CATALYTIC REFORMING OF PURE HYDROCARBONS AND NAPHTHA USING MONO AND BI-METALLIC REFORMING CATALYSTS

by

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ABSTRACT

The catalytic role of mono and bi-metallic of reforming catalysts is studied for the conversion of pure hydrocarbons: i.e: n. hexane, n. heptane, n. octane, methylcyclopentane, cyclohexane and naphtha in the reforming reaction.

I. INTRODUCTION

The rapidly increasing demand for aromatic hydrocarbons as petrochemical feedstock and the high octane number of gasoline has promoted refiner to seek methods of improving yields of these valuable product.

Catalytic reforming of naphtha is one of the aromatic and gasoline produstion from petroleum (1,2). As paraffin and naphthene hydrocarbons are usually the mayor component in the naphtha feedstocks, thus the high conversion of these hydrocarbons to aromatic hydrocarbons plays an important role.

In order to obtain more information about conversion of paraffin and naphthene hydrocarbons of naphtha to aromatic hydrocarbon and the catalytic role of mono and bi-metallic of reforming catalysts for aromatization of those hydrocarbons, an experiment has been carried out to study the conversion of pure hydrocarbons, paraffins: i.e. n. hexane, n. heptane and n. octane, and naphthenes: cyclohexane and methylcyclohexane and methylcyclopentane; and naphtha with the operating temperatures from 370° to 500°C, pressure: $15 kg/cm^2$ hydrocarbon to hydrogene ratio: 8 mole/mole, using mono and bi-mettalic reforming catalysts having the same acidity.

Dehydrogenation of cyclohexane to benzene has been used as reaction model to determine the activity of metal site of reforming catalysts.

A micro-catalytic-activity-test (Catatest) unit operated in a continuous system was used in these experiments. Gas and Liquid products samples taken from gas and liquid samples respectively were analyzed by using a Gas-Liquid Chromatography.

II. EXPERIMENTAL

Pure grade of hydrocarbons: i.e: n.hexane, n.heptane, n.octane, methylcyclopentane, cyclohexane and naphtha, were used as feedstock. The purified hydrogen, containing impurity less than 0,5% by vol, mono and bi-metallic reforming catalysts were used in this experiment.

Experiment was carried out in a Micro Activity Test (Catatest) Unit, without gas recycle, operated contineous system (Figure 1).
The volume and inside of the reactor are 220 cc and 19 mm respectively. The reactor temperature is regulated automatically.

Gas and liquid produst samples were taken from gas and liquid sampler respectively and these products were ghen analysed by using Gas - Liquid Chromatography.
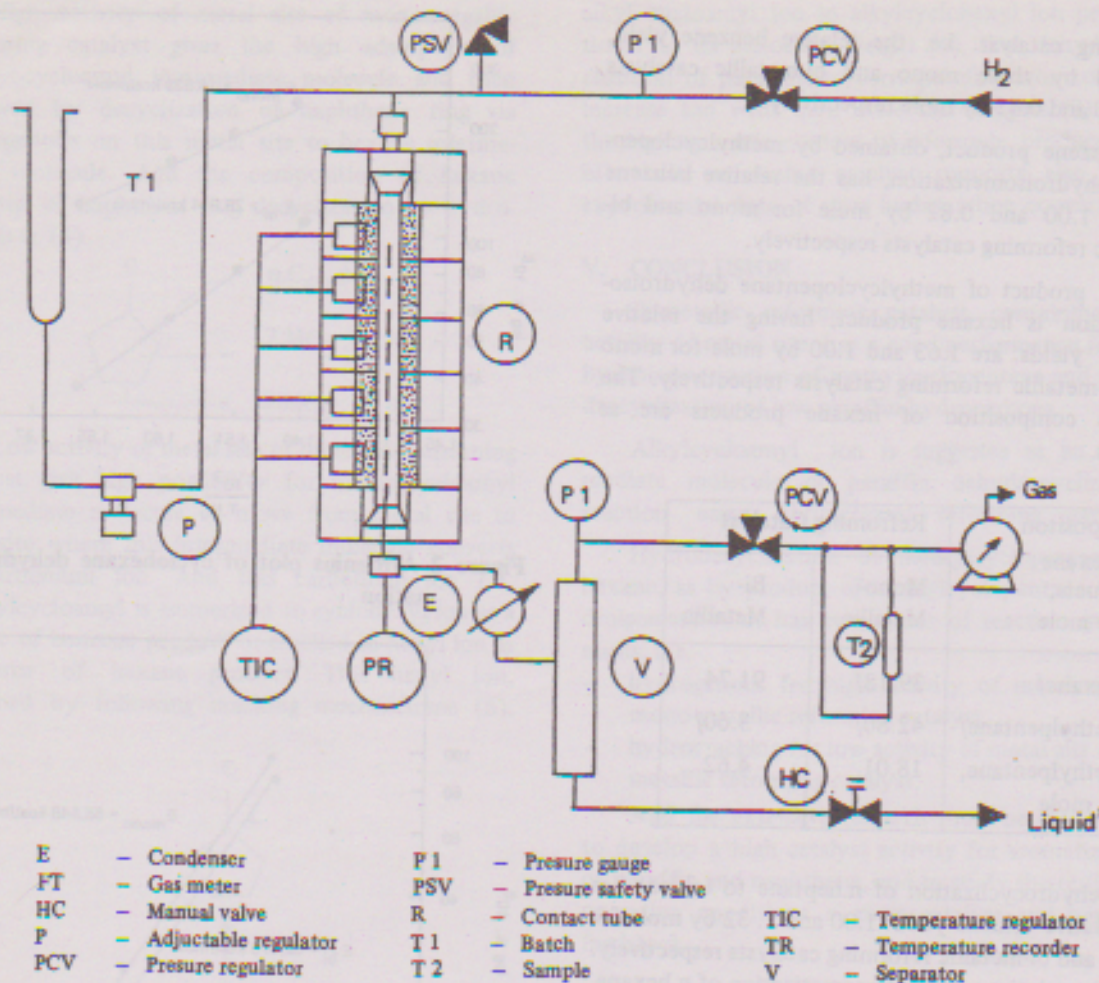
E	— Condenser	P 1	— Presure gauge	TIC	— Temperature regulator
FT	— Gas meter	PSV	— Presure safety valve	TR	— Temperature recorder
HC	— Manual valve	R	— Contact tube	V	— Separator
P	— Adjuctable regulator	T 1	— Batch		
PCV	— Presure regulator	T 2	— Sample		

