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H/D Exchange Reaction between Isobutane and Acidic USY Zeolite: A Mechanistic Study by Mass Spectrometry and *in Situ* NMR

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The H/D exchange reaction between isobutane and acidic USY zeolite was studied using mass spectrometry and *in situ* ^{1}H NMR. An inhibiting effect of hydrogen on this reaction was observed. The H/D exchange is enhanced by both *in situ* and *ex situ* addition of small amounts of isobutene. A kinetic isotope effect of 1.5 was found for the H/D exchange of isobutane and 2-deuterium-labeled isobutane over D_2O-exchanged HUSY (DUSY), as well as nondeuterated and perdeuterated isobutane over HUSY. The occurrence of a primary kinetic isotope effect (KIE) indicates that the slow step of the H/D exchange reaction involves a cleavage of the tertiary C–H (or C–D) bond in isobutane. After addition of small amounts of isobutene to the feed or pretreating the catalyst with small amounts of isobutene before starting the H/D exchange reaction, the KIE still exists, suggesting that the limiting step for the H/D exchange reaction between isobutane and acidic zeolite is the hydride transfer from an alkane to the exchanged cation.

Key Words: **H/D exchange; acidic zeolite; alkane activation; kinetic isotope effect; *in situ* NMR, mechanism.**

1. INTRODUCTION

Acid zeolite catalysis is one of the economically and ecologically important fields in catalysis, and acidic zeolites have been used in a wide variety of industrial processes (1). Acid-catalyzed hydrocarbon conversions, such as catalytic cracking, isomerization, and alkylation, are large-scale industrial processes that use solid or liquid strong acids, such as acidic zeolites, chlorinated aluminas, sulfuric acid, and hydrogen fluoride (1–4). However, in the catalytic conversion of alkanes over acidic zeolites, several reactions, such as cracking, isomerization, dehydrogenation, and oligomerization, often take place simultaneously, resulting in very complex reaction pathways. This often hampers a detailed investigation of the reaction mechanism. In order to gain more information regarding the mechanistic aspects of alkane activation on acidic zeolites, the simplest and most elementary reaction involving alkane activation is H/D exchange, which takes place readily in the absence of side reactions.

In a series of recent papers (5–12) we have shown that H/D exchange between light alkanes (C_3–C_6) and various D_2O-exchanged strong solid acids, such as SZ, FMSZ, HEMT, HBEA, HUSY, HMAZ, HZSM-5, HSAPO, and HPAs, occurs readily in the temperature range 25–200°C in the absence of cracking and isomerization. The observed regiospecific H/D exchange in branched alkanes for which only the protiums vicinal to the branching carbon were exchanged was rationalized by the intermediate formation of carbenium ions and olefins (6). This H/D exchange mechanism, as shown in Scheme 1 using isobutane as a model, is very different from the one observed with deuterated liquid superacids, in which the exchange process takes place via the reversible protonation of the alkane, leading to the H/D exchange in all C–H positions.

Unlike the clear picture now available for alkane activation in liquid superacids (13–15), some fundamental questions concerning alkane activation on solid acids remain unanswered (4, 16). How are the reactive intermediates formed from the starting alkane and at which steady state concentration? Moreover, what is the true nature of the cations: (i) adsorbed carbenium ions (i.e., alkoxy species); (ii) bona fide highly energetic carbenium ion intermediates; or (iii) carbocation-like transition states? At the present state, nuclear magnetic resonance (NMR) spectroscopy, hydrocarbon chemistry, and theoretical approaches have not provided the conclusive answer. As our results as well as generally acid-catalyzed hydrocarbon chemistry are best rationalized using classical carbocationic intermediates (carbenium ions), we use this general term in the text for simplification, being well aware that the exact nature of these species on the solid is still under debate. In this work, H/D exchange of isobutane over acidic USY zeolite was investigated using gas chromatography (GC)-mass spectrometry (MS) and *in situ* ^{1}H NMR. The slow step for this H/D exchange reaction was discussed on the basis of kinetic isotope effects (KIEs).

