# **FULL PAPER**

## Alkane Activation over Acidic Zeolites: The First Step

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**Abstract:** The heterogeneous acid-catalyzed activation step of alkanes leading to the reaction intermediates (carbocationic or alkoxy species) was up to now the matter of a longstanding controversy. Gas chromatography and online mass spectroscopy measurements show that  $H_2$  and methane are formed over H-zeolites, whereas HD and  $CH_3D$  are formed over D-zeolites as the primary products in the reaction with isobutane. These results indicate

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that  $\sigma$ -bond protolysis by strong acid sites is the first step for hydrocarbon activation on these catalysts at mild temperatures (473 K), in analogy to the activation path occurring in liquid superacid media.

#### Introduction

Acid-catalyzed transformation of hydrocarbons, such as cracking and isomerisation, are of prime importance for the petrochemical industry.<sup>[1,2]</sup> The chemical inertness of the starting alkanes is generally overcome by the use of high temperatures and strongly acidic catalysts, such as proton-exchanged zeolites.<sup>[3]</sup> The activation step of alkanes is well demonstrated in liquid superacids,<sup>[4]</sup> whereas the initial step involved on solid acids has not, up to now, received a clear answer.<sup>[5]</sup> It is generally believed that zeolites lack sufficient acid strength<sup>[6]</sup> to allow direct C–C or C–H bond protolysis at mild temperatures (below 500 K), thus excluding the formation of a transient pentacoordinated carbonium ion. Zeolite-catalyzed alkane transformations are generally per-

formed above 573 K, but many authors have shown that H/ D exchange between iso-alkanes and zeolites or other solid acids occurs readily and, regioselectively at temperatures below 473 K, in the absence of significant cracking or isomerisation reactions.<sup>[7-11]</sup> These results were rationalised by the involvement of adsorbed carbenium ions in equilibrium with the corresponding olefin by a fast protonation/deprotonation process before desorption by hydride transfer according to Scheme 1. Nevertheless the questions "what is first: alkene or carbenium ion? or which is the first step in alkane activation?" were left open.

Herein we describe our recent results which, we believe, clearly confirm the hypothesis of an initial protolytic cleavage of C-H and C-C bonds in the activation of alkanes



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Scheme 1. H/D exchange for isobutane over acidic D-zeolite.

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even at temperatures as low as 473 K. Scheme 2 presents the two possible protonation pathways, as observed in liquid superacids.



Scheme 2. Protonation of saturated alkanes.

### **Results and Discussion**

In 1946, Bloch, Pines and Schmerling<sup>[12]</sup> observed that *n*butane isomerises to isobutane, under the influence of pure aluminium chloride only in the presence of HCl. They proposed that the ionisation step takes place through initial protolysis of the alkane as evidenced by formation of minor amounts of hydrogen in the initial stage of the reaction. Whereas all studies involving isomerisation, cracking and alkylation reactions under acidic conditions agree that carbocations are key intermediates, the mode of the formation of these reactive species from barely reactive hydrocarbons is still under debate nowadays.

Owing to this long-lasting controversy concerning the initial step in hydrocarbon conversion over solid acids, the following pathways can be found in the literature: Protolysis,<sup>[13]</sup> hydride abstraction by a preexisting carbenium ion,<sup>[14]</sup> hydride abstraction by a Lewis acid,<sup>[10,15]</sup> oxidation by means of traces of metal impurities or protonation of traces of alkenes impurities.

In one of the most cited papers in hydrocarbon chemistry, Haag and Dessau,<sup>[16]</sup> described the cracking of 3-methylpentane and *n*-hexane in the presence of acidic zeolites between 623 and 823 K and suggested the coexistence of two competing mechanistic pathways. Whereas one mechanism involved a bimolecular hydride transfer in the rate determining step, the second one described a monomolecular reaction proceeding via a pentacoordinated transition state, as known in superacidic conditions.<sup>[17]</sup> The latter mechanism involved the active acid sites of the aluminosilicate<sup>[18]</sup> and was suggested to predominate at high temperature (823 K).

We have chosen isobutane as the probe molecule to reinvestigate the cracking mechanism. It is the smallest, most reactive alkane due to its tertiary hydrogen. The protolysis of this tertiary C–H  $\sigma$  bond should produce H<sub>2</sub> and a tertiary butylcarbenium ion on the zeolite surface.

These reaction products cannot be accounted by the classical oligomerisation and  $\beta$ -scission mechanism<sup>[5]</sup>

(Scheme 3), in which the smallest alkane cracking product remains propane. All our experiments were carried out at 473 K to monitor the initial product distribution. As H<sub>2</sub>



Scheme 3. Classical oligomerisation and  $\beta$ -scission mechanism showing that methane formation is unfavourable by this mechanistic route.

could also be formed by dehydrogenation reaction, we have completed our study by deuteration of the Brönsted acid sites of the zeolite. Hence, the formation of HD molecule would ascertain a superacid-like alkane activation mechanism.

