

Activation of Small Alkanes on Solid Acids. An H/D Exchange Study by Liquid and Solid-State NMR: The Activation Energy and the Inhibiting Effect of Carbon Monoxide

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The regioselective hydrogen/deuterium exchange taking place between isobutane and acidic OH groups of strong solid acids has been investigated both by *in-situ* solid state ¹H MAS NMR with perdeuterioisobutane and H-ZSM5 and by liquid ¹H and ²H NMR with isobutane on various D₂O-exchanged solid acids. The activation energy of the process was estimated from the variable temperature *in-situ* ¹H MAS NMR kinetic experiments. A drastic inhibition of the hydrogen exchange was observed in all cases when carbon monoxide was present which is rationalized by the interaction of CO with carbocationic reaction intermediates. © 1999 Academic Press

Key Words: zeolites; superacid; alkane activation; carbon monoxide; solid state NMR.

INTRODUCTION

Acid-catalyzed transformation of hydrocarbons such as cracking, isomerization, and alkylation, are of prime economic importance in the petrochemical industry (1). The chemical inertness of the starting material is generally compensated by high temperature, and/or strongly acidic catalysts. In the presence of liquid superacids (2), alkanes can be protolytically activated even at temperatures well below 273 K. Zeolite catalyzed alkane conversion is generally performed above 573 K (3), but the initial activation step is still controversial: oxidation, hydride abstraction, or protolysis mechanisms were proposed. Some of us have shown recently in a series of papers (4) that hydrogen/deuterium exchange in absence of noticeable cracking or isomerization exchange occurs readily at temperatures below 473 K (even at room temperature). It could be shown that this exchange was regiospecific, e.g. for isobutane on zeolite H-ZSM-5 only methyl groups are involved into the H/D exchange. (4a–e, 5). These results were rationalized by the

intermediate formation of olefins in equilibrium with carbenium ions (4b).

On the other hand, the reaction of carbon monoxide with carbocations generated under superacidic conditions is well documented (6). It is also one of the reaction steps in the Koch synthesis of carboxylic acids from olefins (7). This reaction which is generally performed in sulfuric acid was also shown to occur on acidic zeolites under mild temperatures and pressures, as demonstrated by the *in-situ* solid-state NMR observation of the formation of carboxylic acids in HZSM-5 from isobutene, CO, and water (8).

In earlier work, the inhibiting role of carbon monoxide on solid superacid catalyzed alkane isomerization was reported (9). We were interested in the role of CO in the hydrogen/deuterium exchange reaction in small alkanes, and particularly in the question whether CO is interacting with carbocationic intermediates (10a), as observed in reactions of olefins, or whether the CO is intervening via interaction with Lewis acid sites (9). The question was addressed by studying the kinetics of H/D exchange between perdeuterated isobutane and acidic OH groups in zeolite H-ZSM-5 by *in-situ* ¹H MAS NMR. The inhibiting effect of carbon monoxide on H/D exchange reactions was investigated using isobutane and various strong solid acids deuterated with D₂O (H-BETA, H-USY, H-SAPO-5, and sulfated zirconia) and having different Lewis acidities.

EXPERIMENTAL

Materials

Commercially available *isobutane* was purified from olefinic impurities by pretreating it first under stream hydrogen in the presence of Adams platinum (353 K) and passing it over activated ZSM-5 at room temperature.

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HBEA zeolite (Si/Al = 12) was obtained from P.Q. Corp H β -8: sample with chemical composition H_{4.2}Na_{0.3}Al_{4.5}Si_{59.5}.

HUSY (Si/Al = 4.5) was obtained from Union Carbide LZY-82.

HZSM-5 zeolite (Si/Al = 35) was synthesized according to Ref. (11), calcined at 873 K for 5 h and exchanged with 0.5 M HCl solution.

Sulfated zirconia (SZ) was prepared following Ref. (12). The amount of exchangeable OH sites was determined by exchanging the catalyst with D₂O and measuring by ¹H NMR the amount of protons recovered in the H₂O/HDO/D₂O mixture.

H-SAPO-5 synthesized according to Ref. (13). The chemical composition corresponds to H_{0.04}Si_{0.04}Al_{0.50}P_{0.46}.

