HYDROISOMERIZATION OF CYCLOHEXANE AND N–HEPTANE USING Ni–Mo AND Ni–W CATALYSTS SUPPORTED ON SILICA–ALUMINA *)

By

AS. Nasution

ABSTRACT

An experiment has been carried out to study the influence of hydrogenating site of bi-functional and of n-butylamine on the hydroisomerization cyclohexane and n-heptane. The observed data show that a high activity of hydrogenating ste of bi-functional catalyst, tends to increase the catalytic activity of hydroisomerization reaction and n-butylamine acts as catalyst poison, which reduces the isomer products.

I. INTRODUCTION

Hydroconvension is probably the most versatile of modern petroleum processes. The versatility has been achieved by the development of specific families of catalysts, of processing schemes designed to allow these catalysts to functions efficiently, and optimal refining relationships between hydroconversion and other refining processes. (6)

Hydroisomerization is one of the hydroconversion processes using a bi-functional catalysts, containing both metal site or hydrogenating site, and acid site or isomerization/cracking site. The best choice of this bi-functional catalysts for a specific objective requires a particular balance between these two typical active sites. (4)

The kinetic of hydroconversion processes with respect to the variety of feedstock characteristics gives rise to an interesting case to study, i.e. hydroisomerization of paraffin wax and influence of catalyst acidity on the hydrocracking. (2)

In order to obtain more information about hydroconversion, an experiment has been carried out to study the influence of metal site of bi-functional catalysts and of n-butylamine on the hydroisomerization of cyclohexane and n-heptane at operating conditions : Temperature : from 370 to 400°C Pressure : 30 kg/cm² and H_2/HC ratio : 8 mole/mole

using Ni-W and Ni-Mo catalysts supported on the same acidity of Silica Alumina. And benzene hydrogenation to cyclohexane has been used as molecule model to determine the activity of hydrogenating site of these two bi-functional catalysts.

Experiment was carried out by using a micro-catatest unit, operated in a continous system. Gas and liquid product samples taken from gas and liquid samplers, respectively, were analyzed by using a Gas-Liquid Chromatography.

II. EXPERIMENTAL

Three types of molecules models have been used as feedstock, i.e. benzene, cyclohexane and n-heptane. The purity of these molecules is higher than 99.5% mole. The electrilytic hydrogen having purity 99.5% by volume has been used in this experiment. Two bi-functional catalysts i.e. Ni-W and Ni-Mo catalysys supported on the same silicate alumine, were used in this experiment.

Experiment was carried out in a micro cata-test unit, without gas recycle, operated at high temperature and pressure with a contineous system. The volume and inside diameter of the reactor are 220 cc and 19 mm, respectivelly.

The temperature of inside reactor is measured on the

---

3 (three) zones: i.e. reactor-zone, catalysts-zone and the product-zone, and these reactor temperatures are regulated and recorder. The flow-sheet of this micro catatest unit is shown in the Figure 1.
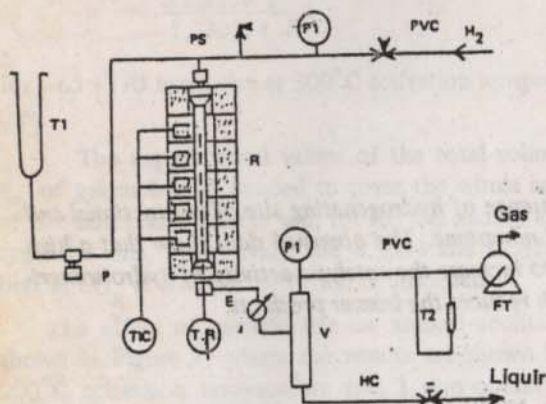
E	— Condensar	R	— Contant tube
FT	— Gas meter	T1	— Batch
P	— Pump	T2	— Sample
PVC	— Pressure regulator	TIC	— Temperature regulator
P1	— Pressure gauge	TR	— Temperature recorder
PS	— Pressure safety valve	V	— Separator

Figure 1. Catatest Unit

Gas and Liquid product samples were taken from gas and liquid sampler respectively and these producte are then analyzed by Gas-Liquid Chromatography. The operating conditions of this experiments are shown on the Table 1.