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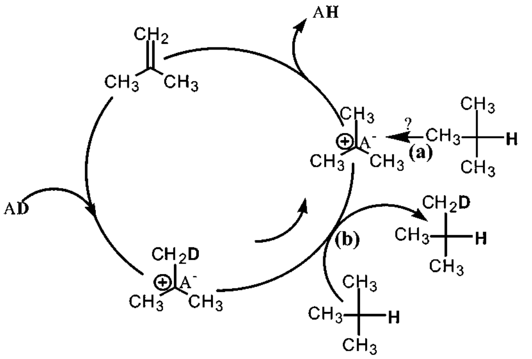


SCHEME 1. Catalytic cycle of H/D exchange between isobutane and deuterated solid acids.

2. EXPERIMENTAL

2.1. *Materials*

HUSY (Si/Al = 4.3) is a zeolite Y dealuminated with $(NH_4)_2SiF_6$, in which some of the framework Al was replaced by Si without leaving extra-framework aluminum. The surface area, micropore volume, and Brønsted acid sites of this sample are 742 $m^2\ g^{-1}$, 0.322 ml g^{-1}, and 2.9 mmol g^{-1}, respectively.

Deuterium labeled isobutane, such as 2-methylpropane-2-d_1 (abbreviated as isobutane-2-d), 2-(methyl-d_3)-propane-1,1,1,3,3,3-d_6 (abbreviated as isobutane-d_9), and isobutane-d_{10}, were synthesized according to Ref. (17). Isotopic purity is higher than 95%.

2.2. *Deuteration of the Catalyst*

For deuteration of the catalyst, an all-glass grease-free flow system was used following Ref. (18). The catalyst was first activated in dry air at 500°C for 3 h. Then the temperature was lowered to 200°C, and the catalyst was deuterated by sweeping D_2O with N_2 (40 ml min^{-1}, ca. 3 mol% D_2O in N_2) for 2 h. Excess D_2O was then removed by flushing the catalyst at the same temperature with dry N_2 (40 ml min^{-1}) for 2 h.

2.3. *Procedure for H/D Exchange*

The H/D exchange reaction between isobutane and the deuterated catalyst was carried out in the same glass system. One gram of the above deuterated catalyst was put in the flow reactor with gaseous isobutane (5.2% in N_2, total rate = 25 ml min^{-1}) at 150°C. The gas phase was analyzed by GC-MS every 2 min during the reaction. The reaction mixture including carrier gas was separated by a GC-8000 gas chromatograph (Carlo Erba Instruments) equipped with a 30-m capillary column DB-624 (JSW Scientific). The oven temperature was constant at 35°C. MS analysis was performed using a QMD-1000 spectrometer (Carlo Erba Instruments) with a ionization voltage of 70 eV.

The correction of mass spectra from the natural abundance (^{13}C contribution) and fragmentation pattern of isobutane was made with a program based on the work of Price and Iglesia (19). The H/D exchange rate was calculated based on first-order kinetics of the hydrocarbon. Taking into account the adsorption and induction period in the first stage of the reaction, the data linearly fitted with first-order kinetics were generally taken from the time range 14–30 min, unless stated otherwise.

2.4. *In Situ NMR Experiments*

HUSY (0.5 g) was activated in dry air at 500°C for 3 h. Then it was placed in an alumina NMR tube from Saphikon (20) under argon. Gaseous deuterated isobutane (isobutane-d_9 or isobutane-d_{10}) (30 ml) was condensed on the catalyst at liquid nitrogen temperature. A teflon cylinder was added on top of the catalyst to decrease the head space in the NMR tube. The tube was then tightly closed.

