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**CATALYTIC REFORMING OF n-HEPTANE ON PLATINUM-
TUNGSTEN SUPPORTED ON GAMMA-ALUMINA**

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ABSTRACT

The mono-metallic and bi-metallic catalysts have been prepared by impregnating with solutions containing a compound of H_2PtCl_6 , WO_3 and 1ml HCl (0.1 mol). It should be noted that the catalysts' activity and selectivity have been determined under these conditions : 450-500⁰C ,and 15-25atm by H_2 . For converting n-heptane , the molar ratio H_2/C_7H_{16} is 5 , and LHSV is 1.5ml/h. It has been proved that , under these experimental conditions , the conversion of n-heptane into branched aliphatic isomers is catalyzed by a bifunctional mechanism. The results indicate that in the presence of W , the catalysts have much higher selectivity and stability for isomerization reaction. At a given conversion , the bi-metallic catalysts produce much lower concentrations of cracked products. According to the tests , W modifies the support acidity resulting to the higher selectivity for isomerization and the lower one for cracking , and it also modifies the Pt properties .

Keywords: Catalytic reforming; n-Heptane; Platinum; Tungsten; Gamma-alumina

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INTRODUCTION

Naphta reformation is a process of increasing naphta octane number by increasing the concentration of Paraffin branched isomers and specially the one of aromatics (1). The overall process involves several reactions promoted by a bifunctional catalyst (2). Catalytic reforming reactions proceed on bifunctional catalyst (such as Platinum) for hydrogenation, dehydrogenation and the active sites on the surface of the support (e.g activate alumina) such as the acid and base sites for the isomerization, cracking and cyclization reactions (3). The Pt/Al₂O₃ has been used as a bifunctional reforming catalyst in the oil industry since the 1950's (4). Later, Pt was promoted with the other metals called bimetallic or multimetallic catalyst which are as follows :

Pt-Re (5-11), Pt-Sn (12-18), Pt-Pb (13), Pt-Ge (19), Pt-Ir (20), Pt-Nd (21-22) and Pt-Nb (23). The most remarkable property of bimetallic catalysts includes the improvement of stability reformation which distinguishes them from the mono-metallic Pt/Al₂O₃ systems . ” bimetallic model “ is one of the theories proposed to explain the stability improvement that attributes the bimetallic to a modification of the Platinum catalytic properties (7,24). The subject of interest is the role of second metal . Baccaud et.al (26) have shown that Sn may preserve activity by poisoning the more acidic sites in the alumina support . Bertolaccini and Pellet (25) found that Re promotes the hydrogenolysis of coke precursor, so it reduces coke formation . Jossens and Petersen (9) observed that Re interacts with Pt to reduce the activity of metal function. However , it is claimed that Pt-Sn interactions of coke formation on the metal surface of small ensembles that do not favor coking also reduce deactivation (12, 15, 27, 28).

This article suggests these catalysts performance (i.e. activity and selectivity) for the n-heptane catalytic reformation .

Experimental

1- Catalyst Preparation

The samples 0.6wt% Pt/Al₂O₃ and Xwt%Pt-YWt%W/Al₂O₃ (X=0.3, 0.5, Y=0.3, 0.1) were prepared by impregnating Gamma-Al₂O₃ (AKZO with surface area=270m²g⁻¹, Pore volume=0.71ml.g⁻¹ and bulk density=0.58g.ml⁻¹, respectively , with solutions of H₂PtCl₆ and W in diluted hydrochloric acid. This process is followed by drying them at 120°C for a period of 24 hours, and heating them in the air from room temperature up to 450°C. At this temperature the chlorine concentration was fixed at 0.05 wt%. The sample was purged with N₂ at room temperature for 30 minutes.

2- Catalyst Testing

Twelve grams of the catalyst were loaded into a 220cc reactor (Geomecanique, Catates Unit, Model BL-2). It was reduced by heating in a hydrogen stream at a constant flow-rate from room temperature up to 500°C for 8 hours. The catalyst was sulfided in a gas flow consisting of 600ppm H₂S in H₂ at 500°C and 1atm for 30 minutes , and then H₂ was passed over for 8 hours at the same temperature (i.e. 500°C). Operating conditions included the following factors : temperature = 450-500°C , pressure = 15-25 atm, LHSV=1.5h⁻¹ molar ratio H₂/C₇H₁₆=5 , and length of run 2 hours. After 2 hours , the total hydrocarbon conversion is taken as a measure of catalyst activity and it is defined as grams of feed transformed into products per 100g of feed total conversion , and selectivity for each type of products of n-heptane reformation is defined as:

Aromatization: Conversion to aromatics×100 / total conversion.

The percentage of product was analyzed by gas chromatography Varian 3600 Star with following characteristics: 6m capillary columns with a diameter of 250 microns , Liquid-Phase (DB-1), FID detector, Varian 4400 integrator and carrier gas is Helium.