Table 1. Operating conditions of benzene hydrogenation, hydroisomerization of cyclohexane and n-heptane.

Operating contions		Type of reaction	
		Hydrogen-nation	Hydroiso-merization
Temperature	°C	290° - 350°	370 - 400°
Pressure	kg/cm²	15	30
H₂/HC	mole/mole	8	8

III. RESULT AND DISCUSSION

Experimental data on hydroisomerization of cyclohexane and n-heptane using Ni-Mo and Ni-W catalyst supported on silicate-alumine will be dis-

cussed into two following subjects :

- Activation energy
- Influence of n-butylamine

A. Activation energy

Activation energy of reaction can be calculated by using the following Arrhenius equation,

$$k = A\,e^{-E/RT}$$

The initial reaction rate (r_o) is proportional with the rate constant (k), then the Arrhenius-equation can be written as follows,

$$r_o\,k = A\,e^{-E/RT} \text{ or}$$

$$\log r_o = -\frac{E}{2,303.R}\frac{1}{T} + 2,303 \log A$$

The slope $(tg\varphi)$ of the straight line $\log r_o = f(1/T\,K)$ is equal to $tg\,\varphi = -E/2,303.R$, than the activation energy of reaction (E) can be calculated.

Log r_o against 1/T K for benzene hydrogenation, hydroisomerization of cyclohexane and n-heptane are shown on the Figure : 2, 3 and 4.
Data on the Figure 2, 3 and 4 show that :
Activation energy of hydrocarbon hydroconversion are as follows :

* Hydrogenation of benzene to cyclohexane are 17.282 and 20/982 kcal/mole for Ni -W/ Al_2O_3 - SiO_2 and Ni - Mo/Al_2O_3 - SiO_2 catalysts respectively.

* Hydroisomerization of cyclohexane to methylcyclopentane and of n-heptane to isoheptane, are 23.004 ÷ 26.987 and 24.78 ÷ 26.228 kcal/mole for Ni-W/Al_2O_3 SiO_2 and Ni-Mo/Al_2O_3-SiO_2 catalysts respectively.

Base on these observeed activation energy, the order of activity of these two bi-functional catalysts is Ni-W/Al_2O_3—SiO_2 Ni-Mo/Al_2O_3—SiO_2 for benzene hydrogenation and hydroisomerization of cyclohexane and n-heptane.

High activity of metal site of bi-functional catalysts become extremely active for hydroisomerization reaction. It is suggested as follows :

Metal site may dehydrogenate the hydrocarbon to an unsaturated hydrocarbon which moves to the acidic site where chain branching or in-
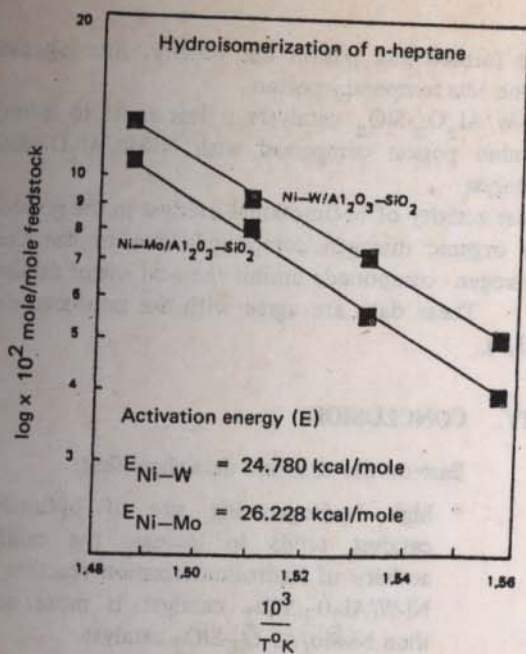
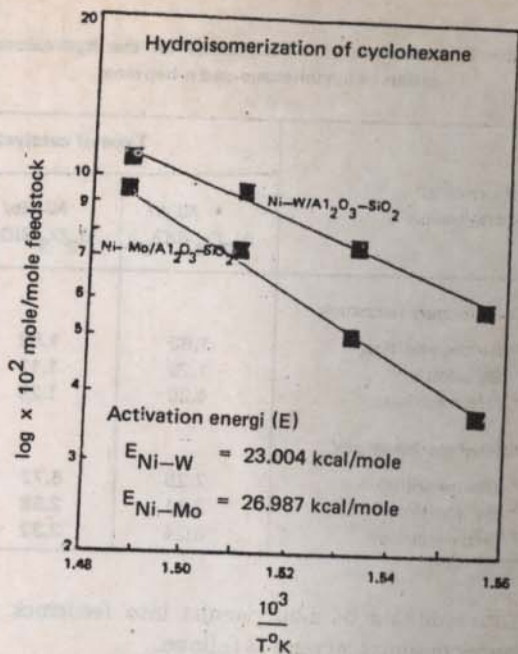**Figure 2.** Arrhenius plot of hydroisomerization of n-heptane using Ni-W/Al_2O_3-SiO_2 and Ni-Mo/Al_2O_3-SiO_2 catalysts.