In situ ^1H NMR kinetic measurements were performed using a Bruker MSL 300 spectrometer at a Larmor frequency of 300 MHz. Angle pulses (45°) were used with a relaxation time of 2 s and each spectrum represented an accumulation of 48 scans. A BVT 1000 Bruker temperature controller equipped with a Cu-Const thermocouple was used for temperature regulation. The temperature inside the NMR tube was calibrated based on the chemical shift of the ethylene glycol. For nonadeuterated isobutane, the reaction temperature ranged from 70 to 100°C and for perdeuterated isobutane from 80 to 110°C.

The rate of H/D exchange between deuterated (non-deuterated or perdeuterated) isobutane and acidic OH groups of zeolite HUSY was determined by an exponential fit,

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

where I_t and I_∞ denote the amplitude of signals from methyl groups of isobutane in the ^1H NMR spectra at the observation time t and at $t = \infty$ (equilibrium), respectively.

3. RESULTS AND DISCUSSION

3.1. *Effect of Hydrogen*

Figure 1 presents the graphic determination of the H/D exchange rate of isobutane at 150°C on D_2O-exchanged HUSY, namely DUSY, measured using N_2 and H_2 as carrier gases. Under the same experimental conditions, when replacing N_2 with H_2, the H/D exchange rate of isobutane decreases by one half (from 0.0145 to 0.00669 min^{-1}). In order to check in more detail the influence of H_2 on this H/D exchange reaction, we performed a recirculation (4 ml min^{-1}) with a mixture of 200 ml of D_2 and 50 ml of isobutane on 1 g of HUSY at 150°C. After continuous-flow recirculation for 50 min, isobutane was condensed and analyzed using

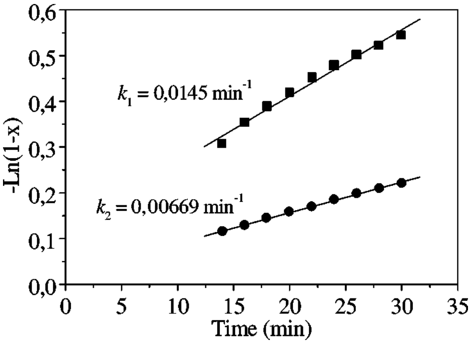


FIG. 1. Effect of hydrogen on the H/D exchange rate between isobutane and deuterated HUSY at 150°C. (■) N_2 as carrier gas; (●) H_2 as carrier gas.

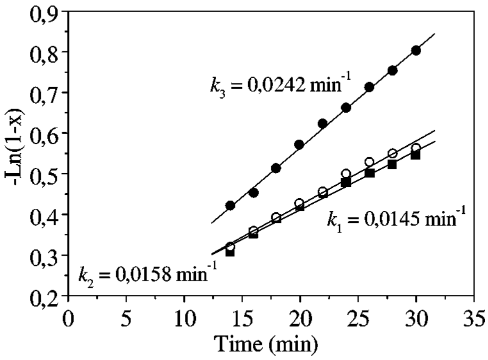


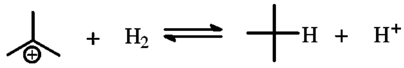
FIG. 2. Effect of isobutene addition in the isobutane feed on the H/D exchange rate between isobutane and deuterated HUSY at 150°C. (■) 0%; (○) 2%; (●) 5% (5% isobutene: 95% isobutane, 5.2% in N_2).

400-MHz ^1H and ^2H NMR after addition of an adequate amount of a $CF_2ClCFCl_2$ solution of a $CDCl_3/CHCl_3$ mixture used as internal standard. Deuterium (1.3%) was incorporated into the primary position of isobutane, but no deuterium was detected in the tertiary position. This suggests that no direct hydrogenation of alkenes, which are required as intermediates by the H/D exchange reaction (Scheme 1), takes place on HUSY under these conditions. Otherwise, the incorporation of deuterium in the tertiary position of isobutane would be expected. The incorporation of a small quantity of deuterium in the primary position can be interpreted as a deuteration of the catalyst by D_2 followed by an exchange reaction between isobutane and deuterated sites on the catalyst.