Deuteration of the Catalyst

For the deuteration of the catalyst as for the H/D exchange between the catalyst and the alkane, an all-glass grease-free flow system was used following Ref. (14).

The solid acids (200 mg) were first activated at 773 K for 2 h under stream nitrogen 20 cc/min and the temperature lowered to 473 K. Deuteration was then carried out at this temperature by sweeping D₂O with nitrogen (20 cc/min during 90 min). Excess D₂O was then removed by flushing the catalyst at 473 K with dry nitrogen (20 cc/min during 30 min).

Procedure for H/D Exchange

The alkane (ca 6 mol% in N₂) was passed at 473 K during 50 min at a rate of 20 cc/min over the (200 mg) deuterated solid acid, collected in a cold trap, and analysed by 400 MHz ¹H and ²H NMR, after addition of an adequate amount of a CFC₃ solution of a CDCl₃/CHCl₃ mixture used as an internal standard for the H/D distribution measurement (4).

Sample Preparation for the in-situ NMR Experiment

Zeolite H-ZSM-5 (Si/Al = 35) samples for NMR were prepared by heating 80-mg zeolite in glass tubes 5-mm outer diameter. The temperature was increased at a rate of 10 K h⁻¹ under vacuum. Samples were maintained at 673 K at less than 10⁻² Pa for 24 h, loaded at room temperature with four molecules of deuterated isobutane-*d*₁₀, C₄D₁₀ (98% ²H isotope enrichment) per unit cell and sealed off (10-mm length of the glass tube). This corresponds to a loading of 700 μ mol isobutane per gram of dehydrated zeolite. Some samples were loaded, in addition, with an equal quantity of CO. ¹³C and ¹H MAS NMR techniques for the analysis of the reaction products were described earlier (10a).

Kinetic Measurements

In-situ ¹H MAS NMR kinetic measurements were performed on a Bruker MSL 300 spectrometer at 296–423 K at a Larmor frequency of 300 MHz and a rotation frequency of ca 4 kHz. Free induction decay's (FID) were recorded with 45° flip-angle preparation pulses of 3.5 μ s duration, 25 μ s ring down delay, 2–4-s recycle delay, and 24–48 scans for accumulation. The interval between two steps in the time scale of the kinetics ranged from 1 to 10 min in dependence on the temperature and the corresponding rate of the hydrogen transfer. The accuracy of determination of the relative line position with respect to TMS was 0.05 ppm.

The measuring temperature was controlled by the Bruker BVT-2000 variable-temperature unit. The calibration of the temperature inside the sample could be made with an accuracy of ± 2 K by means of a lead nitrate sample as ²⁰⁷Pb MAS NMR chemical shift thermometer (15).

The rate *R* of the H/D exchange between deuterated isobutane and acidic OH group of the zeolite was determined by fitting with first-order kinetics (16),

$$I_t = I_\infty [1 - \exp(-Rt)], \quad [1]$$

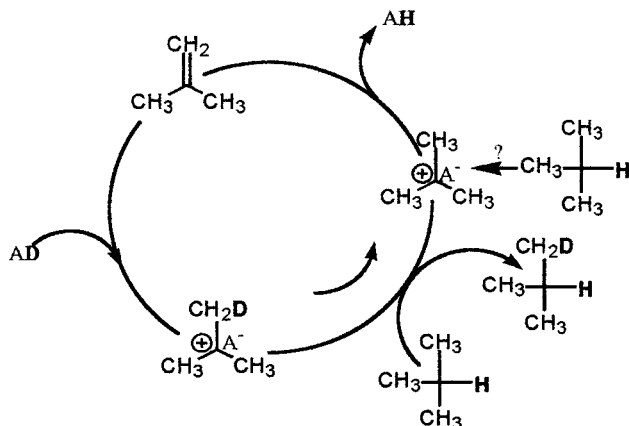
where *I_t* and *I_∞* denote the integral intensities of signals from CH_{*n*} groups (*n* = 1 or 3) in the ¹H MAS NMR spectra at the observation time *t* and at *t* = ∞ (equilibrium), respectively. The time *t* = 0 corresponds to the start of the experiment, when the temperature was increased from room temperature to the desired exchange temperature.