Activation energy (E)

E_{Ni-W} = 24.780 kcal/mole

E_{Ni-Mo} = 26.228 kcal/mole

Figure 4 Arrhenius plot of Hydroisomerization of Cyclohexane using Ni-W/Al_2O_3-SiO_2 and Ni-Mo/Al_2O_3-SiO_2 catalyst

Activation energi (E)

E_{Ni-W} = 23.004 kcal/mole

E_{Ni-Mo} = 26.987 kcal/mole
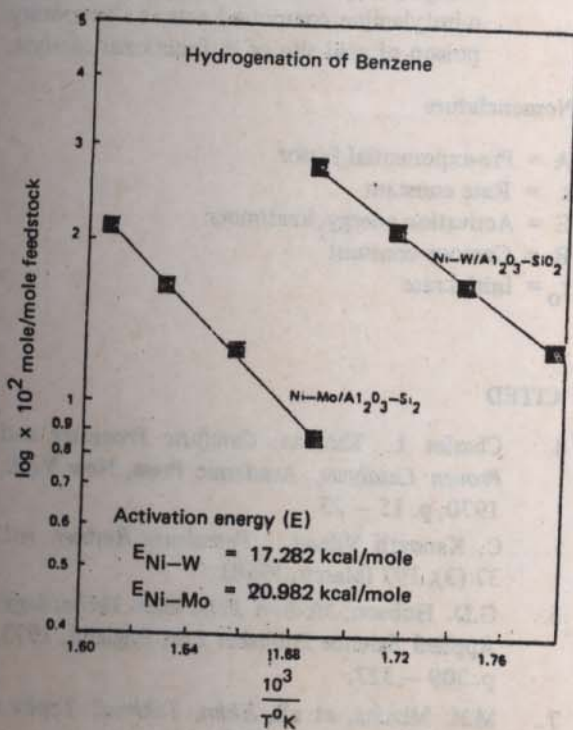
Figure 3 Arrhenius plot of hydrogenation of Benzene using Ni-W/Al_2O_3-SiO_2 and Ni-Mo/Al_2O_3-SiO_2 catalysts

Activation energy (E)

E_{Ni-W} = 17.282 kcal/mole

E_{Ni-Mo} = 20.982 kcal/mole

somerization occur, and the isomerized unsaturated hydrocarbon moves back to the metal site where it is hydrogenated to the isomer products.

The published data (1,7) are agree with these experimental data.

B. Influence of n-butylamine

The experimental data on the influence of n-butylamine on the hydroisomerization of cyclohexane and n-heptane at the operating conditions : Temperature = 380°C and H_2/HC ratio = 8 mole/mole, are shown on the Table 2.

