Catalytic Reforming of n-Heptane on Platimum - Rhenium Supported on Gamma-Alumina

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ABSTRACT

Catalyitic reforming is one of the refinery processes in catalyst conversion that results to an increases in octane number of naphtan which leads to production of gasoline with higher octane number. Hydrocarbons with high octan number that are produced in reforming process are as; aromatics, paraffins, isomers and etc.

Not only Aromatics are used as fuel for motors but they are also useful in petrochemical industry. Also hydrogen is produced as a subsidiary in the process. In this research, platinium-rhenium is used as a catalyst with the combination of "Re=0.4"and"Pt=0.3".the activity and selectivity of the catalysts have been determined under condition at 350- 450oC and 30at. Pressure molar ratio H2/C7H16=5 and VVH=1.5 mL/h.

Our results proved that this catalyst produces good products under 30 atmosphere pressure and temperature ranges between 350 - 450oC but at higher temperatures such as 490 oC and over will generate lots of cracking and low quality black products that can not be analyzed by chromatography. This shows that in these temperatures the action of cracking is very much. However in temperature lower than 490 oC, the products have yellow color and this shows the existence of aromatic compounds.

In comparison between two catalysts with different percentages 0.3Pt=0.4Re catalyst has more activity. It also shows more selectivity in aromatization in comparison with 0.3Pt-0.3Re catalyst.

Keywords: Catalytic reforming; n-heptane; Platinum; Rhenium; Gamma-Alumina

INTRODUCTION

Catalytic reforming is a process of desirable gasoline production with high octan number that in a suitable condition and by using desirable catalyst cycloid hydrocarbons could be changed in to aromatics and paraffins to paraffin isomers. Mixture of gasoline and heavy cycloid compound are needed to feed this process that is made of paraffins, olefins, cycloid compounds and aromatics that are well known in oil industry [1] .

In fact transformation of hydrocarbon molecules is named reforming.

The food for this process is made of oil materials with low octan number and low percent of aromatics with boiling point of 80 oC [2] . Reactions of the reforming process are divided in seven groups , some of these reactions are performed with metal catalyst and some of them on the acidic base catalyst and some others are performed on the both bases of acidic and metallic for example aromatization reaction on the metal base,hydrocracing reaction on the acidic base and isomerization and cyclization performed on the bases of

metallic and acidic.This 7 kinds of reactions are divided in to groups of desirable (aromatization, isomerization ,cyclization) and undesirable.

The best condition for the process is thermodynamic balance between desirable and undesirable reactions[3]. The Pt/Al2O3 as a bifunctional reforming catalyst has been used since the 1950's in the oil industry[4]. Later Pt was promoted with other metals called bi or multimetallic catalyst which are Pt-Re[5-6],Pt-Sn[7-8] , Pt-Pb[9] , Pt-Ge[10], Pt-Ir[11], Pt-Nd[12-13]and Pt-WO3 [14] the most interesting feature of the bimetallic catalyst which distinguishes them from the mono – metallic Pt/Al2O3 system is the improvement in reforming stability . One of the theories put forward to explain the improvement in stability is the "alloy"model which attributes the alloy to a modification of catalytic properties of platinum when alloyed with a second metal [15-16] . The role of the second metal has been the subject of much attention. Jossen and Peterson [17] suggest that Re interacts with Pt to reduct the activity of the metal function.Bertolaccini and pellet [18] found that Re promotes the hydrogenolysis of coke precursor,thereby reducing coke formation. Baccaud et.al [19] has shown that Sn may preserve activity by poisoning the more acidic sites in the alumina support .However Pt-Sn interaction,resulting in the formation of coke on the metal surface of small ensembles that do not favour coking , have also been suggested to reduce deactivation [7,21,22,] .The most interesting feature of the bimettalic catalysts which distinguishes them from the mono-metallic Pt on alumina systems is the improvement in reforming stability.One of the theories put forward to explain the improvement in stability is the "alloy" model which attributes the alloy to a modification of the catalytic properties of platinum when alloyed with second metal[21,23].A number of bimettalic reforming catalysts have been patented and Pt-Re catalysts are used commercially.With Pt-Re catalysts it seems probable that the rhenium is zero-valant state and forms an alloy,or at least a solid solution,with platinum.The role of other additives is less clear,although it has been suggested recently that widely different

