MECHANISM OF HEXANE DEHYDROCYCLIZATION TO BENZENE USING BI—FUNCTIONAL REFORMING CATALYST*

By :

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ABSTRACT

The Mechanism of n. hexane dehydrocyclization reaction to benzene has been studied with pure hydrocarbons and synthetic naphtha feedstock at the operating conditions: $T = 400° - 520°C$ $PT = 10 - 30$ kg/cm^2 and $H_2/HC = 4-10$ mole/mole using a Catatest Unit operated in a continous system. The results show that n. hexadiene has been formed as a mayor source of the intermediate molecule of the methylcycloamil ion, an optimum metal site activity was observed for a given acid-site of bi-functional reforming catalyst and - 1 (minus one) of the total reaction order of n.hexane dehydrocyclization to benzene.

I. INTRODUCTION

The catalytic reforming process is a process to upgrade low octane naphthas to high octane motor gasoline components having a research octane number clear from 85 to over 100. Alternatively, this process may be operated to produce aviation blending stocks or to give high yields of low aromatics. The process is carried out in the presence of hydrogen and utilies a bi-functional reforming catalyst [1].

Paraffin and naphthene are usually the major components in the naphtha-reforming feedstock [2]

In order to obtain data about the conversion of paraffins to aromatics, an experiment has been carried out to study the machanism of hexane dehydrocyclization to benzene using pure hydrocarbons: n-hexane, n.heptane, n. octane, cyclohexane and methylcyclopentane and synthetic naphtha reforming feedstocks having various hydrocarbon compositions using a bi-functional catalyst: i.e. reforming catalyst (mono-and bimetallic) and hydroconversion catalyst (Ni-Mo/Al_2O_3-SiO_2).

Cyclohexane conversion to benzene and methylcyclopentane hydrodecyclization to hexane have been used as mode reaction models to determine the activity of metal site of bi-functi-

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onal catalyst and of optimum balance between metal site and acid site of bi-functional catalyst for n.hexane dehydrocyclization.

The operating conditions are as follows: • temperatures: from 400° to 520°C, • pressure: from 10 to kg/cm², • H_2/C-ratio : from : 4 to 10 mole/mole. A Catatest Unit, operated in a continuous system, was used in this experiment. Gas and liquid product samples taken from gas and liquid samplers respectively were analyzed using Gas-Liquid Chromatography.

II. EXPERIMENTAL

N.hexane, n.heptane, n.octane, methylcyclopentane, cyclohexane and methylcyclopentane with a purity of 99,5 mole %, and synthetic naphtha having various hydrocarbon compositions, have been used as feedstocks in this experiment. Commercially pure hydrocarbon was used in all experiments. Small amounts of oxygen were converted to water over a Deoxo catalyst and water was removed by passage over a silica drier. Bi-functional reforming catalysts (mono-and bi-Metallic) and hydroconversion catalyst (Ni-Mo/Al_2O_3—SiO_2) having the same total acidity has used in this experiment.

The experiment was carried out un a **Catatest Unit** which can be operated in a continuous system (Fig.1). The reactor assembly consisted of a microreactor placed in an electric furnace and joined to inlet and outlet fittings, temperature control panel (not shown), ganses for measuring gas flow and pressures and a continuous high pressure oil feeding pump. The microreactor was constructed from stainless steel tubing, 220 cc volume, 19 mm inside diameter and 7 mm outside diameter couple well tubing.

Feedstock and hydrogen were fed from the upper part of the reactor. The products were moved from the cooler to the high pressure receiver, where they were separated into gas and liquid. Gas was released after its volume was measured by a wet gas meter. Gas and liquid products samples taken from gas and liquid samples respectively were analyzed using a gas-liquid chromatography.

