

## Weak Hydrogen Bonds and Alkane C-H Bond Activation by Solid Acid Catalysts

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### Introduction

Mechanistic steps for the initiation and subsequent reaction of saturated paraffins on solid acid zeolites are ambiguous when compared to their olefin and oxygenate counterparts. Carbenium ion chemistry initiated by trace olefinic contaminants is considered the most probable route to activation as zeolites are not classified as superacids capable of forming pentavalent carbonium ions. Regardless, many current publications propose this direct protonation step [1,2]. Alternatively, trace Lewis acidic sites in the catalyst could serve to generate carbenium ions through the process of hydride extraction, further complicating the determination of the operative mechanism. Spectroscopic H/D exchange experiments are obvious choices for the determination of the fate of protons over the course of catalytic hydrogen transfer reactions. Several authors have reported <sup>1</sup>H MAS (Magic Angle Spinning) NMR data observing the exchange between perdeuterated paraffins and protonated catalysts using “in-situ” techniques. These works, however, do not follow the fate of the reactant peaks, but only that of the product. Additionally, the reaction was sometimes carried out off-line, and subsequently analyzed. It has been shown previously, that following the fates of both the reactant and product peaks using truly in-situ techniques is vital to the determination of accurate mechanistic information. In this work, we present both spectroscopic data and ab-initio quantum-chemical calculations to propose a viable mechanistic pathway for the exchange of protons between the zeolitic catalyst H-ZSM-5 and the light alkane isobutane.

### Materials and Methods

ZSM-5 (Si:Al=15) samples were obtained from Zeolyst. Isobutane-d<sub>10</sub> (99.1% D) and isobutane-2-<sup>13</sup>C (99% <sup>13</sup>C) were obtained from CDN Isotopes and Icon Isotopes, respectively. The as received reagents were treated with D<sub>2</sub> (99.8% D - Isotec) over a supported 0.5% Pt/alumina catalyst to remove unsaturated impurities. Calcined and dehydrated zeolite samples were prepared in a stainless steel reactor body using a gradual, stepwise dry-air calcination up to a final temperature of 723 K. Samples were sealed under positive pressure and immediately placed in the glovebox to avoid exposure to moisture. Gas adsorptions were carried out using a CAVERN type apparatus [3]. 7-mm MAS rotors were loaded with 50-55 mg of catalyst and placed into the apparatus which was then evacuated on a vacuum line. Stoichiometric samples were prepared by adsorbing one isobutane molecule per Bronsted acid site. MAS NMR data were collected on a Bruker DSX 300 MHz spectrometer.

Ab-initio calculations were carried out at the Hartree Fock self-consistent field/single determinant (SCF) and configuration interaction multi-determinant (CI) expansion levels of theory using a flexible basis set on a cluster model of the zeolite reacting with isobutane. The cluster used is the same as that illustrated in Figure 1. A Nelder Mead [4] simplex algorithm was used for energy minimization allowing simultaneous optimization of 27 geometrical

parameters. Most optimizations were carried out at the SCF level, followed by CI calculation of the energy. The transition state optimization, however, was done directly at the CI level.

### Results and Discussion

The activation of isobutane C-H bonds by the zeolite H-ZSM5 was directly observed, and the rate of proton transfer between the solid catalyst surface and gaseous isobutane is quantitatively measured using isotopic <sup>1</sup>H/<sup>2</sup>H exchange methods. An observable adsorption complex forms between the isobutane and the primary Bronsted acid site of ZSM-5, which leads to proton exchange between the zeolite surface and the isobutane methyl groups at temperatures (273 K) much lower than previously reported. Simultaneous detection of protium loss from the Bronsted acid site and protium gain by perdeuterated isobutane reveals a common rate constant equal to  $4.1 - 4.6 \times 10^{-4} \text{ s}^{-1}$  at 298 K, but at lower temperatures, the transition between this and a much slower rate process is resolved. The results are consistent with direct proton exchange between the zeolite surface and the methyl groups of isobutane.

Ab initio calculations at the SCF and CI levels of theory calculated 15 kcal/mole for the activation barrier, which agrees with the experimentally determined value of 13.7 kcal/mole. Figure 1 illustrates the mechanism of reaction and the energies of each state. Overall, the mechanism described in this contribution demonstrates that weak C-H to O hydrogen-bonding leads to complexes at the zeolite acid site that can facilitate C-H bond activation.

### Significance

The commercialization of a solid acid catalyzed alkylation process has not proceeded due to a lack of information concerning the operative mechanisms. This research provides an important consideration as to how saturated alkanes become activated on a solid acid.

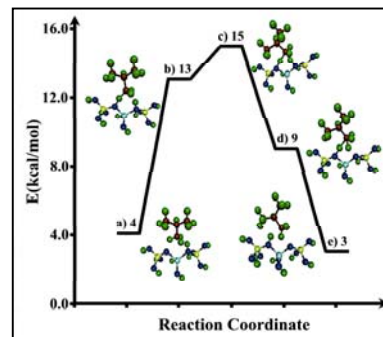


Figure 1. Mechanism for the surface catalyzed H/D exchange for isobutane/ZSM-5.

### References

1. Walspurger, S.; Sun, Y.; Sido, A. S. S.; Sommer, J., *J. Phys. Chem. B* 110, 18368 (2006).
2. Esteves, P. M.; Nascimento, M. A. C.; Mota, C. J. A. *J. Phys. Chem. B* 103, 10417 (1999).
3. Munson, E. J.; Ferguson, D. B.; Kheir, A. A.; Haw, J. F. *J. Catal.* 136, 504 (1992).
4. Nelder, J. A.; Mead, R. *Comput. J.* 7, 308 (1965).