RESULTS AND DISCUSSION

H/D Exchange between Isobutane and D₂O Exchanged Solid Acids in the Absence of Carbon Monoxide

The amount of isotope exchange which can take place between the alkane and the D₂O-exchanged solid acid is directly related to the number of Brønsted acid sites present on the solid. The exchange reaction has been shown to be very fast (4b) at 473 K and the catalyst is rapidly depleted in deuterons replaced by the primary hydrons from isobutane. In accord with the catalytic cycle of Scheme 1 only primary protium in isobutane can be exchanged for deuterium. This mechanism is very similar to the one described for H/D exchange between isobutane and D₂SO₄ by Otvos and Stevenson (17).

The Brønsted acid site density can in this way be estimated and the results obtained for a series of solid acids are collected in Table 1, column A. The values are close Brønsted acid site (BAS) concentration determined by other methods. For sulfated zirconia the value of 0.43 corresponds with one acidic group per sulfur (18).

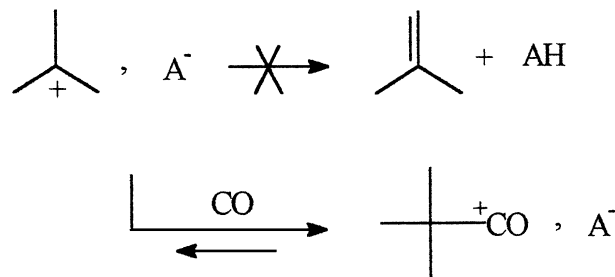


Scheme 1. Catalytic cycle of H/D exchange on solid acids.

H/D Exchange between Isobutane and D₂O-Exchanged Solid Acids in the Presence of Carbon Monoxide

The hydrogen/deuterium exchange reactions have been conducted as before with the same catalyst, but N₂ was replaced by carbon monoxide. Analysis of the deuterium content in isobutane recovered after reaction shows that the H/D exchange is “almost” completely suppressed in all cases, i.e. with the various catalysts. The results are collected in Table 1, column B.

In accordance with the proposed mechanistic scheme (Scheme 1) and in agreement with our earlier work showing that alkenes do react at these temperatures with carbon



Scheme 2. Trapping of the reactive carbenium ion by carbon monoxide.

monoxide on HZSM-5 (8), we rationalize these results with the interaction of the carbenium ion reaction intermediate with carbon monoxide shifting the equilibrium towards the oxocarbenium ion side and blocking in this way the deprotonation step (Scheme 2). Nevertheless, despite various attempts we have no direct experimental evidence for stable oxocarbenium ions in these solid acids. This is not surprising as the decarboxylation constant of *t*-butyl oxocarbenium ion was estimated in liquid superacids to be of the order of 10⁵ at 273 K (6c). The chemical trapping of these oxocarbenium ion intermediates by water in HZSM-5 has been, however, demonstrated (8).

A supplementary argument for the proposed carbocationic intermediate comes from the results obtained with HZSM-5 and H-SAPO-5. For the H-ZSM5 (Si/Al = 35) used for the NMR *in-situ* experiments described below, the ²⁷Al MAS NMR spectra reveal the absence of extra-framework aluminium and H-SAPO-5 is known to contain only some very weak Lewis acid sites (19, 20, 23, 24). We do consider that in both catalysts, Lewis sites are absent and we notice that CO blocks the reaction as well.

These results indicate that the exchange is inhibited for all catalysts independently of the presence or not of Lewis acid sites and also support our suggestion that the interaction takes place instead with the carbocationic intermediates.

We found it also of interest to investigate how much carbon monoxide was necessary to block the isotope exchange. For this reason we have measured the isotope exchange occurring between DBEA and isobutane by changing progressively the N₂/CO ratio of the vector gas. The influence of the carbon monoxide/N₂ ratio on the H/D exchange can be seen in Fig. 1. The curve shows the strong dependence of the isotope exchange rate on the CO/N₂ ratio and supports the hypothesis of interaction between the cationic intermediates and carbon monoxide.