In this investigation, the experimental conditions were selected as follows: • the reaction temperatur : from 400° − 520°C, • the total pressures : from 10 to 30 kg/cm² the hydrogen to hydrocarbon mole ratio : from 4 to 10.
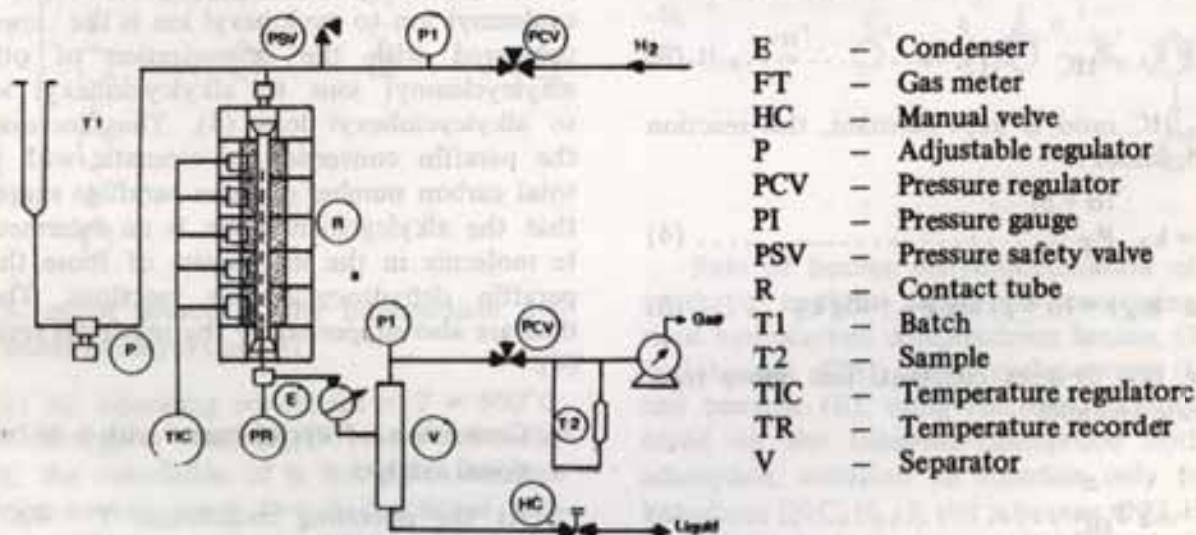

E	—	Condenser
FT	—	Gas meter
HC	—	Manual velve
P	—	Adjustable regulator
PCV	—	Pressure regulator
PI	—	Pressure gauge
PSV	—	Pressure safety valve
R	—	Contact tube
T1	—	Batch
T2	—	Sample
TIC	—	Temperature regulatorc
TR	—	Temperature recorder
V	—	Separator

Figure 1. Catatest unit

III. RESULTS AND DISCUSSION

A. Reaction rate

The initial reactions rate (r), for conversion of hydrocarbon feedstock, is calculated by using the following equation (3).

$$r = X \frac{F}{W} \quad \dots \dots \dots \dots \dots \quad (1)$$

Where :

X = Conversion of hydrocarbon feedstock, in mole/mole

F = Rate of hydrocarbon feedstock, in mole/hour

W = Weight of catalyst used, in grams.

As the rate constant (k), is proportional to the initial reaction rate, thus the activation energy (E), of conversion of hydrocarbon is obtained by using the following Arrhenius equation :

$$r \approx k_1 = A. e^{-E/RT} \quad \dots \dots \dots \quad (2)$$

Reaction rate can be written by the following power series,

$$r = k_2 \ P_{HC}^{\alpha} \ P_{H2}^{\beta} \quad \dots \dots \dots \dots \quad (3)$$

If H_2/HC ratio is kept constant, this reaction rate becomes :

$$r = k_3 \ P_T^{(\alpha + \beta)} \quad \dots \dots \dots \dots \quad (4)$$

$$\text{or} \quad \log r = (\alpha + \beta) \log P_T + \log k_3 \ \dots \dots \quad (5)$$

If the P_{H_2} is kept constant, this above reaction rate becomes :

$$r = k_4 \ P_{HC}^{\alpha} \quad \dots \dots \dots \dots \dots \quad (6)$$

$$\text{or} \log r = \alpha \log P_{HC} + \log k_4 \ \dots \dots \dots \quad (7)$$

The activation energy (E) from equation 2, the total order $(\alpha + \beta)$ from equation 5, and the partial reaction order on the hydrocarbon feedstock (α) from equation 7, can be obtained by variation of the temperatures (T), the total pressure (P_T), and the hydrocarbon partial pressure (P_{HC}) respectively. And then the experimental reaction rate can be obtained.

B Reaction mechanism

1. Intermediate molecule of dehydrocyclization reaction

At operating conditions : T = 500°C; P_T = 30 kg/cm² and H_2/HC ratio = 8 mole/mole, conversions of n. hexane, n. heptane and n. octane to aromatic, using reforming bi-metallic catalyst, are obtained as follows : 0,55: 2,02 and 6,55 % by mole respectively. The mole ratio of the aromatic products of n. octane dehydrocyclization between xylene and ethylbenzene is higher than 2 (two).

