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CATALYTIC REFORMING OF n-HEPTANE ON PLATINUM-NIOBIUM SUPPORTED ON GAMMA-ALUMINA

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ABSTRACT

The series of mono-metallic and bi-metallic catalysts have been prepared by impregnating with solutions containing compound of H_2PtCl_5,$NbCl_5$ and 1ml HCl (0.1 mol). The activity and selectivity of the catalysts have been determined under conditions at 450-500^{0}C، 15-30atm. Molar ratio $H_2/C_7H_{16}=5$ and VVH=1.5/h for converting n-heptane. Under these experimental conditions it has been established that the conversion of n-heptane into branched aliphatic isomers is catalyzed by a bifunctional mechanism. The results show that when Nb is present, the catalysts are much more stable and have much higher selectivities for isomerization reaction. At a given conversion the bimetallic catalysts produce much lower concentrations of cracked products. It is shown that Nb modifies the acidity of the support, resulting to higher selectivity for isomerization and lower selectivity for cracking and also modifies the properties of the Pt.

Keywords : n-heptane; Platinum; Niobium; Gamma-Alumina; H_2PtCl_5; $NbCl_5$; HCl

INTRODUCTION

The reforming of naphta is a process in which the naphta octane number increases by increasing the concentration of Paraffin branched isomers and mainly of aromatics (1). The overall process involves several reactions which are 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/Al_2O_3 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 (5-11), Pt-Sn (12-18), Pt-Pb (13), Pt-Ge (19), Pt-Ir (20), Pt-Nd (21-22) and Pt-WO_3 (23). The most interesting feature of the bimetallic catalysts which distinguishes them from the mono-metallic Pt/Al_2O_3 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 a second metal (7,24). The role of the second metal has been the subject of much attention. Jossens and Petersen (9) suggest that Re interacts with Pt to reduce the activity of the metal function. Bertolaccini and Pellet (25) found that Re promotes the hydrogenolysis of coke precursor, thereby reducing coke formation. Baccaud et.al (26) has shown that Sn may preserve activity by poisoning the more acidic sites in the alumina support. However Pt-Sn interactions, 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 (12, 15, 27, 28). Pt-Nb/Al_2O_3 has been the subject of much less study. As part of a study of bimetallic reforming catalysts attention has been focused on the performance of Pt/Al_2O_3 and Pt-Nb/ Al_2O_3.

The present paper reports studies of the performance (i.e. activity and selectivity) of these catalysts for the catalytic reforming of n-heptane.

EXPERIMENTAL

1- Catalyst Preparation

The samples 0.6wt% Pt/Al_2O_3 and Xwt%Pt-YWt%Nb/Al_2O_3 (X=0.4, 0.5, Y=0.2, 0.1) were prepared by impregnating Gamma-Al_2O_3 (AKZO with surface area=$270m^2g^{-1}$,Pore volume=$0.71ml.g^{-1}$and bulk density=$0.58g.ml^{-1}$ respectively with solutions of H_2PtCl_6 and $NbCl_5$ in diluted hydrochloric acid. This process is followed by drying at 120°C for period of 24 hours, heating in air from room up temperature to 450°C. At this temperature the chlorine concentration was fixed at 0.05 wt%. The sample was purged with N_2 at room temperature for 30 minutes.

2- Catalyst Testing

12g of the catalyst was loaded into a 220cc reactor (Geomecaninque, Gatates 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 H_2S in H_2 at 500°C and 1atm for 30 minutes and then H_2 was passed over for 8 hours at the same temperature (500°C). Operating conditions included temperature: 450-500°C , pressure: 15-30 atm, VVH=$1.5h^{-1}$ molar ratio $H_2/C_7H_{16}=5$ 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 feed total conversion and Selectivity for each type of products of n-heptane reforming is defined as:

Aromatization: Conversion to aromatics×100 / total conversion.

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 integrator and carrier gas is Helium .

RESULTS AND DISCUSSION

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

The relative importance of the two processes depends on the acidity of the support, activity of the metal and the experimental conditions. Preliminary experiments with our bimetallic Pt-Nb catalysts showed that in addition to higher activity (conversion) they had higher selectivity for the formation of toluene. The Pt-Nb catalysts showed that in addition to higher activity, they had lower selectivity for the formation of cyclization as compared to the Pt-Sn catalysts (15).

