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Ring contraction and selective ring opening of naphthenic molecules for octane number improvement

Malee Santikunaporn [a], Walter E. Alvarez [b], Daniel E. Resasco [a,*]

[a] School of Chemical, Biological, and Materials Engineering, The University of Oklahoma, Norman, OK 73019, United States
[b] Conoco Phillips Research Center, Bartlesville, OK 74004, United States

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Abstract

Different catalytic strategies have been evaluated to maximize the production of non-aromatic compounds with high octane number, starting from naphthenic molecules, which are typically obtained from the saturation of aromatics. The research octane number (RON), the motor octane number (MON), and the specific volume of the product mixtures were evaluated in each case. The product distribution obtained on acidic and Pt-containing zeolites was investigated in the temperature range 533–563 K in the presence of hydrogen at a total pressure of 2 MPa. It was found that skeletal isomerization (ring contraction) was the primary reaction in both HY and Pt/HY catalysts. The presence of Pt was found to enhance the stability of the catalyst, but also greatly altered the distribution of RC products, enhancing 1,1-dimethylcyclopentane. This enhancement can be explained in terms of a higher rate of hydride transfer caused by the presence of the metal. Evaluation of the octane numbers of the product indicated that a mixture of RC products results in rather high RON, but the MON and specific volume were about the same as that of the feed. To improve MON and specific volume an Ir/SiO_2 catalyst with high hydrogenolysis activity was added to realize the ring opening (RO). The combination of RC and RO was tested on physical mixtures and segregated beds of Pt/HY and Ir/SiO_2 catalysts in order to optimize the production of the iso-alkanes with highest octane number. It was found that with segregated catalyst beds, a better control of the selective breaking of C–C bonds of RC isomers can be achieved, which optimizes octane number and specific volume.

Keywords: Methylcyclohexane; Ring opening; Ring contraction; Cracking; Gasoline; Octane number; RON; MON; Pt; HY zeolite; Ir/SiO_2

1. Introduction

Environmental regulations set limits in the content of aromatics in motor gasolines and impose a challenge to refiners, who need to maintain high octane numbers while decreasing aromatic content [1–3]. Hydrogenation of aromatics into alkylcyclohexanes (naphthenes) would result in significant losses of octane number [4–6] and hydrocracking would lead to losses in molecular weight with consequent losses, in gasoline yield [7,8]. An interesting aspect to investigate is the conversion of naphthenes into non-aromatic compounds with the same number of carbon atoms as the original molecule, but with higher octane number. Octane number provides an indication of the ability of a gasoline to resist knocking as it burns in the engine. There are two test methods to measure the octane number of a gasoline. These methods use different engine conditions, mainly the intake temperature and the engine speed. The research octane number (RON) method represents engine operations typical of mild driving, without consistent heavy loads on the engine, while the motor octane number (MON) method represents severe, sustained high speed, high load driving. The pump octane number is the average between the two methods (RON + MON)/2. For most gasoline fuels, RON is higher than MON. The difference between the two (RON–MON) is called Sensitivity. Modern fuels are expected to have low sensitivities. Therefore, refiners are concerned about keeping both high RON and high MON.

The conversion of naphthenic molecules has been extensively investigated on metal, acidic, and bifunctional (metal/acid) catalysts for many years. Several reactions are known to occur, such as isomerization (including ring contraction), ring opening, dehydrogenation, and cracking, depending mainly on the reaction conditions, the feed, and the catalysts used [9]. Methylcyclohexane (MCH) is an interesting probe molecule

* Corresponding author. Tel.: +1 405 325 4370; fax: +1 405 325 5813.
E-mail address: resasco@ou.edu (D.E. Resasco).

