

INFLUENCE OF THIOPHENE ON THE CONVERSION OF METHYL-CYCLOPENTANE AND N. HEXANE TO BENZENE USING MONO-AND BI-METALLIC REFORMING CATALYSTS

by
A.S. Nasution

I. INTRODUCTION

Paraffin and naphthene hydrocarbons are usually the major component in the naphtha reforming feedstock. Thus the conversion of these hydrocarbon to high octane motor gasoline and aromatic hydrocarbon is one of the important reactions of the catalytic reforming process. (Montamal., 1965). And aromatization reaction is guided by both metal and acid sites of bi-functiona reforming catalyst (Hobson 1973).

In order to obtain more information about the conversion of paraffin and naphthene to aromatic hydrocarbons and the role of bi-functional reforming catalyst on those hydrocarbon conversion, an experiment has been carried out to study the influence of thiophene on conversion of methylcyclopentane and n.hexane to benzene using mono-and bi-metallic reforming catalysts having the same acidity.

The activity of metal site of mono-and bi-metallic reforming catalysts has used hydrogenation and cyclohexane dehydrogenation as a molecule model. The operating conditions are as follows: temperatures: from 698 to 728 K, pressure: 19.4 atm and H_2/HC ratio mole/mole. A catatest unit operated in a continuous system was used in this experiment. Gas and liquid products samplers taken from gas and liquid samplers, respectively, were analyzed by using gas liquid chromatography.

II. EXPERIMENTAL

Pure hydrocarbon feedstocks: n.hexane methylcyclopentane, cyclohexane and benzene, commercially pure hydrogen and industrial mono-, bi-metallic reforming and $NI-Mo/Al_2O_3-SiO_2$ catalysts, have been used in this experiment.

The experiment was carried out on a catatest unit which can be operated in contineuous system. (Figure 1). The volume and inside of the reactor are 220 cc and

19 mm, respectively. And the operating temperature of the reactor is regulated autimatically.

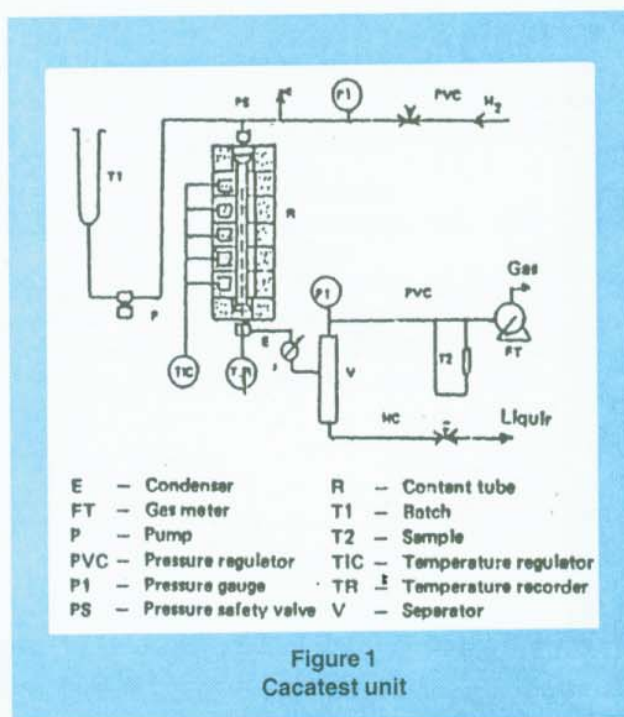
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III. RESULTS AND DISSCUSSIONS

A. Results

1. Activation Energy of the Benzene Hydrogenation

Initial reaction rate ($r = \text{mole/hour.g.cata}$) is proportional to the conversion of the feedstocks (mole/mole) and the hydrocarbon feedstock (mole/hour) and the weight of the catalyst (gr) (Sinfelt, 1961). And for low feedstock conversion, this initial reaction rate is propor-



tional to the reaction rate constant (k). Activation energy of the benzene calculated by following arrhenius equation:

$$rvk = A \exp (-E/RT)$$

Benzene hydrogenation at T from 528 to 558 K, $P = 19.4$ atm, and $H_2/HC = 6$ mole/mole is given on the Figure 2. Calculated activation energy of benzene hydrogenation from Figure 2 are obtained : 10.112; 20.210 and 21.982 koal/mole for mono-,bi-metallic and Ni-Mo/ Al_2O_3 - SiO_2 catalyst respectively.

2. Composition of Products

Composition of products of the fresh feedstock of the cyclohexane hydrogenation at $T =$ from 643 to 673 K, $P = 19.4$ atm and $H_2/HC = 6$ mole/mole and the methyl cyclopentane hydroisomerization at $T =$ from 698 to 728 K, $T = 19.4$ atm and $H_2/HC = 6$ mole/mole are given on the Figure 3, Figure 4 respectively.

At the temperature 673 K the relative initial rate of the cyclohexane dehydrogenation for production of the benzene: 11.3; 5.4, 1.0, and of the methylcyclopentane: 0.4, 0.8, 1.0 for mono-metallic,bi-metallic and Ni-Mo/ Al_2O_3 - SiO_2 catalysts, respectively. And at temperature 728 K the methylcyclopentane dehydroisomerization gives the relative initial reaction rate for production of the benzene: 1.2, 1.0, and of the hexane: 5.0, 1.0 for mono-metallic and bi-metallic reforming catalyst respectively.

