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Communications to the Editor

Alkene Formation during Low-Temperature Alkane Activation on Various Solid Acids or Superacids

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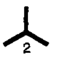
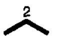
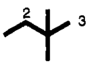
From an economic standpoint, solid acid-catalyzed transformations of hydrocarbons, such as fluid catalytic cracking, isomerization, and alkylation, are far and away the most important reactions.[1] For the understanding of these reactions, there is, however, a surprising contrast between the general agreement on the role of carbocations as reaction intermediates and the long-lasting controversy[2] over their mode of formation: protonation of the alkane by Brønsted superacidic sites,[3] hydride abstraction by a strong Lewis acid site,[2,4] or protonation of traces of alkenes present as impurities in the feed. In comparison with the clear picture now available for superacid-catalyzed activation of alkanes,[5,6] the mechanistic aspects of solid acid alkane activation need further investigation.

We have shown recently that the acid-catalysed H/D exchange observed in C4-C6 isoalkanes implied a different mechanism on HUSY zeolite in comparison with liquid superacids. In this paper we suggest that the regiospecific H/D exchange observed in small alkanes on various solid acids or "superacids" can be best rationalized by the formation of alkenes as reaction intermediates at temperatures much below the usual working temperature of these catalysts. The catalysts which we have used are the following: H-USY,[7] H-BETA,[8] HZSM-5,[9] and ZrO_2/SO_4^{2-}.[10]

Table 1. H/D Exchange between Alkanes and Deuterated Solid Acids[a]

alcane	exp no.	catalyst	T, °C	C1	C2	C3
	1	Zr/SO_4^{2-}	100	1.31	—	
	2	H-USY	100	2.63	—	
	3	H-BETA	100	9.02	—	
	4	HZSM-5	100	0.53	—	
	5	Zr/SO_4^{2-}	170	0.03	—	
	6	H-USY	200	0.03	—	
	7	H-BETA	200	0.24	—	
	8	HZSM-5	200	0.15	tr	
	9	H-BETA	150	0.11	—	—

[a] Average values measured on the total amount of alkane trapped during 40 min at GHSV ≅ 3000 and expressed in atom % of D at each position.

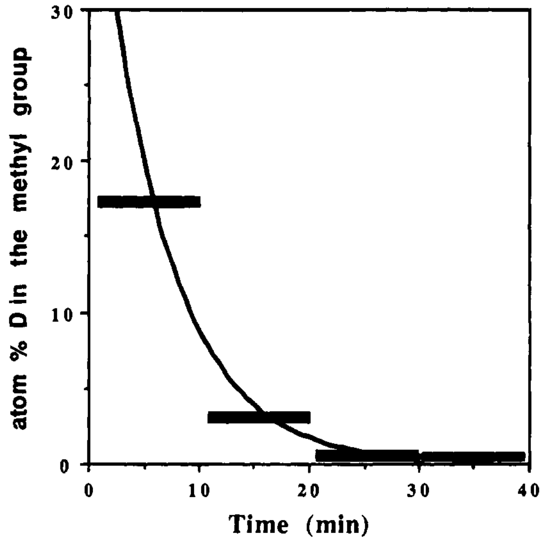


Figure 1. H/D exchange measured in isobutane at 200 °C with D_2O-exchanged H-BETA zeolite as a function of time (trapping time, 10 min each point).

The purity of the hydrocarbons was checked by GC and all alkanes, commercially available, were used without further purification.

The reaction was carried out in an all-glass, grease-free flow system.[11] The experimental procedure was the same for all catalysts. About 500 mg of the solid catalyst was pretreated with dry nitrogen (38 mL/min^{-1} for the zeolites and 20 mL/min^{-1} for the sulfated zirconia) at 500 °C for 30 min. Deuteration was carried out with 3 mol % D_2O in N_2 at 200 °C for 60 min, followed by an N_2 purge of 15 min. The alkane (ca. 6 mol % in N_2) was passed at a rate of 20 mL/min over the zeolites, collected in a cold trap, and analyzed by 400 MHz ^1H and ^2H NMR after addition of an adequate amount of a $CFCl_3$ solution of a $CDCl_3/CHCl_3$ mixture used as internal standard for the H/D distribution measurement. The results are collected in Table 1.

When isobutane was used as starting material, the ^2H NMR spectrum of recovered isobutane showed only one line at 0.9 ppm, corresponding to the methyl deuterons independently of the catalyst. The methine proton was not exchanged.

We have also tested the exchange reaction at room temperature by recirculating the alkane: 45 mL of gaseous isobutane

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(7) Obtained from Union Carbide, zeolite LZY-82 (Si/Al = 4.5).

(8) Obtained from PQ Corp., HB-8 (Si/Al = 12).

(9) Obtained from PQ Corp., CBV 5020 no. ZH 39.3 (Si/Al = 19).