From the above experiment we can rule out the possibility that the inhibiting effect of H_2 on the H/D exchange rate of isobutane on deuterated HUSY is caused by hydrogenation of isobutene (i.e., a decrease in the concentration of alkene intermediates). We suggest that hydrogen diminishes the exchange rate by reacting directly with the carbenium ions, as shown in Scheme 2, thus decreasing the formation of carbenium ion intermediates, viz., the initial step of alkane activation. This kind of reaction, which was initially reported by Hogeveen and Bickel (21) to take place in liquid superacids, was also suggested by Guisnet and co-workers (22–25) to explain the decrease in the rate of toluene disproportionation in the presence of hydrogen, and to interpret the large inhibiting effect of hydrogen on *n*-butane isomerization over H–mordenite zeolites. The observation of maximum rate as a function of hydrogen pressure has also been reported (26, 27).

3.2. *Effect of Isobutene*

The effect of addition of isobutene on the H/D exchange rate of isobutane on DUSY at 150°C is shown in Fig. 2. The addition of 2% isobutene (relative to isobutane, 2% isobutene: 98% isobutane) to the feed (5.2 mol% hydrocarbons in N_2, total rate = 25 ml min^{-1}) changes the exchange rate very slightly (only from 0.0145 to 0.0158 min^{-1}). However, when the amount of isobutene is increased to 5%, the H/D exchange rate of isobutane increases substantially (from 0.0145 to 0.0242 min^{-1}). It is well known that isobutene is easily protonated by the acid sites of zeolite to give *t*-butyl carbenium ions, which are proposed as intermediates for the H/D exchange of isobutane. If the initial alkane activation (Scheme 1) was the slow step, an obvious increase in the H/D exchange rate would be expected when adding 2% isobutene to the isobutane feed due to *in situ* generation of more *t*-butyl cations. It seems that hydride transfer could be the rate-limiting step of the H/D exchange reaction.



SCHEME 2. Reaction of carbenium ions with hydrogen.

In another series of experiments DUSY zeolite was first pretreated with isobutene for a short time, and then placed in contact with isobutane to start the H/D exchange reaction. Figure 3 shows the H/D exchange rate of isobutane on DUSY at 150°C after pretreatment with isobutene (5.2 mol% in N_2, total rate = 25 ml min^{-1}) for various time intervals. The H/D exchange rate was calculated based on the initial period. After isobutene pretreatment, the H/D exchange rate of isobutane increased by a factor of 2–4. This

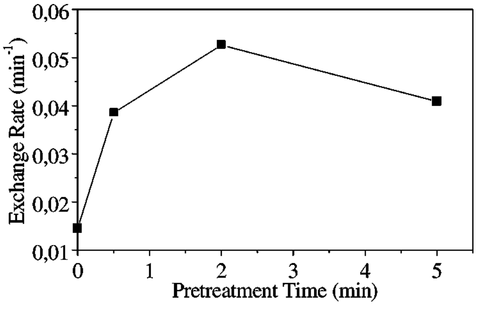


FIG. 3. Effect of isobutene pretreatment time on the H/D exchange rate between isobutane and deuterated HUSY at 150°C.

can be rationalized by the rapid initial generation of *t*-butyl cations before starting the H/D exchange reaction. The exchange rate is obviously dependent on the pretreatment time, viz., the amount of isobutene added. It first increases rapidly during pretreatment, and then declines slowly. This can be understood as follows. Increasing the addition time of isobutene means that more *t*-butyl cations are generated on the surface of the zeolite, thus leading to an increase in the H/D exchange rate of isobutane with longer addition time of isobutene. However, introduction of more isobutene does favor oligomerization and thus deactivates the catalyst.