Figure 1 Catalytic activity test unit

III. RESULTS

Activation energy of hydrocarbon conversion (E) is calculated by using the following Arrhenius equation,

$$k = Ae^{-E/RT}$$

Figure 2 and 3 show the plot of log r_o against 1/T for cyclohexane dehydrogenation and methylcyclopentane dehydroisomerization, and calculated activation energies for those two reactions are obtained as follows

Type of hydro-carbon conversion	Reforming Catalysts	
	Mono-Metallic	Bi-Metallic
Cyclohexane-dehydrogenation	19.839	25.864
Methylcyclopentane dehydro-isomerization.	66.548	69.476

Mono-metallic reforming catalyst gives the high aromatization of this cyclohexane than bi-metallic
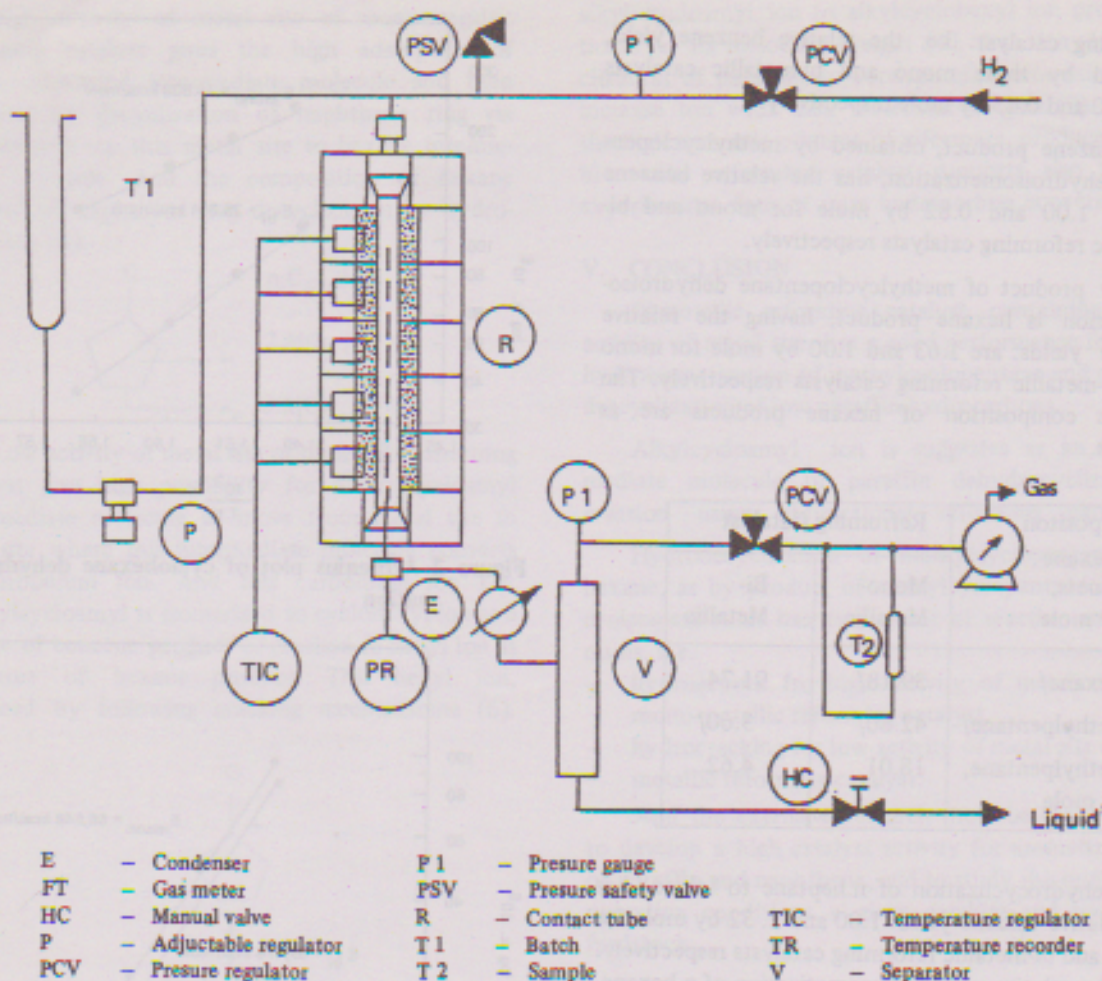
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TR	—	Temperature recorder
V	—	Separator