Data on the Table shows that :

By addition of n-butylamine into feedstocks the isomer products decrease as follows.

* Product ratios (methylcyclopentane/benzene) of cyclohexane hydroisomerization are 70,49 and 74.34% mole on fresh feedstock for Ni-W/Al_2O_3-SiO_2 and Ni-Mo/Al_2O_3-SiO_2 catalysts respectively.

* Products of n-heptane hydroisomerization are : 31.86 and 45.10% mole on fresh feedstock for Ni-W/Al_2O_3-SiO_2 and Ni-Mo/Al_2O_3-SiO_2 catalysts respectively.

Table 2. Influence of n-butylamine on the hydroisomerization of cyclohexane and n-heptane.

Influence of n-butylamine	Type of catalysts	
	Ni-W/ Al_2O_3-SiO_2 ↓	Ni-Mo/ Al_2O_3-SiO_2
Cyclohexane feedstock		
* Before addition	1.83	1.52
* By addition	1.29	1.13
* After addition	1.36	1.29
N-Heptane feedstock		
* Before addition	7.25	5.72
* By addition	2.31	2.58
* After addition	3.24	3.32

After addition of n-butylamine into feedstock the isomer products increase as follows.

Product ratios (methylcyclopentane/benzene) of cyclohexane hydroisomerization are 74.32 and 84.87% mole on fresh feedstock for Ni-W/Al_2O_3-SiO_2 and Ni-Mo/Al_2O_3-SiO_2 catalysts respectively.

Products of n-heptane hydroisomerization are 44.69 and 58.04% mole on fresh feedstock for Ni-W/Al_2O_3-SiO_2 and Ni-Mo/Al_2O_3-SiO_2 catalysts respectively.

Base on these experimental data show that in hydroisomerization, nitrogen containing feedstock over bi-functional catalysts, hydroisomerization is partially suppressed because ammonia and amines are formed and posion the activity. And n-butylamine acts temporary poison.

Ni-W/Al_2O_3-SiO_2 catalysts is less resist to n-butylamine poison comparred with Ni-Mo/Al_2O_3-SiO_2 catalyst.

Lost activity of bi-functional catalyst in the presence of organic nitrogen compounds due to the these nitrogen compounds inhibit the acid site of catalyst.

These data are agree with the previeous data (3,5).

IV. CONCLUSION

Base on the observed data show that;

* high hydrogenating site of bi-funtional catalyst tends to increase the catalytic activity of hydroisomerization reaction, i.e. Ni-W/Al_2O_3-SiO_2 catalyst is more active than Ni-Mo/Al_2O_3-SiO_2 catalyst.

* By addition of n-butylamine into feedstock, the isomer products of cyclohexane and n-heptane hydroisomerization decrease. And n-butylamine compound acts as a temporary poison of acid site of bi functional catalyst.

Nomenclature

A = Pre-exponential factor
k = Rate constant
E = Activation energy, kcal/mole
R = Gaseous constant
r_0 = Initial rate

LITERATURE CITED

1. Ahusa, *Etudes des Catalyseours d'hydrotreatment,* These Universite de Paris, December 2, 1967.

2. A.S. Nasution, *Papers :* on 2nd ASCOPE Conference and Exhibition, Manila, Philipines, October 7 – 11, 1981; and on 3rd International Congress on Catalyst, West Berlin, West-Germany, July 2 – 6, 1984.

3. Asselin, G.F., and Erickson, R.A., *Chem. Eng. Prog.* 58, No. 4, 47 (1962).

4. Charles L. Thomas, *Catalytic Processes and Proven Catalysts,* Academic Press, New York, 1970, p. 15 – 23.

5. C. Kenneth Viland. , *Petroleum Refiner, vol.* 37 (3), 197 (March, 1958)

6. G.D. Hobson, *Modern Petroleum Technology,* Applied Science Publisher Ltd, England, 1973, p. 309 – 327.

7. M.H. Mizcha, et all, *Khim, Tekhnol. Topliv i Masel,* No. 4, 23 – 25 (1961)