modifiers(Au,Sn,S,C) all effect the platinum in a similar way by dividing the surface into very small ensembles of Pt atoms[24].It is thought that these ensembles are too small to form partially dehydrogenolysis and coke forming reactions,where as the stability to form partially dehydrogenated molecules,which can isomerise on acidic oxide sites,is hardly affected[20].

EXPERIMENTAL AND METHOD
Catalyst preparation

The samples Xwt%Pt-Ywt%Re/Al2O3(X=0.3,Y=0.3,0.4) were prepared by impregnating gamma – Al2O3(AKZO with surface area = $270 m2g-1$, pore volume= 0.71 mL.g-1 and bulk density=0.58g.mL-1).Respectively with solution of H2PtCl6 and ReCl5 in diluted hydrochloric acid . This process is followed by drying at 120 °C for period of 24 hours, heating with air from room temperature untill obtained 450 C temperature. At this temperature (450 C) the chlorine concentration was fixed at 0.05 wt%. the sample was purged with N2 at room temperature for 30 minutes .

Catalyst testing

12 g of the catalyst was loaded into a 220cm^3 reactor(Geomecaninque ,Gatates Unit.Model BL-2).It was reduced by heating in hydrogen stream at constant flow-rate from room temperature up to 500 °C for 8 hours.The catalyst was sulfided in a gas flow consisting of 600 ppm H2S in 500 °C and 1 atmosphere for 30 minutes and H2 was passed over for 8 hours at same temperature.Operating condition included temperature:450-500 °C, pressure:15-30 atm. ,VVH = 1.5mL/h,molar ratio H2/C7H16=5 and length of run 2 hours .The total hydrocarbon conversion after 2 hours is taken as a measure of catalyst activity and is defined as grams of feed transformed into products per 100g of food conversion and selectivity for each of products of n-heptan reforming is defined as:Selectivity= 100X product. The percentage of product was analysed 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 integrat or and carrier gas is helium.

RESULTS AND DISCUSSION

The activity (conversion) and selectivity of the catalysts have been determined under flow condition at 490-510 °C and 15-30 tm. For the conversion n-heptane. Under these experimental conditions it has been estabilished that the conversion of n-heptane into branched aliphatic isomers is catalysed by a bifunctional mechanism,but excess acidity gives lower selectivity due to enhanced cracking.

Benzene is formed directly form n-heptane on metal sites and do not require acidic sites .The results show that when rhenium is present ,the catalysts are much more stable for conversion ,and have much higher selectivities for aromatization and isomerization veactions .At a given conversion the bimetalic catalysts produce much higher concentrations of cracked products. It is concluded that rhenium can not modifies the acidity of the support.It is tentatively suggested that similar electronic effects may be important in other bimetallic catalysts [20].

The products obtained in temperature higher than 490 °C by using chromatography gas can' t be recognized because they are not transparent. This shows that in these temperatures the action of cracking is very much. However in temperature lower than 350-450 °C, the products have yellow color and this shows the existence of aromatic compounds.

In comparison between two catalysts with different percentages 0.3Pt=0.4Re catalyst has more activity. It also shows more selectivity in aromatization in comparison with 0.3Pt-0.3Re catalyst. However the percentage aromatization in 0.3Pt-0.3Re catalyst is more than 0.3Pt-0.4Re catalyst. And this shows that in 0.3Pt-0.4Re catalyst, the compounds which resulted from isomerization were changed into aromatic compounds.