Following the observation that the sulfated zirconia catalyzed *n*-butane isomerization was suppressed when the vector gas N₂ was replaced by CO, Pinna and co-workers (9) suggested that carbon monoxide was complexing the Lewis acid sites necessary for enhancing the superacid character. Considering our results we cannot discard this hypothesis in the case of sulfated zirconia, but it appears also that the

TABLE 1

Number of Exchangeable H Atoms (mmol/g) in the Presence or Absence of CO

Catalyst	BAS ^a	LAS ^a	Sites exchanged for D	
			Under N ₂	Under CO
HBEA	1.07 ^b	0.22 ^c	0.97	0.01
SZ	0.50 ^d	0.50 ^e	0.43	0.01
HUSY	2.90 ^f	1.80 ^c	2.89	0.02
SAPO-5	0.66 ^g	0.00 ^h	0.51	0.04
HZSM-5	0.49 ^b	0.00 ^c	— ⁱ	0.00

^a Brønsted, Lewis sites in 10⁻³ mol g⁻¹.

^b From total Al content (chemical analysis) minus extra framework Al (²⁷Al MAS NMR).

^c From ²⁷Al NMR, assuming that each extra-framework Al represents one Lewis acid site.

^d Experimental.

^e Data from Ref. (12b).

^f From ²⁹Si MAS NMR.

^g From the Si(4Al) concentration determined by chemical analysis and ²⁹Si MAS NMR.

^h According to the literature, SAPO-5 does not contain any Lewis acid sites.

ⁱ Amount not quantified (*in-situ* NMR experiment).

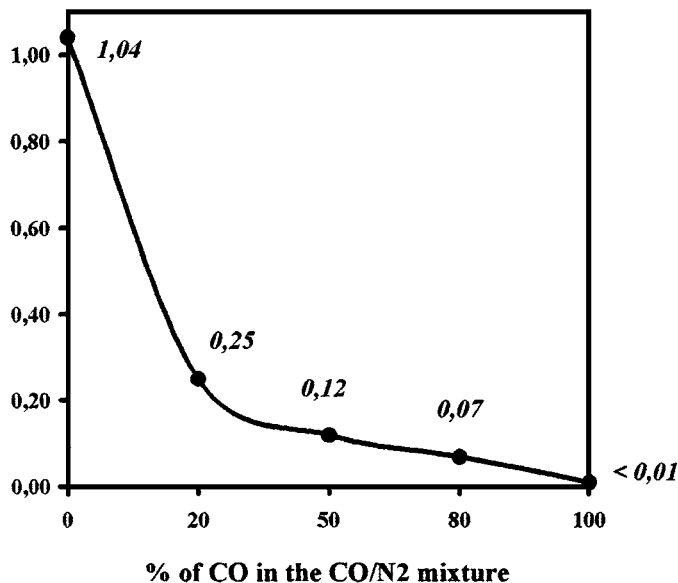


FIG. 1. Equivalent acid sites exchanged in DBEA as a function of the CO/N₂ ratio.

inhibiting effect of carbon monoxide is very general in solid acid catalysis.

In fact, CO shifts the equilibrium described in Scheme 2, and from the shape of the curve in Fig. 1 it appears that a large excess is necessary to suppress completely the exchange. For example, for the first point (25% CO in the CO:N₂ mixture) the relative molar ratio iC₄:CO:N₂ is 6:23.5:70.5. The amount of CO should be large enough to block the Lewis sites but it is insufficient to prevent partial deprotonation of the *t*-butyl intermediates.

The probability of CO to compete with iC₄ for the same Brønsted sites in the activation step can be considered as not very probable as it is known from earlier studies in liquid strong acids and superacids that CO does not prevent the ionization step (6). This shows again that H/D exchange occurs only after generation of the carbenium ion intermediate on the solid.

In-situ ¹H MAS NMR Observation of H/D Exchange between Isobutane d₁₀ and HZSM-5 without and with CO; A Variable Temperature Study

A sample of HZSM-5, maintained at 10⁻² Pa, was loaded at room temperature with four molecules of isobutane-d₁₀ per unit cell and sealed off. The ¹H MAS NMR spectrum at 295 K of isobutane (98% ²H enriched) adsorbed on H-ZSM-5 showed the following characteristics: the broad signals at 4.9 and ca 2.0 ppm (Fig. 2A) belong to Si-OH-Al and Si-OH groups of the zeolite, correspondingly. The signal at ca 1.0 ppm arises from the methyl groups of the residual 2% protium isotope in isobutane-d₁₀.

