INFLUENCE OF POISON COMPOUNDS UPON THE ACTIVITY OF MONO AND BE-METALLIC REFORMER CATALYSTS *

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Abstract. Catalytic reforming process uses a bifunctional catalyst. An experiment has been carried out to study the influence of sulphur, nitrogen, oxygene and lead compound upon the activity of the metal site of mono and be-metallic reformer catalysts using hydrogenation of benzene as a reaction model in a contineous catatest unit.

1. INTRODUCTION

Catalytic reforming is one of the catalytic processes used to convert naphtna fraction into high octane gasoline and also to get low aromatic hydrocarbons (benzene, toluene, xylene, and ethyl benzene) with the assistance of bifunctional heterogenous catalyst. 1,2)

The increase of naphthena and aromatic hydrocarbon contents in naphtha will raise the quality of reformer product (3) and on the contrary, the high content of non-hydrocarbon and metal (such as Pb) can deactivate the catalysts which decrease the quality and quality of reformer product (4).

Bi-functional heterogenous catalysts used in the catalytic reforming process has two types of the active sites, metal active site and acid active site (5).

The success of a catalytic reformer process in many ways depends on the activity of metal site catalyst, because this active metal site activity cannot be stabilized as acid active site during operation.
This means that the activity of active metal site will decrease due to the coke deposit and poison compounds (6,7).

A series of experiments have been carried out to study the influence of various poison compounds such as tiophene, n. butylamine, ethylalcohol and tetra ethyl lead, upon the activity and stability of three mono-metallic and two bi-metallic heterogenous reformer catalysts has been carried out.

A hydrogenation reaction of benzene into cyclohexane has been used as a reaction model in this experiment.

This experiment has been carried out in a contineous catalytic-activity test (Catatest) unit.

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2. EXPERIMENTAL

Reactant.

Benzene and poison compounds, which have been used in this experiment have a pure grade.

Pure benzene and a mixture of the poison compound have been used as feedstocks.

The electrolitic hydrogene has been used in this experiment, having the purity 99,5% mol.

The catalyst used of the type commonly employed in catalytic reformer processes i.e. three mono-metallic (M_1, M_2, M_3) and two metallic (B_1, B_2) reformer catalysts.

Apparatus

Hydrogenation of benzene into cyclohexane has been carried out in a contineous micro-Catalytic-Activity (CATATEST) unit, without gas recycle. The volume and the inside diameter of the reactor are 100 cc and 18 mm respectively.

The operating procedures

The operating conditions of the experiment are as follows: Catalyst weight: 2,5 g; H_2/HC ratio = 4 mole/mole, Feed ratio = 0,064 gmole per hour, Pressure = 1 kg/cm^2 and Temperature = 275°C.

The operating procedure used in this experiment is as follows :

- If the temperature rises up to 100°C, the hydrogen injection is set out, and then reactor temperature increased by about 10°C per minute.
- At temperature 200°C, feedstock is pumped to the reactor, and then operating conditions is set out.
- Gas and liquid product samples are taken from gas and liquid samplers respectively. Their chemical compositions are analyzed by using gas-liquid chromatography.

3. RESULTS AND DISCUSSION

The experiment on the influence of the poison compounds upon the activity of reformer catalysts has been carried out to determine the two following subjects :

- Influence of the poisons compounds upon the activity of bi-metallic reformer catalyst (B_2).
- Stability of mono and bi-metallic reformer catalysts upon the various poison compounds.

3.1 Influence of the poison compounds upon catalyst activity of bi-metallic reformer catalyst (B_2)

Influence of tiophene, n. buthyl amine, ethyl alcohol and tetra ethyl lead upon catalyst activity of bi-metallic reformer catalyst has been carried out to determine the poisoning coeficient. Experimental data are shown on the table 1 and figure 1.

Data can be divided into two types of poisons :

First type is sulphur, nitrogene and oxygene poison compounds, can reduce the activity of bi-metallic reformer catalyst as follows :

- First, a small amount of poison compounds in the reactant will strongly reduce the conversion of benzene into cyclohexane due to the high deactivation of bi-metailic reformer catalyst where this deactivation is proportional to the poison content in the feedstock.
- Then by increasing the poison content in the feedstock, the catalyst activity of the bi-metallic will slowly decrease.
- And then the rate of catalyst deactivation will be equilibrium.

These experimental data agree with the previous one (4).

By varying of the operating conditions the reaction rate constant of adsorption of these poison compounds can be reduced, this means the catalyst can be reactivated (or regenerated). And such poison are classified as temporer poisons (6).