**Reaction on H-ZSM5**: Isobutane was recirculated over H-ZSM5 (acid form of MFI Zeolite) at 473 K and the following product distribution was observed (see Figure 1). Isobutane reacts readily on H-ZSM5 even at that low temperature. However, its conversion remains very low, 1-2% after 150 min of reaction. During the first 20 min on stream, only H<sub>2</sub> was produced, in agreement with a direct protolysis of the alkane by a Brönsted acid site of the zeolite.<sup>[9]</sup> Accord-



Figure 1. Product distribution during isobutane recirculation on H-ZSM5 at 473 K  $\bullet$  methane,  $\bullet$  ethane,  $\bullet$  propane,  $\blacksquare$  *n*-butane,  $\blacksquare$  ethylene,  $\bullet$  isopentane,  $\bullet$  hydrogen.

ing to the  $\sigma$ -reactivity of hydrocarbons,<sup>[19,20]</sup> the protolysis is favoured on the tertiary C–H bond, which leads to H<sub>2</sub> formation, prior to the appearance of light alkanes. Following the initial release of H<sub>2</sub>, the following products were detected: CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>8</sub>. With the exception of methane, the formation of these light products can be best rationalised by the classical cracking mechanism, involving β-scission.<sup>[3]</sup> Scheme 3 shows some of the reactions and products involved in these paths, thus further supports the absence of methane. Hence, methane can only be formed through a non-classical mechanism (Scheme 2b).

Nevertheless, H<sub>2</sub> was formed in extremely low amount,  $\approx 10^{-3}$  mmol, suggesting that at 473 K only few acid sites are strong enough to operate a direct protolytic cleavage of isobutane to produce H<sub>2</sub> and adsorbed *tert*-butyl carbenium ion.

To investigate the dependence between the number of Brönsted acid sites of the zeolite and the production of hydrogen from isobutane cracking, we have varied the amount of zeolite (hence the number of acid sites), monitoring the quantity of  $H_2$  produced for the different experiments. By dividing the mass of zeolite by two, the production of hydrogen was also divided by the same factor. These results indicate that only 0.1% of zeolite acid sites reacted with isobutane to form  $H_2$ . Hydrogen, in this closed recirculation system, is only produced as long as the acid sites are consumed in the protolytic step forming the carbocation. Figure 1 shows that later on, its amount remains constant, in contrast with the secondary products resulting from classical autocatalytic oligomerisation-cracking reaction of isobutane.

The protonation of saturated alkanes may result in the formation of a non-classical pentacoordinated carbonium ion, which decomposes into a trivalent carbonium ion and hydrogen or methane (Scheme 2). Route a) is predominant over b) according to the  $\sigma$ -reactivity concept proposed by Olah.<sup>[19,20]</sup>

Reaction on D<sub>2</sub>O-exchanged ultra stable faujasite (D-USY):

Table 1 presents a detailed characterisation of the acid sites present on both ZSM5 and USY (ultra stable faujasite) zeolites. The Brönsted acid sites were titrated by means of a H/ D isotope exchange technique developed in our group.<sup>[21a-c]</sup> *n*-Hexane cracking was used as a model reaction to evaluate the performance of the two catalysts. The HUSY (an acidic, ultra-stable, faujasite-type zeolite) zeolite exhibited a much higher cracking rate when compared to H-ZSM5, 2370 versus 364 mmol *n*-hexane converted per g per min. To get a higher resolution of the signal in the mass spectrometer, we have therefore performed the cracking reaction over deuterated USY zeolite, D-USY.

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In this sense, to overcome the doubt that hydrogen could result from isobutane dehydrogenation, and further confirm our working hypothesis, we have deuterated the zeolite, replacing all Brönsted acid sites by O–D groups<sup>[21]</sup> (see the Supplementary Information). Likewise liquid superacid media, the mechanism proposed (Scheme 2, routes a) and b)) may be valid, if HD or CH<sub>3</sub>D were detected. The partial pressures, monitored by on-line MS, are presented in Figure 2. Neither isobutene (m/z 56), nor H<sub>2</sub> was observed.



Figure 2. Profiles of the primary products of  $[D_1]$  isobutane reaction on DUSY: HD  $(m/z \ 3) \rightarrow -$ , CH<sub>3</sub>D $(m/z \ 17) \rightarrow -$  and  $[D_1]$  isobutane  $(m/z \ 59) \rightarrow -$ .