RESULTS AND DISCUSSION

Under reforming conditions , specially at high temperatures , n-heptane reactions can occur either by metal catalyzed processes or a bifunctional mechanism involving both the metal and acidic sites on the oxide.

These two processes are of great importance which depend on the following factors : the support acidity , the metal acidity , and the experimental conditions. We conducted some experiments on the bimetallic Pt-W catalysts . Based on these experiments it is proved that they had lower selectivity for the cyclization formation in addition to their higher activity, specially when we compared them with the Pt-Sn catalysts (15). It is also shown that the Pt-W catalysts had higher selectivity for the toluene formation in addition to higher activity (conversion).

1- Effect of metal percent on the activity and selectivity of n-heptane

1-1-Activity

In regard to the bi-metallic catalysts we can say that by increasing the amounts of W , the total conversion will also increase . Under experimental conditions of this work , 0.3Ptwt%-0.3Wwt% is a slightly active catalyst at all temperatures and pressures

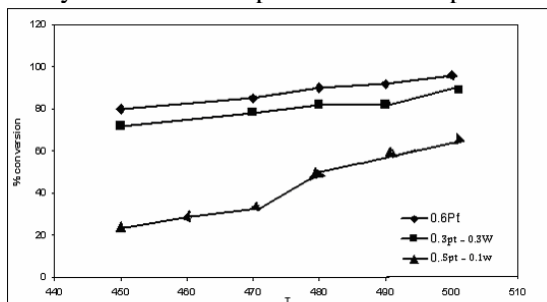


Figure1. Effect of Temperature on conversion % (P=20atm)

1-2- Selectivity

In regard to the catalysts with the large amounts of W ,the aromatics selectivity increases ; it is shown in figure 2 . We obtained the best results for the bi-metallic

catalysts 0.3wt%Pt-0.3wt%W. But larger amounts of W lead to decrease in selectivity.

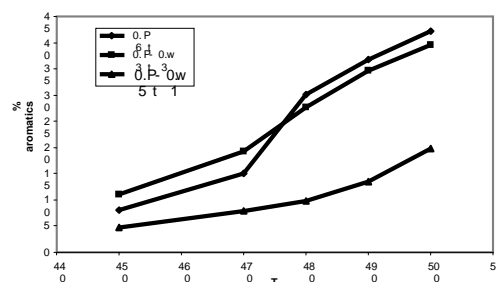


Figure2. Effect of Temperature on selectivity aromatization % (P=20atm)

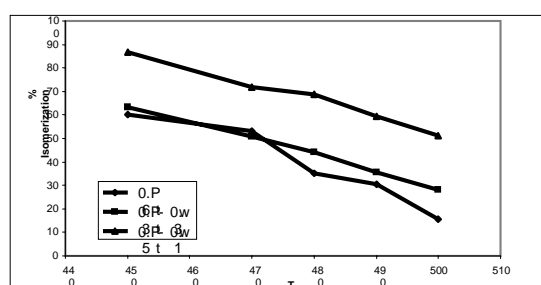


Figure3. Effect of Temperature on selectivity isomerization % (p=20atm)

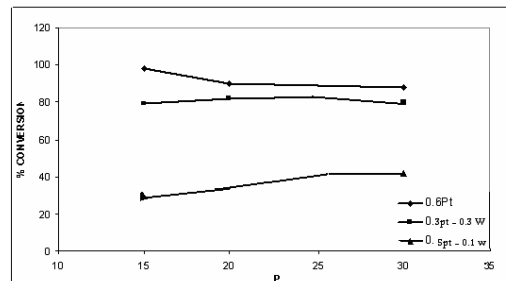


Figure4. Effect of pressure on conversion % (T=480)

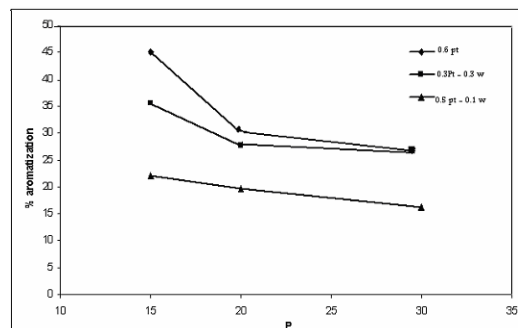


Figure5. Effect of Pressure on selectivity aromatization % (T=480)

