Dealkylation and ring opening: Comparison of energetics from ab initio calculations

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Introduction

Selective ring opening (RO) of naphthenic molecules is an important step in upgrading Canadian bitumen into refinery feedstocks. Achieving higher ring opening yields is a challenge to the researchers as these are hampered by exocyclic cracking reactions such as side chain cracking and dealkylation (DA) [1]. Cycloparaffins ring opening can be catalyzed on the Brønsted acid sites via carbenium intermediates through protolytic cracking [2]. The high cetane number ring opening products are resulted from the endocyclic C-C bond breakage of the cyclic compounds. The endocyclic C-C bond cracking in cycloparaffins is much slower than in aliphatics [3]. As a result, the overall ring opening rates are predominated by isomerization and subsequent dealkylation of side chains of cyclic hydrocarbons, particularly of those having substituents with more than five carbon atoms, leading to significant dealkylation of pendant substituents on the ring. Consequently the ring opening yields are low due to the undesired dealkylation reactions which are confirmed in the literature. The present study aims to understand the detailed kinetic mechanism of the dealkylation and ring opening reaction of propenylcyclopentane on a Brønsted acid site using Hartree-Fock and Density Functional Theory (DFT) methods.

Materials and Methods

The dealkylation and ring opening reaction of propenylcyclopentyl ion has been examined in the gas phase by using HF and DFT-PBEPBE level theories using standard 6-31G* basis set. The "ab initio" quantum calculations were performed by using GAUSSIAN 03 program and using clusters to model the Bronsted acid sites of the zeolites. Elementary steps are postulated and transition state structures are identified as saddle points, having not more than one negative frequency. In addition, intrinsic reaction coordinate method (IRC) was applied for passing from each transition state to the initial and the final products. Corrections for zero-point energy (ZPE) obtained from frequency calculations and were included in final activation energies. Information about the structure of the intermediates, elementary steps and corresponding activation barriers obtained from this study are expected to help in rational design of suitable catalyst systems for selective ring opening of naphthene molecules.

Results and Discussion

The gas phase dealkylation and ring opening of propylcyclopentane ion was studied and the activation energies are shown in Figure 1. With both the theories the RO reaction is difficult compared to dealkylation due to its high activation energies. The Arrhenius activation energies and frequency factors also indicated that RO and DA reactions are very competitive due to their similar range of activation energies. The dealkylation reaction on Bronsted acid

sites is carried out using 1T and 5T clusters. The overall reaction is carried out through three elementary steps. 1) proton transfer between the catalyst surface and the reactant molecule. 2) dealkylation. 3) desorption of the proton from the product molecule. All the transition states for three elementary steps are identified and both 1T and 5T cluster energetics clearly show that surface reaction step requires high activation energy and is the rate limiting step. There is a decrease in the activation energies when we move from 1T to 5T. 5T structure represents high acidic in nature due to the higher level of the cluster and may lead to less activation energy.
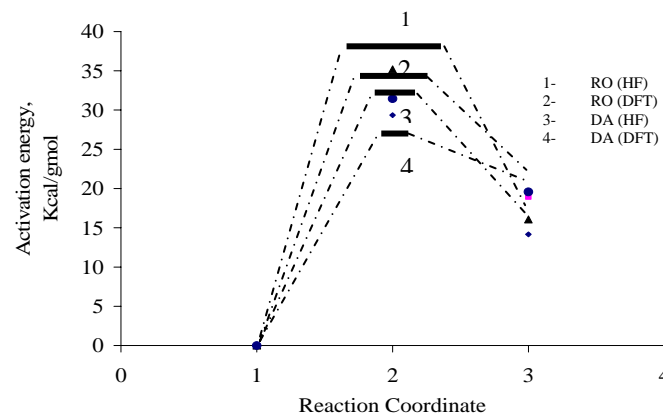

Fig.1. Activation barriers for ring opening and dealkylation reactions in gas phase using HF and DFT theories.

Significance

The use of heavy gas oil as FCC feedstock involve severe problem because of its high aromatic and naphthenic content. In order to upgrade HGO quality as FCC feedstock, selective ring opening of naphthenes is necessary. To improve the ring opening yields, it is necessary to know about the energetics and kinetics of competitive RO and DA reactions

References

1. Mc Vicker, M. daage, G.B, Touvelle, M.S, Hudson, D.P Klein, W. C Baird, Jr., B.R Cook, J.G.Chen, S.Hantzer, D.E.W.Vaughan, E.S Ellis, and O.C. Feeley, J. Catal. 210 (2002) 137.
2. L.B. Galperin, J.C. Bricker, J.R. Holmgren, Appl. Catal. A 239 (2003) 297.
3. J.Weitkamp, S. Ernst, H.G. Karge, Erdol undKohle Erdgas 37 (1984) 457.