

## Selective ring opening of decalin -Thermodynamics

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### Introduction

Removal of polynuclear aromatics from diesel fuel has become a focus of intense research due to the stringent environmental legislation associated with clean fuels. In addition to their negative environmental impact, polynuclear aromatics decrease the cetane number and diminish the overall quality of the diesel. Cetane number (CN) can be increased by dearomatization. However, the enhancement may not be sufficient, as the CN of naphthenes obtained by dearomatization is rather low, and additional upgrading may be needed. The ring opening of the naphthenic ring is a promising option for achieving high cetane number values. But it is not straight forward as high cetane number products can be achieved only by reducing the branched ring opening products [1]. The use of bifunctional catalysts, such as metals supported on zeolites, have been studied for ring opening reactions [2] and showed low ring opening products selectivities. Preparation of highly selective ring opening catalysts for improving CN is not straight forward task and thorough understanding of thermodynamic limitations of ring opening reaction is necessary. In this work, the equilibrium compositions for the decalin ring opening reaction were estimated using thermodynamic parameters. These thermodynamics predictions of products selectivity for decalin ring opening reaction are validated experimentally over Pt-Ir/Zr-MCM-41 catalyst.

### Materials and Methods

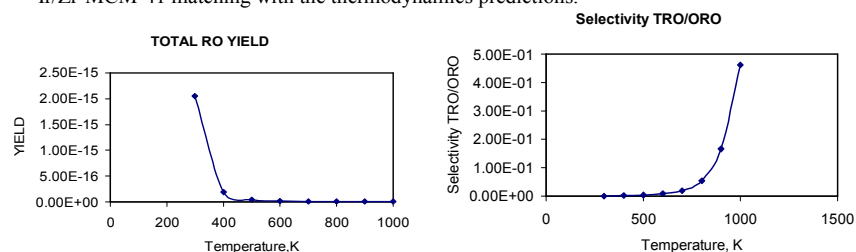
About 50 major products from the decalin ring opening reaction are identified and classified as cracking [CP], one ring opening [ORO], two ring opening[TRO], ring contraction [RC] and dehydrogenated products[DH]. Standard Gibb's free energy change of formation for some of the compounds is not available in the literature. These properties are obtained from the energy optimization of the molecules using G03-MP[2] theory and using West Grid super computer facility. Equilibrium compositions for the decalin ring opening reaction are calculated by the procedure listed in the literature [3]. MATHCAD professional is used for solving nonlinear equations.

Decalin ring opening reaction is carried out experimentally on bifunctional Pt-Ir/Zr-MCM-41 catalyst. 1.5 wt% Pt and 0.75 wt% Ir are incorporated on the support by pore volume impregnation. The catalyst is characterized by using NH<sub>3</sub>-TPD, BET surface area, DRIFTS of CO and DRIFTS of NH<sub>3</sub>. Down flow continuous trickle bed reactor is used for the reaction. The reaction temperature is varied from 573 to 673K while keeping the pressure at 5MPa. LHSV and H<sub>2</sub> flow rate are 1.5h<sup>-1</sup> and 50 ml/min respectively.

### Results and Discussion

Molecular energy optimization was done successfully to get the standard free energy of formation for the complex products at different temperatures. At equilibrium ORO and TRO yield are decreased with temperature up to 600K. Above 600K TRO yield is increased with temperature but total ring opening yield is decreasing with temperature. There is no much change in RC yield up to 600K, but drastic increase from 600 to 700K. Dehydrogenation is predominant at higher temperatures. Even though low temperature favors total RO yield, high cetane number products are dominant at high temperature [Fig.1].

The thermodynamic results of decalin ring opening were evaluated experimentally over Pt-Ir/Zr-MCM-41 catalyst. The Pt-Ir/Zr-MCM-41catalyst was characterized extensively. NH<sub>3</sub>-TPD of the catalyst show moderate acidity. DRIFTS of NH<sub>3</sub> show the presence of both Bronsted and Lewis acid sites. DRIFTS of CO show that Ir particle size is low and Pt is in Pt<sup>0</sup> and Pt<sup>1</sup> states. The catalytic studies showed that the dehydrogenated products from decaling ring opening are increased with the temperature from 573 to 673K. Total RO yield and less branched RO products yield of decalin ring opening are increased with temperature. Selectivity of RO products is maximum at 623K. Thus, the results from the decalin ring opening over Pt-Ir/Zr-MCM-41 matching with the thermodynamics predictions.



### 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. The good matching of thermodynamic predictions with experimental results of decalin ring opening showed that optimum experimental conditions for selective ring opening of different naphthenic molecules of HGO can be determined by thermodynamic calculation.

### References

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