The n. hexane, n. heptane and n. octane dehydrocyclization can produce methylcycloamil, dimethyl/ethylcycoloamyl and three - methyl/methyl-ethyl/propylcycloamil ions respectively. The isomerization of this methylcycloamyl ion to cyclohexyl ion is the lowest compared with the isomerization of other alkylcycloamyl ions to alkylcyclohexyl ions to alkylcyclohexyl ions (4). Thus increasing the paraffin conversion to aromatic with the total carbon number of these paraffins suggests that the alkylcycloamyl ion is an intermediate molecule in the mechanism of those three paraffin dehydrocyclization reactions. These data are also supported by the previeous results (4).
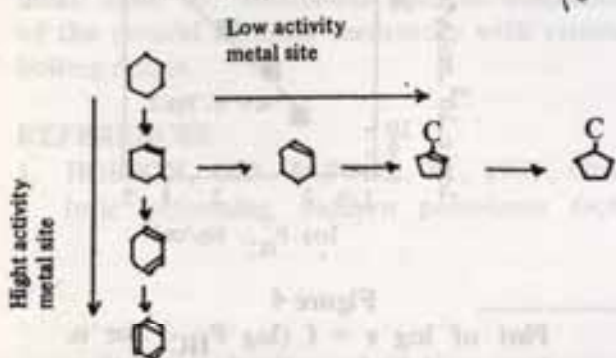
2. Conversion of cyclohexane with a bi-functional catalyst

At the operating conditions: T - 400°C, P_t = 15 kg/cm² and H_2/HC ratio = 8 mole/mole, the conversion of cyclohexane to benze-

ne and methycyclopentane using bi-functional catalyst: reforming mono-metallic and Ni-Mo/Al_2O_3-SiO_2 having the same total acidity is observed as follows:

Products	Conversion = X % by mole	
	Mono-Metallic	Ni-Mo/Al_2O_3-SiO_2
Benzene	28,71	3,03
Methyl cyclo-pentane	1,98	4,65

The dehydrogenation activity of the metal-site of the reforming mono-metallic catalyst is higher than the Ni-Mo/Al_2O_3-SiO_2 catalyst. The high activity of cyclohexane hydroisomerization to methylcyclopentane given by the low dehydrogenation activity of the metal-site of this bi-functional catalyst Ni-Mo/Al_2O_3-SiO_2 suggests that the high migration of the cyclohexane from this metal site to the acid-site where it is isomerized to methyl-cyclopentene via the intermediate molecule methylcycloamyl ion proceeds as show below :


3. **A major source of the intermediate molecule of alkycycloamyl**

At the operating conditions = T = 500°C, P_T = 20 kg/cm² and H_2/HC ratio : 6 mole/mole, the conversion of n. hexane to benzene and iso-hexane using two bi-functional catalysts: reforming mono-metallic catalyst and Ni-Mo/Al_2O_3-SiO_2 are obtained as follows.

Bi-functional catalysts	Coversion = X. % by mole	
	Benzene	Iso-hexane
Mono-metallic	3,77	52,84
Ni-Mo/Al_2O_3-SiO_2	0,92	71,06

This hexadiene suggests as a major source of intermediate molecule of methylcycloamyl ion in the mechanism of n. hexane dehydrocyclization reaction. The high migration of n. hexane from the low metal-site activity (Ni-Mo/Al_2O_3-SiO_2) to the acid site, suggests that, this n. hexane seems to be an intermediate molecule in the n.hexane hydroisomerization reaction. It suggests that for a given acid-site of a bi-functional catalyst for n.hexane isomerization has the lower metal site activity compared with n. hexane dehydrocyclization. It is supported also by the previous data (5). The mechanism of n.hexane conversion using a bi-functional catalyst as follows.
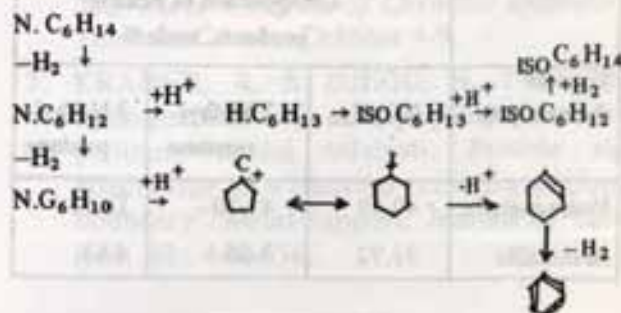
Rate of hexane dehydrocyclization of the synthetic naphtha feedstocks containing various hydrocarbon compositions: hexane, (NC_6) cyclohexane (CH), methylcyclopentane (MPC) and benzene (B), using reaction rate equation based on the Langmuir-Hinselwood isotherm adsorption, obtained an equation only for n. hexadiene (N-C_6H_{10}), not n.hexane (NC_6H_{12}). as a source of the intermediate molecule of methycycloamyl, as follows :

$$r = [12.119 \cdot P_{HC6} \cdot P_{H2}^{-2}]/[1 + 0.217 \cdot P_{HC6} \cdot P_{H2}^{-2} + 4.629 \cdot 10^{-4} \cdot P_{MCP}$$
$$+ 2.745 \cdot 10^{-6} \cdot P_{CH} + 0.276 \cdot 10^{-6} \cdot P_B + 2.12 \cdot 10^{-3} \cdot P_{H2}]$$