In conclusion, the H/D exchange reaction of isobutane on deuterated HUSY is enhanced by both *in situ* and *ex situ* addition of appropriately small amounts of isobutene (i.e., by *in situ* and *ex situ* generation of an excess of *t*-butyl carbenium ions). This is consistent with the reported results on the reaction of butane. Pines and Wocker (28) observed in an early experiment that the efficiency of *n*-butane to isobutane conversion increased significantly when butene was added to the feed. The promoting effect of butene or isobutene on the conversion of *n*-butane or isobutane was reported by several other groups (29–33).

3.3. *Kinetic Isotope Effect*

Isotope effects on the rate of chemical reactions arise from difference in the zero-point energy (34, 35). Since the first paper concerning isotope effects was published by Bigeleisen *et al.* (36), KIEs have been widely used to gain insight into reaction mechanisms (37–40).

As is seen in Fig. 4, the replacement of isobutane by isobutane-2-d shows a substantial decrease in the H/D exchange rate, representing a primary KIE. A k_H/k_D of 1.5 was found for the H/D exchange of isobutane and isobutane-2-d on DUSY zeolite at 150°C. This KIE is close to the recently reported result ($k_H/k_D = 1.4$) by Schoofs *et al.* (41) for the H/D exchange reaction with isobutane over acidic MFI-type zeolites at similar temperatures. The occurrence of primary KIE indicates that the slow step or limiting step of the H/D exchange reaction involves a cleavage of the tertiary C–H (or C–D) bond in isobutane. If one looks at the proposed H/D exchange mechanism presented in Scheme 1, there are only two steps comprising such a cleavage. One (step a) is activation of the alkane to give a t-butyl cation. The other (step b) is hydride transfer from an incoming alkane to the exchanged cation. Thus, one important question remains unanswered. Which is the rate-limiting step in the H/D exchange reaction: alkane activation or hydride transfer?

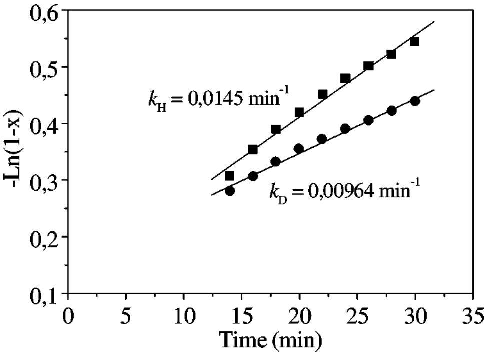


FIG. 4. H/D exchange reaction of isobutane and isobutane-2-d on deuterated HUSY at 150°C. (■) Isobutane; (●) isobutane-2-d.

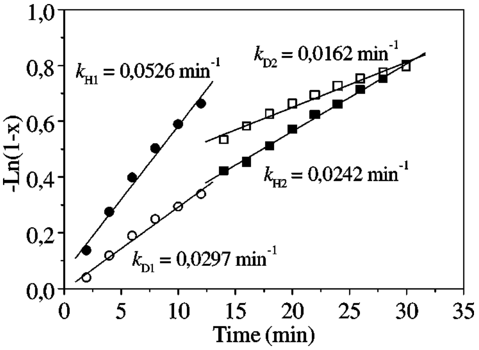


FIG. 5. H/D exchange reaction of isobutane and isobutane-2-d on deuterated HUSY at 150°C after isobutene addition or pretreatment with isobutene. (■, □) 5% isobutene:95% isobutane or isobutane-2-d, 5.2% in N_2; (●, ○) pretreatment with isobutene (5.2% in N_2) for 2 min. Solid symbols, isobutane; open symbols, isobutane-2-d.

Figure 5 shows the H/D exchange rate of isobutane and isobutane-2-d over deuterated HUSY at 150°C after *in situ* or *ex situ* addition of isobutene. Without the addition of isobutene, the k_H/k_D for zeolite DUSY at 150°C is 1.5. It changes to 1.5 and 1.8, respectively, after *in situ* or *ex situ* addition of isobutene. It is obvious that a KIE still exists after the addition of isobutene (i.e., after both *in situ* and *ex situ* generation of an excess of *t*-butyl carbenium ions). Comparison of the k_H/k_D with and without isobutene shows that the addition of isobutene does not affect the KIE so much. Hence, it seems clear that for the H/D exchange reaction of isobutane on acidic zeolites, the slow step is the hydride transfer from an alkane to the exchanged cation.