total conversion as follows : 38% at 450°C , 71% at 500°C with 0.3 Pt- 0.3Nd , and 26% at 450°C , 100% at 540°C with 0.37Pt- 0.24Ge , but conversion is 72 at 450°C and reaches 93 at 500°C. When n-heptane participates in the aromatization reaction for Pt-W and Pt-Nd , its conversion trends in a similar direction , but its conversion towards aromatization for Pt-W is higher than Pt-Ge. For 0.3Pt-0.3W, results show that the total conversion of Pt-W is 51% more than that of Pt-Ge , specially at low temperatures (28) . It was found that isomerization played an important role to Pt /Al₂O₃ and Pt-W , since when temperature increased , it conversely decreased . This reaction was Also important on Pt-Sn/Al₂O₃ (12). Addition Sn to Pt has a main effect on reducing coke formation and increasing selectivity for dehydrocyclization . It was claimed by Beltramini and Trimm (12) .This effect is not due merely to the presence of the second metal since the activity/selectivity patterns of the mono-metallic catalysts differ greatly from those of the bimetallic catalysts , but most of them are resulted from interactions between the two metals. When W is added to Pt , the effect may be observed , too .

Figures 2 and 3 show the conversion of n-heptane to each group of products. In fact , it is a function of temperature. Always , the percentage of aromatization increases , but that of isomerization decreases. At low temperature , the main reactions of all catalysts are among the isomerization type.

3- Effect of pressure on activity and selectivity

3-1- Activity

When pressure is increased the total conversion remains approximately constant. Thus we can say that the second metal has a lot of influence on the n-heptane conversion at the pressure of 15-25atm . It is shown in the activity – pressure curve (Fig.4) for Pt/Al₂O₃, Pt-W/Al₂O₃ catalysts.

3-2- Selectivity

When the pressure is increased the percentage of total aromatics is usually decreased , but the selectivity for isomerization is increased . The

n-heptane conversion to each group of products is shown in figures 5 and 6 . In fact , it is a function of pressure.

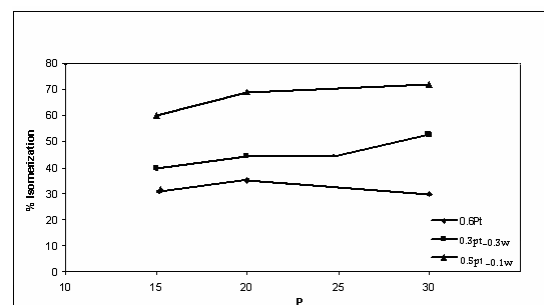


Figure6. Effect of Pressure on selectivity isomerization % (T=480)

4- Effect of Tungsten on platinum

One of the main advantages of bimetallic catalysts is to reduce the amount of self-poisoning by adding wolfram to Pt. If dehydrogenated hydrocarbons on residues are adsorbed very strongly on metal sites , poisoning will occur. Hence , any changes in the surface properties of the Pt, which decrease the binding energy of Pt and carbon, should increase the stability. Scientists believe that self-poisoning parallels deep hydrogenolysis in requiring several continuous metal sites for reaction to proceed (29-31). For instance , In Ni-Cu alloys (32,33) , when Cu is added several orders of magnitude decrease the rate of ethane hydrogenolysis . It can be illustrated on the base of reducing the number of Ni ensembles large enough to catalyze this reaction. In some other bimetallic systems such as Ru-Cu (34) , Ir-Re ,and Ir-Cu(35), the electronic effect has necessarily been invoked to account for the loss of hydrogenolysis activity since the degree of surface dilution by inactive atom is much less than what required for a geometric model. The bimetallic catalysts have a greater stability than the others that a similar explanation has been proposed to account for it (7) . If a small amount of wolfram is present in Pt as a solid solution , the wolfram will either donate electrons to Pt or will cause Pt to redistribute its electrons , so as it will reduce the density of states at the Fermi Level. It would be expected that a lower

density of states localized on the surface of Pt atoms leads a weaker bond joining carbon ; so self-poisoning and hydrogenolysis would be reduced . Wolfram clearly has the electronic role rather than the geometric one . Furthermore , there is a common explanation for the establishing effects of many other second metal additives in terms of electronic modification of the active metal. A small amount of wolfram will be sufficient to modify the Pt because wolfram had valence electrons available.

CONCLUSION

This article focuses on the activity (i.e. total conversion) and the catalysts selectivity for different reactions. The conversion of n-heptane into branched aliphatic isomers is catalyzed by a bifunctional mechanism , under experimental conditions .

The main effect of addition of W to Pt is to reduce the hydrocracking reaction and to increase the selectivity for total aromatics , specially for small amounts of Wolfram.

We suggest that altering the local density of states at surface Pt atoms , and modifying the catalytic properties of these surface atoms is the role of wolfram in Pt-W catalysts . But its main effect is to reduce the activity in cracking reactions.

The conversion of n-heptane into total aromatics is bifunctional. When W is present the catalyst has a higher selectivity for aromatization reaction. So, wolfram modifies the properties of Pt catalyst in two ways; it modifies the acidity of the support, the result that self-poisoning is reduced and the selectivity for nondestructive reaction increases.

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