If the small values of equilibrium constant of adsorption of methylcyclopentane, cyclohesane, benzene and hydrogen can be negleted, thus the total order of this n.hexane dehydrocyclization reaction using a synthetic naphtha feedstock, is-1 (minus one), which is nearly the same with the total order of dehydrocyclization reaction rate of pure n.hexane, obtained from Figures 2, 3 and 4, as follows:

$$r = 6.113 \cdot 10^{18} \cdot e^{-71,228/RT} \cdot P_{HC}^{0.7863} \cdot P_{H2}^{-1.8727}$$

4 Polyadsorption of hydrocarbon by the metal -site

At the operating contions : T = 425°-455°C, P = 15 kg/cm² and H₂/HC = 6 mole/mole, the hydrodecyclization of methylcyclopentane to hexane using mono-and bi-metallic reforming catalysts are, as follows:

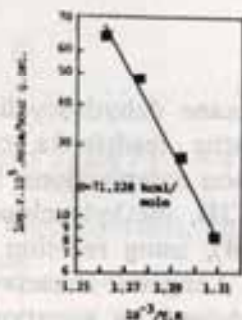| Type of the catalysts	Composition of hexane products, mole %		
	NC₆H₁₄	2 Methyl-pentane	3 Methyl-pentane
Mono-metallic	40.18	43.70	16.12
Bi-metallic	91.72	3.66	4.63

Figure 2
Arrhenius plot of n. hexane dehydro-cyclization reaction
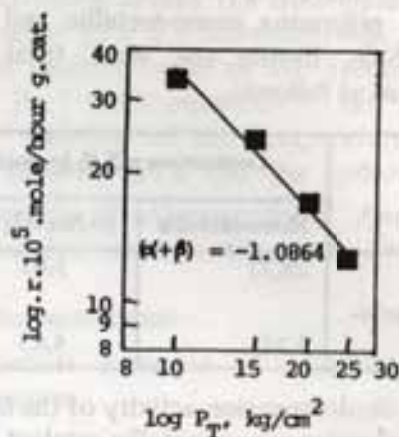
Figure 3
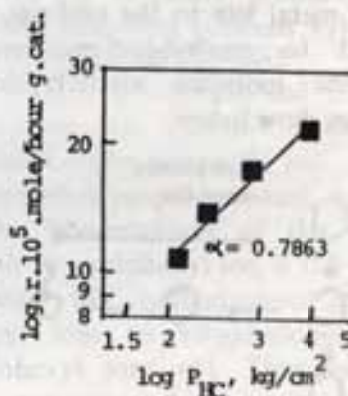Plot of log r = f (log P_T) for n. hexane dehydrocyclization reaction.

Figure 4
Plot of log r = f (log P_{HC}) for n. hexane dehydrocyclization reaction.

These results show that the high metal-site activity of bi-metallic reforming catalyst (6), produces the hexane by methylcyclopentane hydrogenolis reaction (4). And this hydrogenolis reaction suggests that the polyadsorption of the methylcyclopentane on these high ac-

tivity of the metal-site bi-metallic reforming catalyst, has been formed. Thus there is an optimum activity of the metal-site of a given acid site of bi-functional reforming catalyst for n.hexane dehydrocyclization (7).

IV. CONSLUSION

In the mechanism of n.hexane dehydrocyclization to benzene using bi-functional reforming catalyst, it suggests that n. hexadiene has been formed as a mjor source of the intermediate molecule of the methylcycloamil ion.

The dehydrogenation activity of the metal-site of bi-functional reforming catalyst has an optimum value for a given the acid-site of this bi-functional reforming catalyst.

The total reaction order of n.hexane dehydrocyclization to benzene has - 1 (minus one) both for reaction rate equation of power series and of Langmuir-Hinselwood isotherm adsorption.

To study the reaction rate of the paraffin dehydrocyclization to aromatic, the experiment must be continued such as utilization of the natural naphtha feedstocks with various boiling ranges.

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