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reforming catalyst: i.e. the relative benzene yield, produced by these mono and bi-metallic catalysts are 1.00 and 0.45 by mole respectively.

Benzene product, obtained by methylcyclopentane dehydroisomerization, has the relative benzene yields. 1.00 and 0.82 by mole for mono and bi-metallic reforming catalysts respectively.

By product of methylcyclopentane dehydroisomerization is hexane product, having the relative hexane yields: are 1.63 and 1.00 by mole for mono and bi-metallic reforming catalysts respectively. The average composition of hexane products are as follows.

Compositon of hexane products, % by mole	Refroming Catalyst	
	Mono-Metallic	Bi-Metallic
n. hexane/	39.18/	91.74
2 methylpentane/	42.80/	3.60/
3 methylpentane, by mole	18.01	4.62

Dehydrocyclization of n.heptane to toluene has the relative toluene yield: 1.00 and 2. 32 by mole for mono and bi-metallic reforming catalysts respectively. And the relative yields of aromatization of n.hexane, n.heptane and n.octane are 1.00, 7.48 and 12.83 by mole using bi-metallic reforming catalysts.

Catalytic reforming of naphtha produces the reformate with the following performances.

Performance of Reformate, C$_5$+	Reforming Catalysts	
	Mono-Metallic	Bi-Metallic
Yield, % by wt	70.93	75.23
Hydrocarbon Composition, % by vol.		
Paraffin	32.6	21.5
Napththene	10.5	9.2
Aromatic	56.9	69.3
Octane Number	95.2	98.4

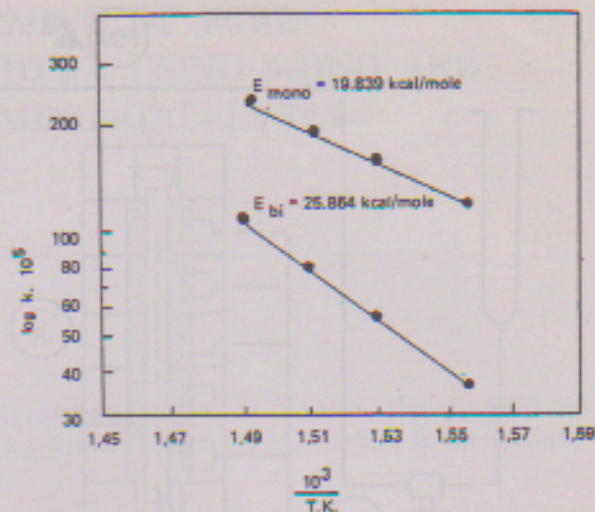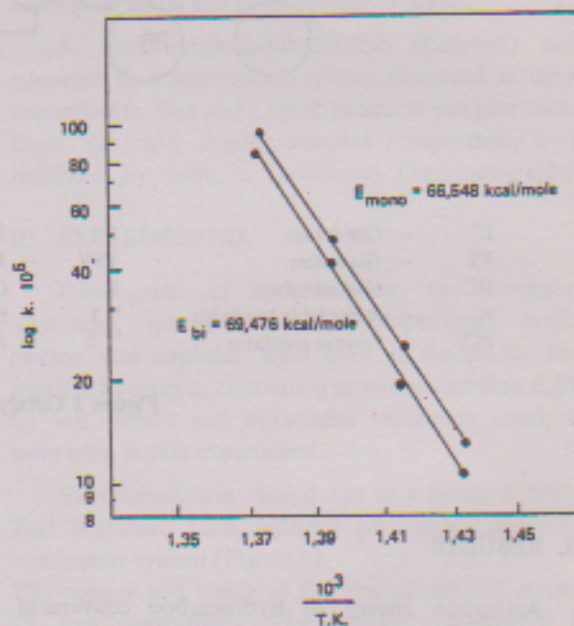Figure 2 Arrhenius plot of cyclohexane dehydrogenation