When the temperature is raised to 354 K and higher, the intensity of the signals at 1.0 ppm from methyl groups of

isobutane increases, while the signal at 4.9 ppm from Al-OH-Si group of the zeolite decreases (Fig. 2B). At the same time, the intensity of the narrow signal at 1.85 ppm from methine group of isobutane does not grow (compare Figs. 2B and 2C). This shows that there is no exchange between Al-OH-Si and methine hydrons. It is interesting to note here that, in contrast with IR spectroscopy (21), ¹H MAS NMR allows us to monitor directly the regioselectivity of the exchange for different hydrons in small alkanes. The signal at ca 2.0 ppm from the zeolite terminal Si-OH groups does not disappear upon heating (Fig. 2B), and therefore, SiOH groups are not involved in the exchange.

Measurements of the NMR signal intensity of the methyl group in dependence on time allowed us to estimate the rate of the H/D exchange under static conditions (Fig. 3). The exchange is finished within 30 min at 457 K, while at 354 K it has not been completed even after 10 h of the kinetics monitoring. Based on kinetics data in Fig. 3 the apparent activation energy for the observed hydrogen exchange can be estimated. An apparent activation energy for this exchange of 50 ± 2 kJ/mol was derived from the Arrhenius plot of the exchange rate versus the reciprocal temperature at 354–457 K (Fig. 4).

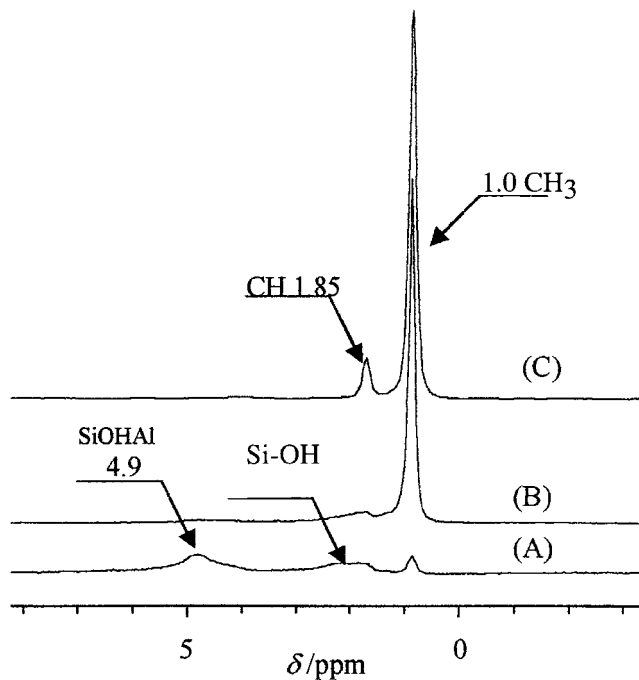


FIG. 2. ¹H MAS NMR spectra for the zeolite H-ZSM-5 loaded with four molecules isobutane per unit cell and measured at 295 K. (A) shows the spectrum of the zeolite loaded with isobutane-d₁₀ before the temperature was increased for the *in-situ* exchange experiment. An identical room temperature spectrum was obtained after keeping the sample 10 h at 457 K, if CO was co-adsorbed. (B) shows the room temperature spectrum of the sample loaded only with isobutane-d₁₀ after keeping it at 425 K for 70 min. (C) shows, for comparison, a spectrum of a zeolite sample which is loaded with nondeuterated isobutane.