The effect of rhenium on activity

A high activity will be reflected either in high productivity from relatively small reactors and catalyst volumes or in mild operating conditions , particularly temperature , that enhance selectivity and stability if the thermodynamics is more

favorable.Figure 1 show that n- heptane conversion the Pt-Re catalyst increases with increasing rhenium , and desreases with increasing reaction temperature to reach 98% at 450 °C. At this temperature, the yield of C7 isomers, in the product is 46wt% , i.e.,the isomerization selectivity is 92% where a conversal of 98% is obtained at 450 °C and P.30atm
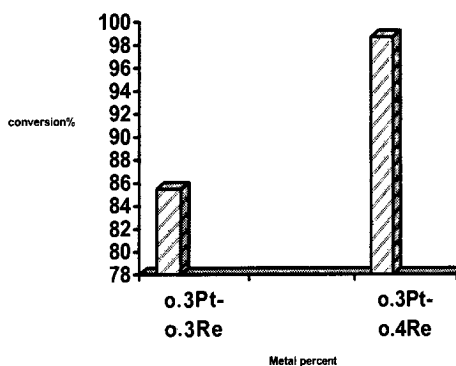

Figure1. Effect of the metal percent on the conversion percent (t=450 °C, P=30atm).

The effect of rhenium on selectivity

High selectivity produces high yields of a desired product while suppressing undesirable competitive and consecutive reactions. This means that the texture of the catalyst (in particular pore volume and pore distribution)should be improved toward reducing limitations by internal diffusion ,which in the case of cones cutive reactions rapidly reducrs selectivity figures 2.3 shows the effect of metal percent on aromatization and isomerisation selectivity .
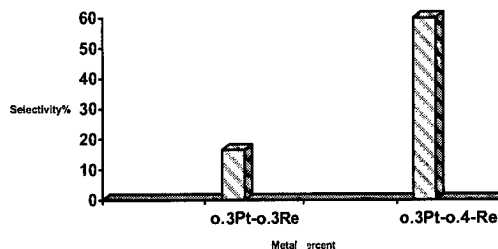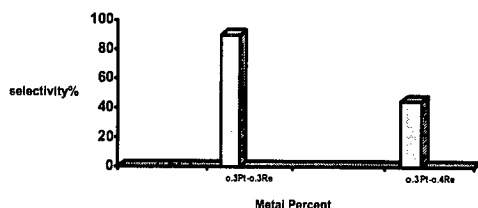

Figure 2. Effect of metal percent on Selectivity aromatization percent (t=450 °C, P- 30atm).

Figure 3 . Effect of metal percent on Selectivity isomerization percent (t=450 °C , P=30atm).

CONCOLUSION

Our results concern to the activity (total conversion) and catalysts selectivity of the catalysts for different reactions. It is show that main effect resulting from addition of Re to reduce the hydrocracking reaction and to increase the selectivity for higher amounts of rhenium . Under experimental condition it has been established that the conversion of n-heptane into branched aliphatic isomers is catalysed by a bifunctional mechanism. The conversion of n-heptane into total aromatics is bifunctional. When Re is present the catalyst has a higher selectivity for aromatisation reactions Therefore, rhenium modifies the properties of Pt catalyst in

two ways, it modifies the acidity of the support and it modifies the Pt electionically with the result that self-poisoning is reduced and the selectivity for nondestructive reaction increases. we believe that role of rhenium in Pt-Re catalyst is to alter the local density of states at surface Pt atom and that this modifies the catalytic properties of these surface atom. The main effect being to reduct the activity in cracking reactions. Under reforming conditions,specially at high temperature ,n-heptane reactions can occur either by metal catalysed process or a bifunctional mechanism involving both the metal and acidic sites on the oxide.These two process 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-Re catalysts.Based on these experiments it is proved that they had higher selectivity for the aromatization in addition to their higher activity,specially when we compared them with the Pt-Sn catalyst[20].

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