Influence of the thiophene on the feedstocks conversion and the product nation at temperature 558 K, $P = 19.4$ atm and $H_2/HC = 6$ mole/mole, and the cyclohexane hydrogenation, the methylcyclopentane dehydroisomerization and the n.hexane dhydrocyclization at temperature 728 K, $P = 19.4$ atm and $H_2/HC = 6$ mole/mole, are shown on the Figure 5 and the Table 1 respectively.

B. Discussions

1. Activity of the Metal Site of The Catalyst

Data on the Figure 2 and Figure 3 show that hydrogenation and dehydrogenation of the metal site of the catalyst, decreases as follows: mono metallic > bi-metallic > Ni-Mo/ Al_2O_3 - SiO_2 . And the initial reaction rate of the benzene hydrogenation is higher than cyclohexane dehydrogenation.

The increasing feedstock conversion and the decreasing isomer products: are methylcyclopentane from cyclohexane dehydrogenation, benzene from methylcyclopentane dehydroisomerization and n.hexane dehydrocyclization with the high metal siteactivity shown on Figure 3, Figure 4 and Table 1, suggest that the high adsorption of the hydrocarbon feedstock on this metal

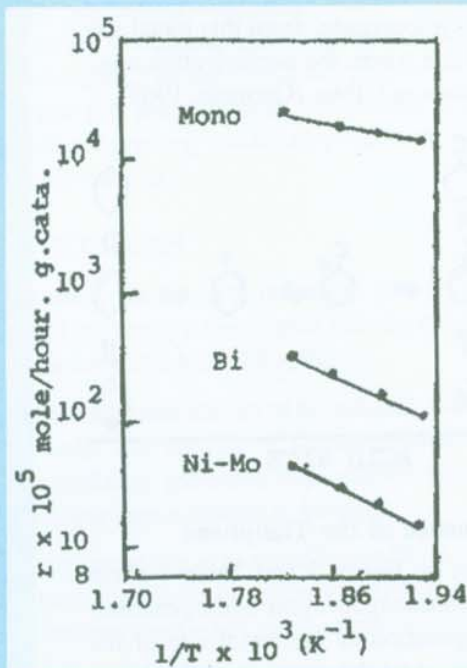


Figure 2
Arrhenius plot of the benzene hydrogenation

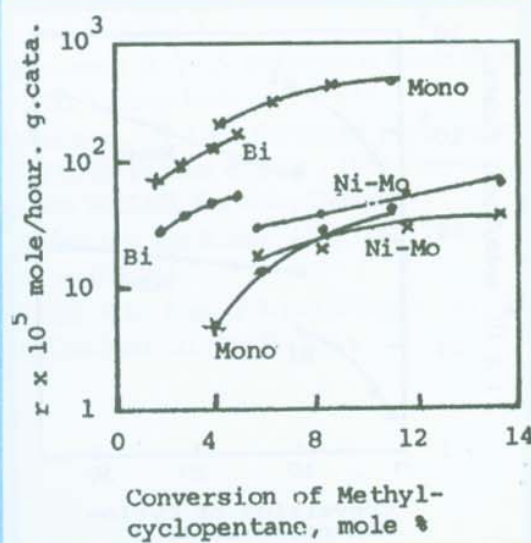
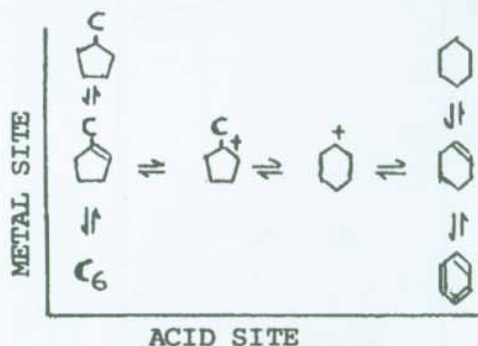


Figure 3
Influence of the conversion of cyclohexane dehydrogenation on the benzene (x) and the methylcyclopentane (o) products

site low migration rate of the olefin intermediate molecules such as: hexane and methylcyclopentane, from this metal site to acid site where the isomerization reaction occurs as follows. (Germain, 1969).



2. Influence of the Thiophene

Data on Figure 5 and Table 1 show that thiophene reduces the hydrogenation-dehydrogenation of the metal site of the catalysts. And the mono-metallic has a relative low sensitivity to thiophene compared to the bi-metallic reforming catalysts, which is supported also by previous data (Nasution, 1981).