3.4. *In Situ ^{1}H NMR Observation of H/D Exchange between Isobutane-d_9 or Isobutane-d_{10} and HUSY*

Figure 6 shows the ^{1}H NMR spectra for zeolite HUSY loaded with isobutane-d_9 or isobutane-d_{10} recorded at 90°C after 10 min of the H/D exchange reaction. The signals at 1.0 ppm belong to methyl groups of isobutane, while the signal at 1.79 ppm (Fig. 6a) arises from the methine group of isobutane. No H/D exchange reaction was observed in the tertiary position of isobutane at temperatures of 80–110°C in the case of isobutane-d_{10} adsorbed on HUSY. This result obtained under static conditions is in agreement with our previous findings of regiospecific H/D exchange for isobutane on deuterated solid acids under flow

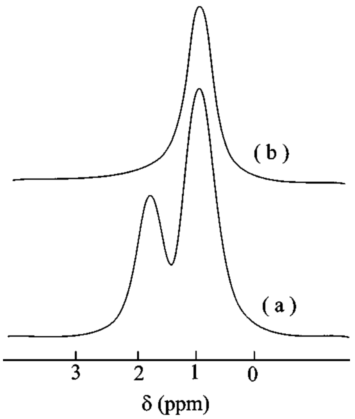


FIG. 6. ^{1}H NMR spectra for zeolite HUSY loaded with (a) isobutane-d_9 and (b) isobutane-d_{10} recorded at 90°C after 10 min of the H/D exchange reaction.

conditions, which can be rationalized by the formation of alkenes and carbenium ions as reaction intermediates (Scheme 1). A recent paper by Stepanov *et al.* (42) using *in situ* ^{1}H magic-angle spinning (MAS) NMR shows that both the methyl and methylene groups of propane were involved in the H/D exchange between acidic OH groups in the zeolite HZSM-5 and adsorbed deuterated propane-d_8 within the temperature range 184–270°C under static conditions. The interpretation by these authors was that H/D exchange for methyl and methylene groups takes place via a penta-coordinated carbonium ion transition state. This hypothesis is however difficult to prove, as it is known that the 2-propyl-cation exchanges very rapidly the primary and secondary hydrons even at low temperature (43). On the other hand, Schoofs *et al.* (41) and Haag and Dessau (44) also suggested that the carbenium ion route for H/D exchange will change to the carbonium ion route when increasing the reaction temperature and the acidity of solid acids.

TABLE 1

Kinetic Isotope Effect for the H/D Exchange Reaction of Isobutane-d_9 and Isobutane-d_{10} on HUSY[a]

Reaction temperature (°C)	80	90	100
k_H/k_D	1.48	1.53	1.39

[a] k_H is the rate for the H/D exchange between isobutane-d_9 and HUSY; k_D is the rate for the H/D exchange between isobutane-d_{10} and HUSY.

The time dependence of the amplitude of signals at 1.0 ppm ascribed to methyl groups of isobutane in the ^{1}H NMR spectra was measured. In the case of H/D exchange between isobutane-d_9 and HUSY (see Fig. 6a), due to the overlapping of two peaks, a peak seperation was done using a Gaussian/Lorentzian function to get the accurate amplitude of signals from methyl groups of isobutane. Figure 7 shows the determination of the H/D exchange rate of isobutane-d_{10} on HUSY at 110°C under static conditions. The solid line in Fig. 7 represents the fit using the rate of H/D exchange (k) for Eq. [1]. Table 1 gives the kinetic isotope effect measured by *in situ* ^{1}H NMR under static conditions. A k_H/k_D of ca. 1.5 was found between deuterated isobutane and acidic OH groups in HUSY, which is the same as that observed for the H/D exchange between isobutane and acidic OD groups in deuterated HUSY under flow conditions. The existence of a KIE suggests that the bond to be broken in the rate-determing step is the tertiary C–H (or C–D) bond in isobutane.