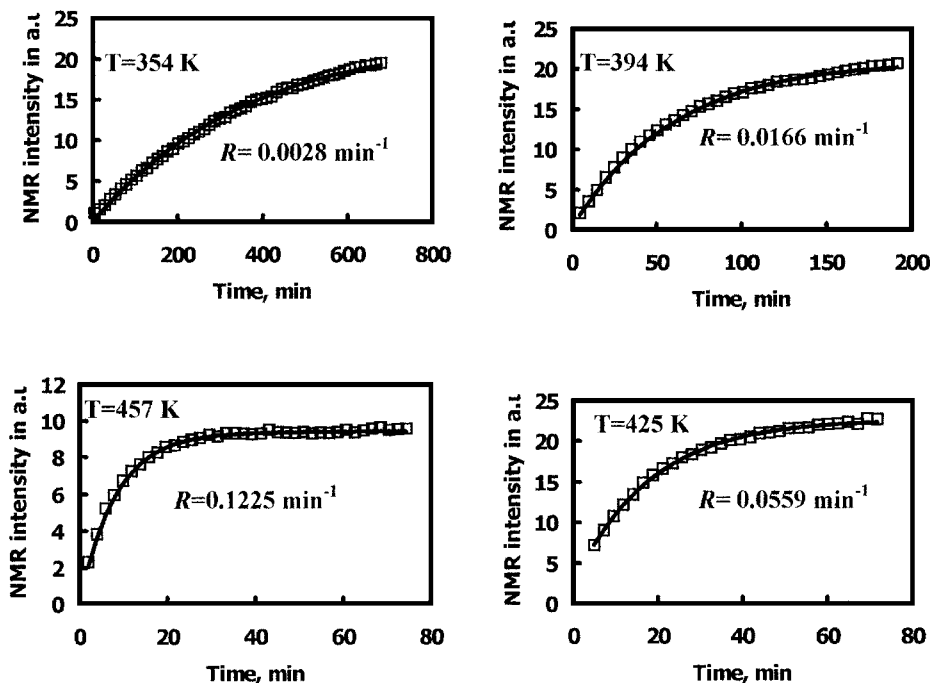


FIG. 3. Kinetics of the proton transfer from the acidic SiOHAl groups of the zeolite HZSM-5 to the methyl groups of the adsorbed isobutane- d_{10} at different temperatures. Solid lines represent the fits using the rates of the H/D exchange R (indicated near each curve) for Eq. [1].

When CO was coadsorbed with isobutane on HZSM-5, hydrogen/deuterium exchange was not observed at all. Indeed, 10 h keeping the zeolite sample with CO and isobutane- d_{10} at 457 K did not show any growth of the intensity of the signal from the methyl groups (Fig. 2A). The present observation by *in-situ* ^1H MAS NMR (19) under static conditions of protium exchange exclusively in methyl group and suppression of the hydrogen exchange with CO are in good accordance with both earlier findings of regioselective hydrogen exchange for isobutane on solid acids (Scheme 1) and with the finding in this work with $^2\text{H}/^1\text{H}$ NMR. The suppression of H/D exchange by CO is observed with two independent techniques, *in situ* and *ex situ*, respectively.

Despite the uncertainties subjacent to experimental determination of activation energies by different methods and

different authors we notice that the value found here for H/D exchange between isobutane and H-ZSM-5 is substantially lower than for *n*-butane and propane, which are 85 kJmol^{-1} (22) and 108 kJmol^{-1} (23), respectively. This sequence is in line with the difference in reactivity between linear and branched alkanes. For methane and ethane the experimental and theoretical values reported (24, 26) are higher and are explained by a pentavalent carbonium ion-type transition state in which exchange may occur as in liquid superacids without ionization.

CONCLUSION

The regioselectivity of the H/D exchange occurring between the hydrons of solid acidic catalysts and isobutane was confirmed both on the catalyst and on the alkane using *in-situ* and *ex-situ* NMR techniques, respectively. The apparent activation energy on H-ZSM-5 is much lower than observed for *n*-butane and propane. The inhibiting effect of carbon monoxide on the H/D exchange process and the regioselectivity are in accordance with the formation of a *t*-butyl cation reaction intermediate.

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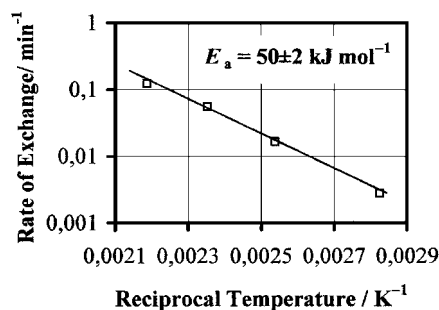


FIG. 4. Arrhenius plot of the hydrogen exchange rate for the methyl groups of isobutane.

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