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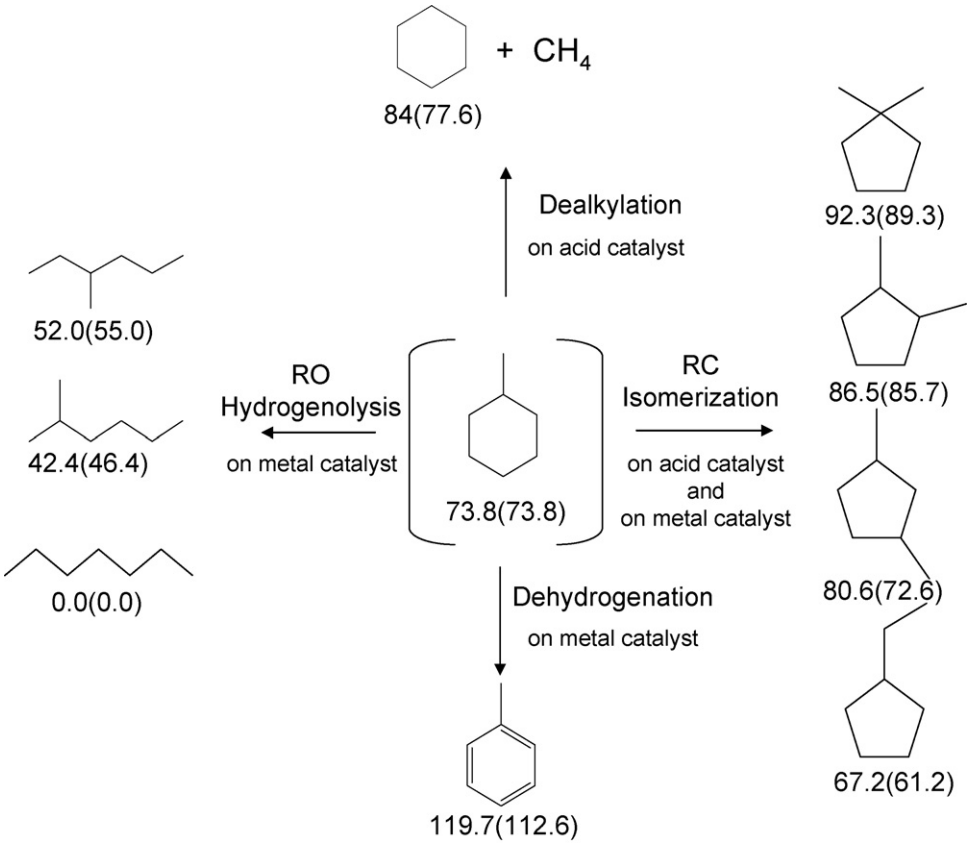
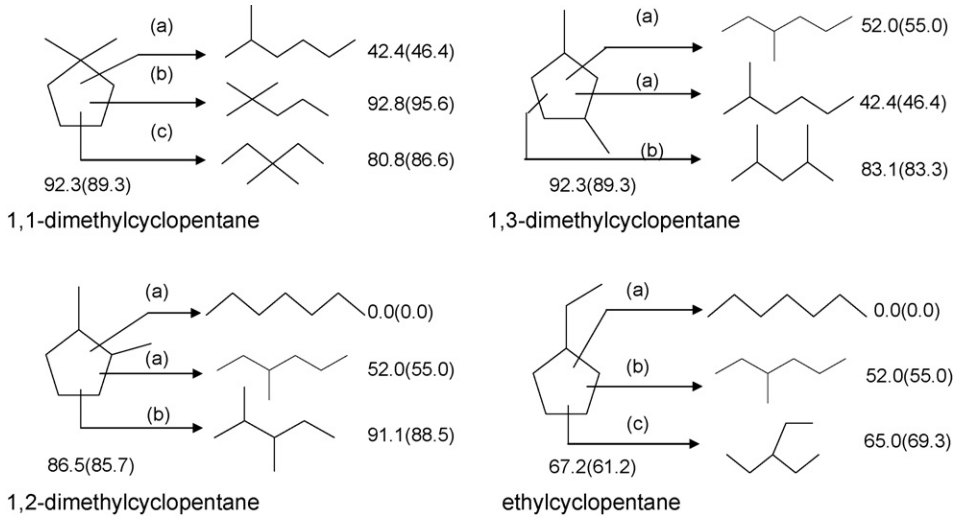


Scheme 1. Possible products from methylcyclohexane and their research octane number (RON) and their motor octane number (MON).

that can undergo all of the reactions mentioned above and can be used as a model feed. Therefore, it is interesting to compare the octane number of each of the different products that can result in the reactions that MCH can undergo and determine which catalyst or combination of catalysts and reaction conditions can be used to maximize octane numbers (both RON and MON).

As illustrated in Scheme 1, a direct ring opening (RO) of the C6-ring is not desirable because all of the resulting RO products have low octane number. By contrast, some ring-contraction (RC) products (dimethylcyclopentanes DMCPs) and some secondary ring opening products of the DMCPs (see Scheme 2) have relatively high octane number and would be a desirable product in gasoline.



Scheme 2. Hydrogenolysis on metal catalysts: product from ring opening reactions of C_7 ring-contraction compounds and their corresponding research octane number and motor octane number.