Based on kinetic data at different temperatures, the apparent activation energy can be obtained from the slope of the Arrhenius plot. Figure 8 shows the Arrhenius plot of the exchange rate versus temperature. An apparent activation energy of 40 ± 1 kJ mol^{-1} for the H/D exchange reaction between isobutane-d_9 and HUSY was observed, which is smaller than that for the H/D exchange between isobutane-d_{10} and HUSY (51 ± 2 kJ mol^{-1}). This is most probably caused by the easier breaking of the C–H bond than the C–D bond, which has already been reflected by the KIE. The apparent activation energy observed for the H/D exchange of deuterated isobutane on HUSY is similar to our previous result for the H/D exchange of deuterated isobutane on HZSM-5 using *in situ* ^{1}H MAS NMR (11).

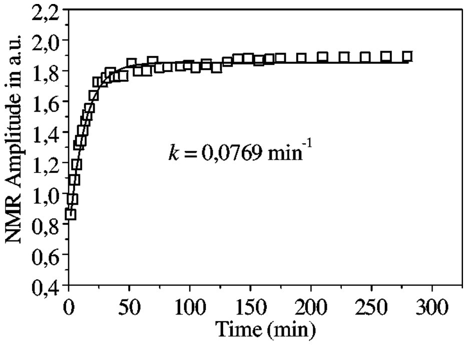


FIG. 7. Evolution of the NMR amplitude vs. time during H/D exchange of isobutane-d_{10} on HUSY at 110°C.

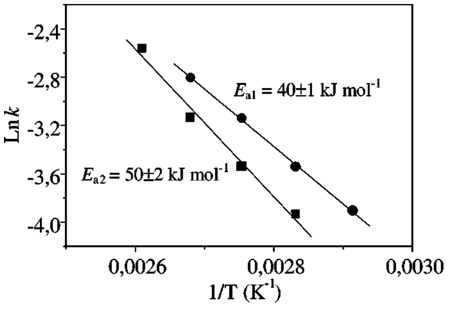


FIG. 8. Arrhenius plot for the H/D exchange of isobutane-d_9 and isobutane-d_{10} on HUSY. (■) Isobutane-d_{10}; (●) isobutane-d_9.

4. CONCLUSION

In this study we have shown that there is an inhibiting effect by hydrogen on the H/D exchange between isobutane and acidic DUSY zeolite, which may be caused by a direct reaction between hydrogen and carbenium ion intermediates. This H/D exchange reaction is accelerated by addition of small amounts of isobutene to the isobutane feed (*in situ* addition) or by pretreating the catalyst with small amounts of isobutene before starting the H/D exchange reaction (*ex situ* addition). The promoting effect of isobutene on the H/D exchange of isobutane over acidic zeolite is related to the rapid generation of t-butyl carbenium ions, which are proposed as the H/D exchange reaction intermediates.

The observed primary KIE for the H/D exchange between isobutane (or isobutane-2-d) and acidic OD groups in D_2O-exchanged HUSY as well as isobutane-d_9 (or isobutane-d_{10}) and acidic OH groups in HUSY indicates that the bond to be broken in the rate-determing step is the tertiary C–H (or C–D) bond in isobutane. After *in situ* or *ex situ* addition of isobutene, the KIE does not change so much, suggesting that the slow step for the H/D exchange reaction between isobutane and acidic zeolite is the hydride transfer from the alkane to the exchanged cation. The lower apparent activation energy observed for the H/D exchange between isobutane-d_9 and HUSY than for that between isobutane-d_{10} and HUSY can also be rationalized by the easier breaking of the C–H bonds in comparison with the C–D bonds.

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