Table 1
Influence of thiophene

Type of reaction	Press feedstock		Addition of thiophene	
	Mono	Bi	Mono	Bi
Cyclodehydro. Conv.	94.43	91.22	87.43	69.77
Benzene	91.75	81.42	79.61	51.91
Met.cyclopen.	2.68	9.80	8.27	17.86
Met.cyclopen. dehydroiso. Conv.	7.39	3.52	4.19	2.08
Benzene	3.35	3.13	2.79	1.92
Hexane	4.04	0.39	1.40	0.16
n.Hexane dehydrocyc. Conv.	68.54	61.78	59.47	43.9
Iso-hexane	53.66	51.84	48.91	38.91
Benzene	3.23	4.97	3.48	2.48
C1-C5	11.65	4.97	7.08	2.51

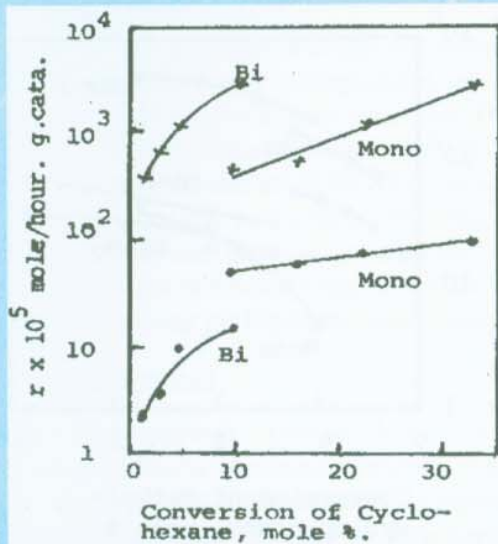


Figure 4
Influence of the conversion of the methylcyclopentane on the benzene (x) and hexane (o) products

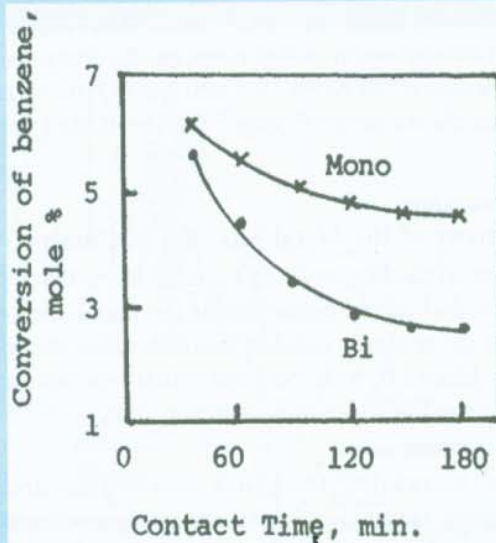
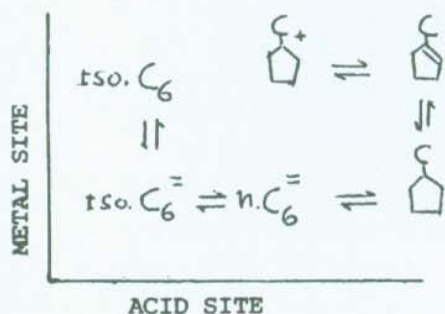


Figure 5
Influence of the contact time on the conversion of benzene added thiophene

The increasing isomer products with the thiophene addition into the feedstock for mono-metallic, suggest an increasing migration rate of this olefin intermediate from the metal site to the acid site of this mono-metallic reforming catalyst.

Due to the high poison sensitivity of the bi-metallic, metal site activity is low enough to produce methylcycloamyl carbonium ion an intermediate molecule for benzene production from and hexane, which is obtained by the hydrogenation of the methylcyclopentane intermediate molecule as following reaction mechanism. (Barron, 1963).



Due to the decreasing n.hexane dehydrocyclization with the operating pressure (Nasution, 1991), the migration rate of those olefin intermediate molecules, seems to be depended by this operating pressure.

The increasing iso-hexane products of n.hexane dehydrocyclization, by addition of the thiophene for both mono- and bi-metallic reforming catalysts, suggest the higher hydrogenation reaction of the iso hexane intermediate molecule compared with the dehydrogenation of this methylcyclopentane intermediate molecule to produce the methylcyclopentane as a source of the methylcycloamyl carbonium ion. And this suggestion is supported also by the lowest metal site activity of Ni-Mo/Al₂O₃-SiO₂ catalyst, which produces a highest iso-hexane and a lowest benzene products from n.hexane dehydrocyclization compared to the both mono- and bi-metallic reforming catalysts (Nasution, 1986).

The high decrease of the hydrocracked products (C₁-C₅) by the thiophene addition for the mono-metallic reforming catalysts, suggest, that n.hexane hydrogenolysis decrease on the poisoned metal site of this mono-metallic. The previous data (Smith et al., 1971) indicated also that the high metal site activity of the bi-functional reforming catalyst produces a high hydrogenolysis reaction.

IV. CONCLUSIONS

The hydrogenation-hydrogenation activity of the metal site of the catalyst decreases follows: mono-metallic > bi-metallic > Ni-Mo/Al₂O₃-SiO₂.

Medium metal site activity of bi-metallic or decreasing high metal site activity of mono-metallic by the thiophene addition, produces high conversion of the methylcyclopentane n.hexane to benzene.

Poisoned metal site of bi-metallic and Ni-Mo/Al₂O₃-SiO₂ catalysts have a low dehydrogenation activity to produce benzene from n.hexane the hydrocyclization.

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