E_{mono} = 19.839 kcal/mole
E_{bi} = 25.864 kcal/mole

Figure 3 Arrhenius plot of dehydroisomerization methylcyclopentane

E_{mono} = 66.548 kcal/mole
E_{bi} = 69.476 kcal/mole

IV. DISCUSSIONS

Low activation energy and high yield of cyclohexane dehydrogenation, promoted by metal site of reforming catalyst (3), shows that the mon-metallic erforming catalyst has high activity of metal site of this mon-metallic reforming catalyst.

High activity of metal site of mono-megallic reforming catalyst gives the high adsorption of methyl-cycloamyl intermediate molecule and then followed by decyclization of naphthene ring via hydrogenolis on this metal site to hexane intermediate molecule. And the composition of hexane produce of naphthene ring decyclization by hydrogenolis is (4).

n.C_6 , 38%

2.MC_5 , 41 %

3.MC_5 ; 21 %
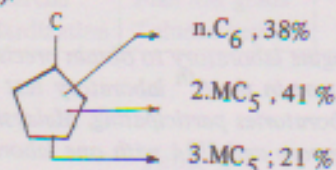
Low activity of metal site of bimetallic reforming catalyst give high possibility for methylcycloamyl intermediate molecule to move from metal site to acid site where this intermediate molecule converts to carbonium ion. And this carbonium ion i.e. methylcycloamyl is isomerized to cyclohexyl ion as a source of benzene product or cracked to hexyl ion as a source of hexane product. This hexyl ion, obtained by following cracking mechanisnme (6).

C

+

C +

Hydroisomerization   Hydrocracking

+   C
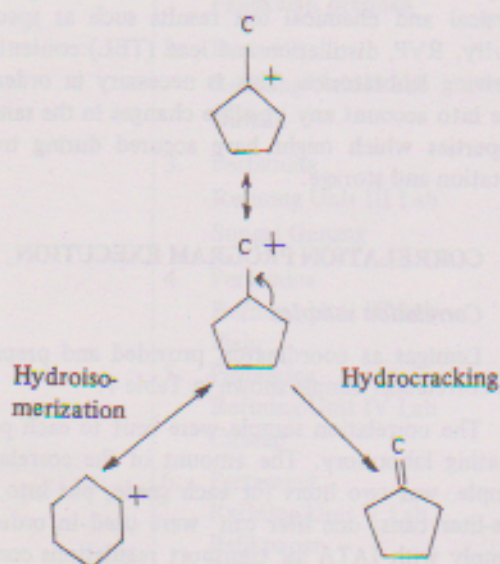
Bi-metallic reforming catalyst has a high activity of methylcyclopentane dehydroisomerization and of paraffin dehydrocyclization. Based on these two reaction, it suggests that alkyl cycloamyl ion is an intermediate molecule of this paraffin dehydrocyclization (5).

As isomerization of intermediate molecule of

alkyl cycloamyl ion to alkylcyclohexyl ion proportional to its melocular weight (4), thus dehydrocyclization of paraffins to corresponding aromatic will increase too with their molecular-weights (7). And the high aromatic content of reformate, produced dy bi-metallic reforming catalyst supports also these experimental data of pure hudrocarbon conversions.

V. CONCLUSION

Bi-metallic reforming catalyst, containing low activity of metal site, has a good performance for dehydroisomerization of methylcyclopentane and dehydrocyclization of low paraffin hydrocarbons.

Alkylcycloamyl ion is suggestes as an intermediate molecule of paraffin dehydrocyclization reaction using bi-functional reforming catalyst.

Hydrodecyclization of methylcyclopentane to hexane, as by product of methylcyclopentane dehydroisomerization has two types of reaction mechanisms, i. e.
- hydrogenolis fro high activity of metal site of mono-metallic reforming catalyst.
- hydrocracking for low activity of metal site of bimetallic reforming catalyst.

And the extensive research must be carried out to develop a high catalyst activity for aromatization of paraffin and naphthene, and to study the optimum operating conditions a given catalyst and naphtha feedstock.

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