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Toward a Reliable Computational Description of Hydrocarbon Activation in Zeolites: A Study of Cracking, Dehydrogenation, and H/D Exchange of Alkanes in H-ZSM-5

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Introduction: During the past decade, quantum-chemical calculations have been used to model hydrocarbon reactions in zeolite acid catalysts. In the interest of computational feasibility, the zeolite has often been represented by a very small cluster model, at times including only one tetrahedrally-coordinated atom (a 1T cluster). The results of such calculations have given important qualitative insights such as possible reaction pathways and transition state geometries, but the calculated activation energies for hydrocarbon reactions have usually been 50 percent or more higher than experimental values. In our recent work we developed a methodology of quantum-chemical techniques and corrections that allowed us to calculate a quantitatively accurate activation energy for protolytic cracking of ethane in H-ZSM-5 [1]. In order to test the limits of our computational method, we have carried out a study of protolytic cracking, dehydrogenation, and H/D exchange of the n-alkanes ethane, propane, and butane using a cluster model of H-ZSM-5. Our goal is to study the dependence of the activation energy on the alkane chain length in these reactions and to determine whether this method can produce results in quantitative agreement with available experimental results [2-5].

Theoretical Methods: We obtained the optimized geometries and zero-point energies of structures on each reaction pathway using the HF/6-31G(d) method and the B3LYP/6-31G(d) level of density functional theory. Our transition state structures have only one imaginary vibrational frequency, corresponding to the reaction coordinate. Our cluster model for the zeolite framework, denoted 5T, has five tetrahedrally-coordinated atoms and is terminated by H atoms at its periphery. This cluster model is much larger than the 1T model used in much previous work [6] and is better able to represent interactions of an adsorbed hydrocarbon molecule with framework oxygen atoms near the Bronsted site in the zeolite. To determine the activation barriers for each reaction, we calculated corrections for (i) scaled zero-point energies and thermal corrections for the experimental reaction temperature of 773 K; (ii) an extended basis set, calculated at the B3LYP/6-311+G(3df,2p) level; and (iii) the long-range electrostatic effects of the zeolite framework. The electrostatic correction was determined by performing a partial optimization of each transition state in a larger 18T zeolite cluster model and then embedding the resulting structure into a much larger 64T cluster model, constructed from the experimental geometry of H-ZSM-5.

Results and Discussion: As an example of our results, a schematic potential energy surface for the complete reaction pathway for catalytic cracking of propane is shown in Fig. 1. Starting from an adsorbed complex ($ZOH\cdots C_3H_8$), the acidic proton attacks a terminal C-H bond. Via an ionic transition state ($ZO^-\cdots C_3H_9^+$) this forms CH_4 and a surface-bound ethoxy species (ZOC_2H_5). In order to close the catalytic cycle, a proton is abstracted from the ethoxy species by a nearby framework oxygen atom. This proceeds through another transition state ($ZO^-\cdots H^+\cdots C_2H_4$) to form a new Bronsted acid site with an adsorbed ethene molecule ($ZOH\cdots C_2H_4$). When the energy corrections described above are used to calculate the true energy barrier for propane cracking, we obtain a final value of 43 kcal/mol, in good agreement with the experimental value of 47 ± 3 kcal/mol [3]. Similar results for dehydrogenation and H/D exchange reactions will be presented and discussed.

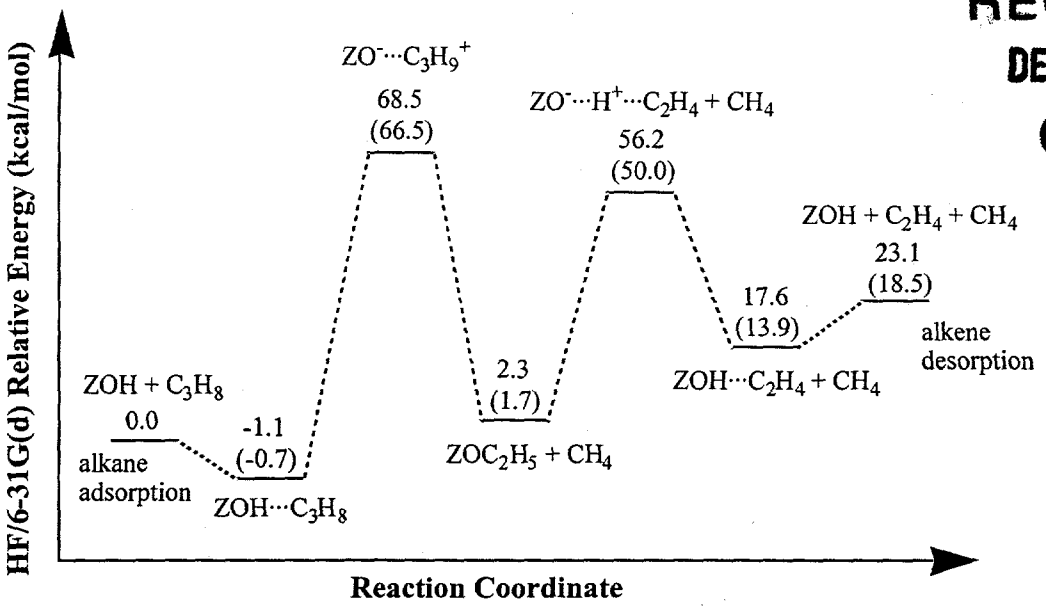

Fig. 1. Schematic potential energy surface for propane cracking. Energies in parentheses include zero-point corrections.

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References:

1. S. Zygmunt, L. Curtiss, P. Zapol and L. Iton, *J. Phys. Chem. B.* 104, (2000) 1944.
2. H. Krannila, W. Haag and B. Gates, *J. Catal.* 135, (1992) 115.
3. T. Narbeshuber, A. Brait, K. Seshan and J. Lercher, *J. Catal.* 172, (1997) 127.
4. A. Stepanov, H. Ernst and D. Freude, *Catal. Lett.* 54, (1998) 1.
5. B. Lee, J. Kondo, F. Wakabayashi and K. Domen, *Catal. Lett.* 59, (1999) 51.
6. S. Blaszkowski and R. van Santen, *J. Am. Chem. Soc.* 119, (1997) 5020.

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