Simultaneously to isobutane (m/z 58) consumption, m/z 3and 17 ascribed respectively to HD and CH<sub>3</sub>D were observed as the primary products followed by [D<sub>1</sub>]isobutane (m/z 59). As m/z 19 and m/z 20 are not observed, m/z 3cannot be formed by molecular-ion fragmentation of water DHO, or  $D_2O$  within the mass spectrometer. Moreover as the profile of m/z 3 did not follow in shape that of m/z 59, consequently m/z 3 can only be ascribed to HD formation and m/z 17 can only be ascribed to CH<sub>3</sub>D formation. It was also observed that the amount of isobutane m/z 58 consumed approximately corresponds to the amount of  $[D_1]$  isobutane (m/z 59) formed. Moreover, ZSM5 and USY frameworks favour the diffusion of reactants toward the active sites.<sup>[23-25]</sup> This leads to a lowering in the energy barrier to activate alkane and, thus mimicking the behaviour of superacids.<sup>[23,24]</sup> It is noteworthy that  $[D_1]$  isobutane (m/z 59)produced was neither accompanied by isobutene nor H<sub>2</sub> for-

Table 1. Characterisation of the acidity of zeolite materials.

	Si/Al <sup>[a]</sup>	Quantity of extra framework Al [%] <sup>[b]</sup>	Total number of Brönsted acid sites [mmolg <sup>-1</sup> ] <sup>[c]</sup>	Rate of <i>n</i> -hexane cracking $[\text{mmol } g^{-1} \text{ min}]^{[d]}$
H-ZSM5	12	_	1.17	364
HUSY	6.2	40	2.26	2370

[a] Determined by X-ray fluorescence; [b] Obtained from the difference of total Si/Al and framework Si/Al (TO<sub>4</sub> vibration by FT-IR); [c] H/D exchange technique reported in Ref. [21b,c] [d] Calculated at iso-conversion between 5 and 8%. Experimental conditions are described in detail in Ref. [22].

mation. In line with H/D experiments reported in the literature,<sup>[7-10]</sup> we suggest that  $[D_1]$ isobutane (m/z 59) is formed by hydride transfer between  $[D_1]$ carbenium ion (m/z 58) and  $[D_0]$ isobutane (m/z 58)according to Scheme 1.

The catalytic transformation of barely reactive alkane by mi-

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croporous solid acids has been industrially implemented in large-scale processes, such as catalytic cracking, reforming, hydroisomerisation, oligomerisation and disproportionation. Considering the economic importance of these reactions a clear understanding of their activation mechanism is of primary interest. It may help researchers to design in a rational manner the solid acid catalyst, through proper control of Brönsted acidity for instance, and thus increase the selectivity toward desired products.

#### Conclusions

The reaction of isobutane over acidic zeolites leads to the formation of  $H_2$  as initial product. The proportionality relation between the amount of  $H_2$  produced and the amount of catalyst indicates that  $H_2$  formation is directly related to the number of Brönsted acid sites involved in the activation step. In the reaction of isobutane with deuterated zeolites, HD and CH<sub>3</sub>D are the initial products. Thus the questions "what is first: alkene or carbenium ion? or which is the first step in alkane activation?" have now a definitive answer; the carbenium ion is formed during the initial step of alkane activation through protolysis of a  $\sigma$  bond, similar to the process that occurs for liquid superacids.

#### **Experimental Section**

Isobutane cracking on H-ZSM5, protolysis experiments: The reaction was run in an all glass grease-free recirculation flow system, as reported earlier.[11] About 8.5 g of H-ZSM5 (AlSi-Penta Zeolite GmbH, Si/Al= 24, particle size: 20–30  $\mu m,\,1.17~mmol~H^{+}/g$  ,  $Na_{2}O<0.03~wt\,\%$  ) was activated at 823 K under N<sub>2</sub> (40 mLmin<sup>-1</sup>) for 1 h. The temperature was then decreased to the reaction temperature (473 K) and a mixture of 60 mL of gaseous isobutane (purified from traces of isobutene on Pt/Adams and checked by GC: 99.99 % purity), 190 mL of N2 was recirculated with a peristaltic pump (Masterflex L/S) at a rate of 5 mLmin<sup>-1</sup>. Samples (1 mL) were withdrawn at regular time intervals and analyzed by using a GC during the initial 150 min on stream. Hydrocarbons were analyzed by using a Hewlett Packard 5840 Series II chromatograph, using a HP-5 capillary column (crosslinked 5% diphenyl and 95% dimethylpolysiloxane, non polar, 30 m×0.32 mmx0.25 mm film thickness) and FID detector. Hydrogen was analyzed by means of an Intersmat IGC 112M gas-chromatograph equipped by a 5 Å molecular sieves column and TCD detector (after external calibration).

**Isobutane cracking on D-USY zeolite, deuterolysis experiments**: About 8.2 g  $\pm$  0.2 g of the protic form (no sodium was detected by X-Ray fluorescence) of ultra-stable Y-type zeolite (HUSY) catalyst, with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio=12.4 (16.4, corrected for extra framework Al), and BET area= 620 m<sup>2</sup>g,<sup>-1</sup> was used in all experiments. The hardware unit consists of a saturator, followed by a fixed-bed reactor, connected on-line to a quadrupolar mass spectrometer (MKS which is able to measure *m*/*z* from 1 to 100). The hardware is described in the supplementary information. This

experiment was repeated three times and a good agreement in each step was observed.

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