The second type is tetra ethyl lead poison compound which shows a different curve compared to the first type, where deactivation of bi-metallic catalyst is proportional with the tetra ethyl lead content in the reactant. These data suggest that active metal of bi-metallic will be covered by lead metal as alloy. And such poison can not be removed from the metal site of the catalyst or regenerated and is called permanent poisons.
Thus the chemical bonds between active metal of bi-metallic reformer catalyst and the temporer poisons (S, N. O) and permanent poison (Pb) are different (5).

Deactivation of catalyst by the poison compound can be expressed by an empirical formula as follows :

$$A/A_0 = 1 - \quad C$$

The value of poison coeficient ( ) of sulphur, nitrogen, oxygen and tetra ethyl lead are shown on the Figure 1.

Poisoning coefficient of tetra ethyl lead (Pb) are much higher than the poisoning coefficient of sulphur, nitrogen and oxygen, i.e, thus the sensitivity of the poison compounds to the bi-metallic reformer catalyst seems to depend on the structure of the poison compounds This result are supported by previous data (6).

3.2 Stability of mono and bi-metallic reformer catalysts upon the various poisons

Stability of mono and bi-metallic reformer catalysts upon, thiophene, normal buthyl amine, ethyl alcohol and tetra ethyl lead has been studied for determination of relation between stability of catalyst and its metal site structure.

On the figure 2 is shown the experimental data.

Data show that :

- Stability of bi-metallic upon sulphur, nitrogene compounds and tetra ethyl lead is less than what is observed on the mono-metallic reformer catalysts, and contrary for ethyl alcohol poisons where bi-metallic are more stable than mono-metallic.

- Stability of two bi-metallic and three mono-metallic reformer catalysts upon the S, N, O and Pb poisons are nearly the same.

The high influence of poison compounds upon the bi-metallic reformer catalysts compared to the mono metallic due to the different structure of the active metal site of the both reformer catalysts. And these experimental data agree with the previous data (3, 5).

4. CONCLUSIONS

Based on the experimental data, the conclusions are as follows :

- Metal site of the bi-metallic reformer catalysts (B_1 and B_2) is more sensitive than metal site of those mono-metallic reformer catalysts (M_1, M_2 and M_3), to the poison compounds (except oxygene compound).

- The sensitivity of the three mono-metallic reformer catalysts (M_1, M_2, and M_3), to the poison compounds used are the same. And these phenomena is also found for the two bi-metallic reformer catalysts. (B_1 and B_2).

- The poison coefficient of these four poison compounds is as follows :

tetra ethyl lead > tiophene > n. buthyl amine > ethyl alcohol

Influence of Various Poisons Upon Relative Activity of Bi-Metallic Reformer Reformer Catalyst. (B_2)

Table 1

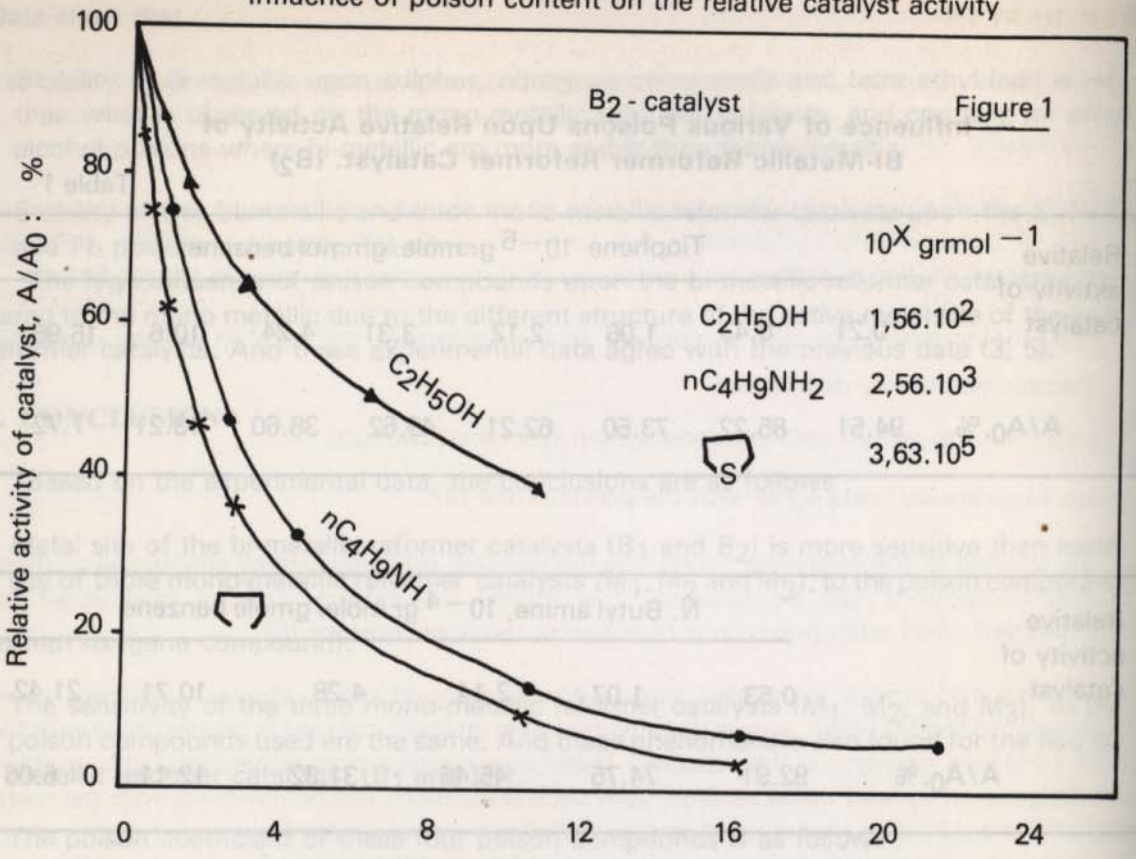
Relative aktivity of catalyst	Tiophene 10^{-6} gr mole/gmmol benzene							
	0.21	0.43	1.06	2.12	3.31	4.24	10.6	15.95
A/A_0.%	94.51	85.22	73.50	62.21	49.62	38.60	13.21	7.72

