Prediction of Hydrogenolysis Product Selectivity of Various Model Hydrocarbons over Ir/Al_2O_3

Steven P. Crossley,[1] Phuong T. Do,[1]Siraprapha Dokjampa,[1] and Daniel E. Resasco[1]*
[1]*University of Oklahoma, Norman, Oklahoma 73119 (US)*
*resasco@ou.edu

Introduction

With increasing demand for cetane number (CN) in diesel fuels [1] and reduction of aromatics in gasoline while maintaining the octane number (ON) [2], selective hydrogenolysis of naphthenic rings has become increasingly important. For the diesel route, naphthenic rings should be selectively broken at the substituted positions in order to produce paraffins with minimal branching and high CN. For gasoline, aromatic levels need to decrease, but hydrogenation to naphthenic rings alone results in significant decreases in ON. Selective hydrogenolysis to branched paraffins needs to be done in order to provide a fuel that has less aromatics without a significant decrease in ON.

In order to gain insight as to the reaction mechanisms involved under specific conditions, it is valuable to be able to predict the product selectivity for a particular model molecule under specific reaction conditions. Prediction of product selectivity has numerous benefits. Many molecules that are present in fuels, or as hydrogenation products of fuels, may be very expensive to synthesize and separate in order to perform reactions. Also, predictions help to save valuable time by getting very quick estimates as to how many different fuels will react over a specific catalyst. If reactivity predictions were performed for numerous catalysts and conditions, one could couple each reaction product with a desired fuel property, and find the best overall catalyst for the desired problem.

Materials and Methods

As a starting point, the catalyst chosen was Ir/Al_2O_3 at 330°C and 500 PSI of Hydrogen, as these conditions are favorable for creating a high CN fuel. Data were taken at low conversions in order to predict only the primary products of the reaction, as secondary cracking at higher conversions leads to numerous products. 17 model feeds consisting of one ring branched naphthenics and paraffins were reacted, and their product distributions recorded. In order to create a reliable database, ratios were taken that corresponded with breaking the reactant at different positions. For example, one ratio, Sub/dic is the ratio of breaking at the substituted to unsubstituted positions on the ring. Other ratios include internal/terminal bond cleavage in an alkyl chain, ring opening/dealkylation, etc.

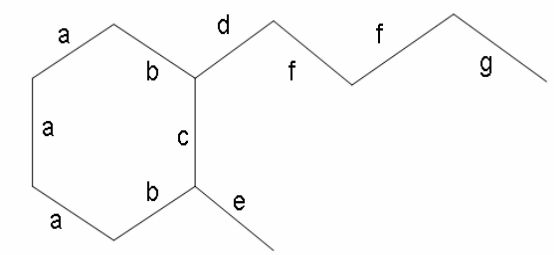
In order to develop a model to predict the product selectivity, some relationship between the ratios of products and the molecular structure of the feed needed to be made. To accomplish this, molecular descriptors were calculated from MDL® QSAR software, and models were created linking each ratio to a particular molecule. In this way, product selectivities can be readily estimated for a new molecule using only the molecular structure.

Results and Discussion

As models were created relating each ratio to the molecular structure, the best models were chosen based on the accuracy of predicting the data, and plotting specific ratios against trends such as alkyl group length, and noting if the models over-fit the data. The leave-one-out method was also used for determining the best model for each predicted ratio. The results for one of the predicted molecules, 1-butyl-2-methylcyclohexane, is shown in figure one. From the ratios, one can gather a great deal of information as to where the molecule will break via primary hydrogenolysis. As more catalysts are tested with a group of molecules, one will be able to learn a great deal of information as to how a catalyst will react with individual model compounds.

Significance

This work provides a first step towards the creation of a useful tool in catalysis. Eventually, these models will be able to predict which primary hydrogenolysis products will be produced for a particular fuel once the composition is determined. This could provide valuable insight as to optimizing the choice of catalyst for a variety of processes.



$$\frac{(2b+c)}{3a} = 2.5$$

$$\frac{(d+e+2f+g)}{(3a+2b+c)} = .56$$

$$\frac{g}{d} = 5.2$$

$$\frac{2f}{d} = 20.0$$

$$\frac{2b}{c} = .28$$

Figure 1. Ratios of predicted selectivity of primary hydrogenolysis products of 1-butyl-2-methylcyclohexane on Ir/Al_2O_3 based on ratios from experimental studies on 17 other molecules.

References

1. Cooper, B.D., *Appl . Catal. A-Gen.*, 137(2), 203 (1996).
2. In "Regulation of Fuel and Fuel Additives: Extension of California Enforcement Exemptions for Reformulated Gasoline to California Phase 3 Gasoline". EPA, Federal Register, 70**,** 244 (2005) 75914.