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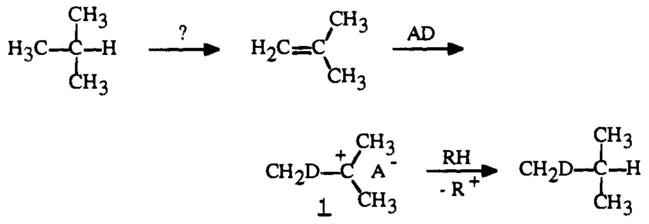
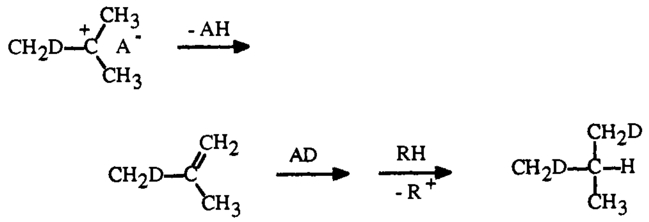
(atmospheric pressure) was recirculated during 24 h at 25 °C at a rate of 4mL/min^{-1} through a microreactor containing 500 mg of D-BETA zeolite pretreated as described above. The ^{1}H and ^{2}H NMR analysis of the isobutane condensed after reaction shows that, even at room temperature, 2.3 atom % of the methyl protons were exchanged for deuterons. Further, the time dependence has been measured at 200 °C on D-BETA, showing that the exchange occurs very rapidly, depleting the catalyst of its deuterons in the first 15 min (Figure 1). No isomerization or cracking products were detected by GC.

These results can best be rationalized by the intermediate protonation (here deuteronation) step of isobutene generated as reaction intermediate on the solid acid. The monodeuterated trivalent carbenium ion, **1**, which is formed exclusively following Markovnikov's rule can be desorbed by the classical hydride (here protide) transfer from incoming isobutane, in accord with the regiospecificity of the isotopic labeling:



$$H_3C-C(CH_3)_2-H \xrightarrow{?} H_2C{=}C(CH_3)_2 \xrightarrow{AD} \underset{\mathbf{1}}{CH_2D-\overset{+}{C}(CH_3)_2\;A^-} \xrightarrow[-R^+]{RH} CH_2D-C(CH_3)_2-H$$

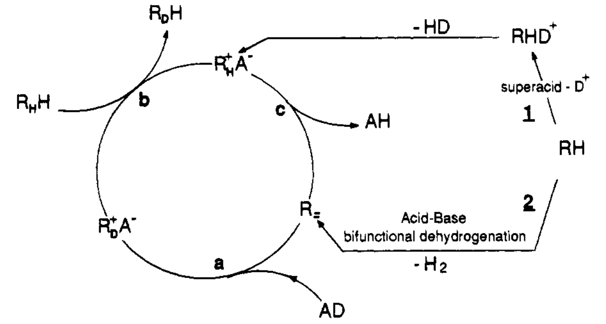
It can, however, also lose a proton and form deuterated isobutene, leading to a second deuteronation, and so on:



$$CH_2D-\overset{+}{C}(CH_3)_2\;A^- \xrightarrow{-AH} CH_2D-C(=CH_2)CH_3 \xrightarrow{AD} \xrightarrow[-R^+]{RH} CH_2D-C(CH_2D)(CH_3)-H$$

These results are remarkably similar to those obtained in the early 1950s by Otvos and Stevenson in H/D exchange studies between isoalkanes and D_2SO_4,[12] showing that only the protons on the carbons adjacent to the branching carbon in isoalkanes were exchanged. Our results are also in good accord with recent acidity estimation of zeolites by Haw and co-workers,[13] who compared H-ZSM-5 with 70% sulfuric acid. The same remark stands for sulfated zirconium oxide, the acidity of which was rated by the group of Vedrine to be not higher than that of sulfuric acid itself.[14] The influence of residual water on the acidity of the zeolite samples has not been taken into account in this work.

Scheme 1



In confirmation of earlier work,[15,16] we notice that linear alkanes do not exchange protons for deuterons on acidic zeolites at 100 °C. The exchange occurs, nevertheless, at higher temperatures, and regiospecificity observed in propane and neohexane is also in accord with the suggested mechanism.

We think that the question which remained unanswered for decades in the field of acid-catalyzed alkane activation. "How is the carbenium formed?" should be envisaged from a different viewpoint: "How is the alkene formed?" or "Which is first?"

Two possible pathways may be considered, as shown in Scheme 1. In pathway 1, the carbenium ion R_H^+ (nondeuterated) is formed by protolytic cleavage of a C−H bond (via a very unstable carbonium ion intermediate), the slow step being the protonation of the alkane. In contrast with the liquid superacids, which do not allow deprotonation, the cation can transfer a proton to the solid, generating the alkene. In pathway 2, the slow step is the acid−base bifunctional dehydrogenation, which needs the simultaneous presence of a strong Lewis acid site (for hydride abstraction) and a basic site (for proton acceptance), following the model generally proposed for bifunctional dehydrogenation and aromatization observed on acidic zeolites at higher temperatures.[17]

In both pathways, alkenes are only reaction intermediates which do not appear in the reaction products, as they are rapidly protonated, leading to the deuterated carbenium ions. Under the usual working conditions of these catalysts, at higher temperatures their formation and oligomerization are the main causes of deactivation of these acidic solids. This is in good accord with our previous work on sulfated zirconia-catalyzed isomerization of *n*-butane, in which we show the beneficial effect of the presence of an adequate amount of hydrogen in the feed.[10]

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