Relative activity of catalyst	N. Butyl amine, 10^{-4} gr mole/gmole benzene					
	0.53	1.07	2.14	4.28	10.71	21.42
A/A_0.%	92.91	74.75	45.46	31.32	12.11	6.06

Relative activity of catalyst	Ethyl alcohol 10^{-4} gr mole/gmole benzene				
	2.54	12.71	25.40	62.72	127.10
A/A_0.%	99.21	80.84	64.65	50.52	40.41

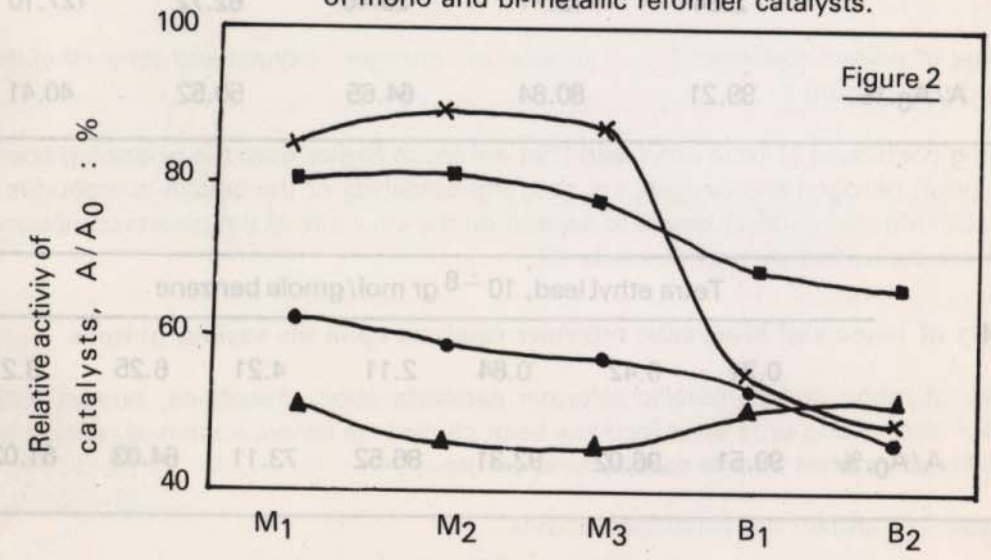
Relative activity of catalyst	Tetra ethyl lead, 10^{-8} gr mol/gmole benzene						
	0.21	0.42	0.84	2.11	4.21	6.25	8.21
A/A_0.%	99.51	96.02	92.31	86.52	73.11	64.03	61.02

Influence of poison content on the relative catalyst activity



(X = 3,4 and 6 for ethanol, n. buthyl amina and tiophene respectively)

Influence of various poison compounds on the relative activity of mono and bi-metallic reformer catalysts.



(X = tiophene, = tetra ethyl lead, = n. buthyl amina; ethyl alcohol.)

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