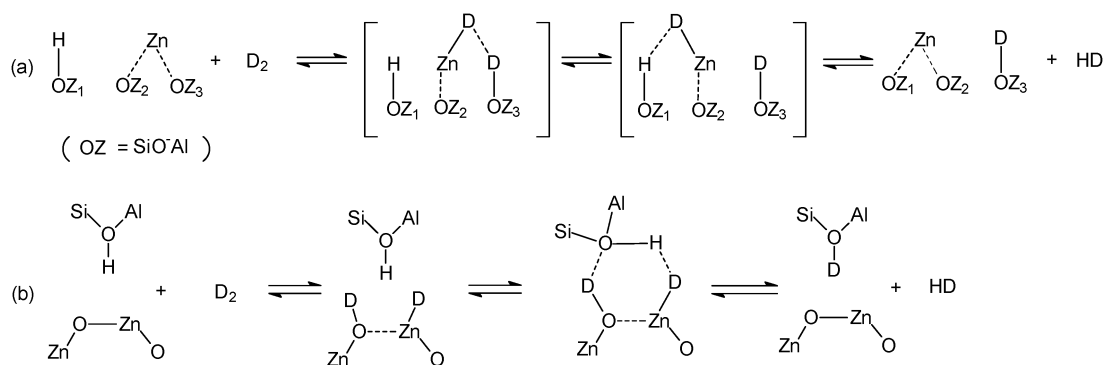
Fig. 8 Potential routes for H/D exchange reaction on Zn- or Ga-modified zeolites. (a) with assistance of metal cation; (b) with assistance of metal oxide species. An example pertains to Zn-modified zeolite.

located in vicinity of SiOHAl groups inside the channels of zeolite BEA, provide a promoting effect of Zn on the H/D exchange.

The promoting effect of Ga on the H/D exchange rate is less profound compared to Zn. Ga exists in a form of small Ga_2O_3 particles (no bulk phase of Ga_2O_3 was detected with XRD and UV-vis). It is assumed that GaO^+ species,[45–48] which is active in alkane aromatization, forms either directly under aromatization conditions or by reducing the zeolite with hydrogen. One can assume that the GaO^+ species, which are expected to provide dissociative adsorption of alkane or hydrogen more effectively than Ga_2O_3, are not formed under the conditions of our experiments. The samples were not treated in a hydrogen atmosphere at higher temperatures, which is used for the activation of Ga-modified zeolite catalysts for aromatization reactions. This may account for a higher activity of the Zn/H-BEA-73 sample compared to the Ga/H-BEA-73 samples in the H/D exchange reaction. The involvement of all acidic sites of the zeolite in the exchange implies that small Zn and Ga oxide species are uniformly distributed over the zeolite channels.

A strong influence of the loaded metal on H/D exchange reaction between molecular hydrogen and zeolite Brønsted sites may evidence that recombinative desorption of hydrogen on Zn- or Ga-containing zeolite catalysts of small alkane aromatization occurs with involvement of both metal species and Brønsted acid sites.

4. Conclusion

Modification of zeolite H-BEA with Zn or Ga provides a promoting effect on the reaction of H/D exchange between molecular hydrogen and Brønsted acid sites of the zeolites. The effect is more remarkable for Zn-modified zeolite. While apparent activation energies of the exchange are similar for the pure acid-form and metal modified zeolites (89–102 kJ mol^{-1}), the rate of H/D exchange increases by two orders of magnitude when the zeolite is modified with Zn, and one order of magnitude with Ga. The strong influence of either Zn or Ga on the rate of H/D exchange is achieved presumably by preliminary dissociative adsorption of molecular hydrogen on metal oxide species and further involvement of M–H species in the interaction with Brønsted acid sites. The data obtained are in favor of involvement of both metal species and

Brønsted acid sites in a possible recombinative desorption of hydrogen on Ga- or Zn-containing zeolite catalysts of small alkane aromatization.

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