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

1-1-Activity

In the case of the bi-metallic catalysts, the increase in amounts of Nb leads to the increase in the total conversion. Under experimental conditions of this work 0.4Ptwt%-0.2Nbwt% is a slightly active catalyst for all the temperatures and pressures (Figure 1).

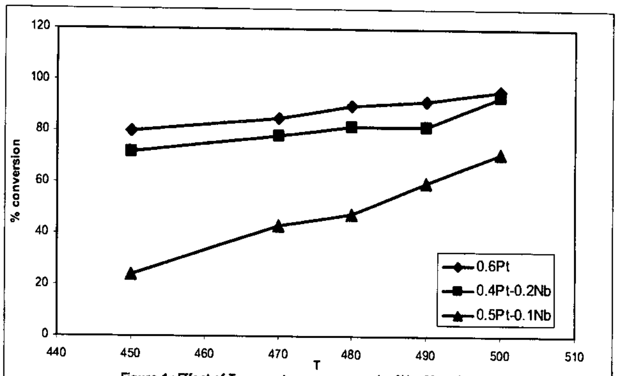

Figure 1 : Effect of Temperature on conversion%(p=20atm)

1-2- Selectivity

Figures 2 shows that in catalysts with large amounts of the Nb the selectivity of aromatics increase. The best results are obtained for the bi-metallics catalysts 0.4wt%Pt-0.2wt%Nb.But larger amounts of Nb results to decrease in selectivity.

2- Effect of temperature on the activity and selectivity

2-1-Activity

Figure 1 shows the total conversion as a function of temperature for Pt/Al_2O_3 , Pt-Nb/Al_2O_3 .It is concluded that the total conversion increase with the increase temperature.

2-2- Selectivity

Figures 2 and 3 show the conversion of n-heptane to each group of products as a function of temperature. The percentage of the aromatization always increases but the amount of isomerization decreases. The main reactions observed on all catalysts are of the isomerization type at low temperature.

The comparison between 0.3 Pt-0.3Nd,0.37Pt-0.24Ge and 0.5Pt-0.1Nd and 0.37Pt- 0.24Ge and 0.4Pt-0.2Nd shows that the n-heptane total conversion is 43% at 450°C and reaches 75% at 500°C with 0.3 Pt- 0.3Nd with 0.37Pt-0.24Ge, it is 24% at 450°C and reaches 100% at 540°C but conversion is 72 at 450°C and reaches 93 at 500°C. For 0.4Pt-0.2Nb, results show that the total conversion of Pt-Nb is 48% more than that of Pt-Ge especially at low temperatures (28). Also the conversion of n-heptane to participate in the aromatization reaction for Pt-Nb and Pt-Nd has a similar trend but the conversion of n-heptane towards aromatization for Pt-Nb in higher as compared to Pt-Ge. Isomerization was found to be important for Pt /Al_2O_3 and Pt-Nb while it decrease with temperature increase. Also this reaction was important on Pt-Sn/Al_2O_3 (12). Beltramini and Trimm (12) have showed that main effect resulting from the addition of Sn to Pt is to reduce coke formation and to increase selectivity for dehydrocyclization. This effect is not due merely to the presence of the second metal since the activity/selectivity patterns of the mono-metallic catalysts are very different from those of the bimetallic catalysts but most results from interactions between the two metals. This effect may also be oberved when adding Nb to Pt.

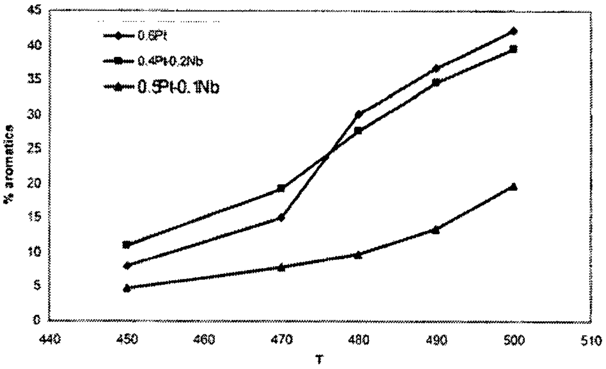

Figure 2 : Effect of Temperature on selectivity aromatization %(p=20atm)

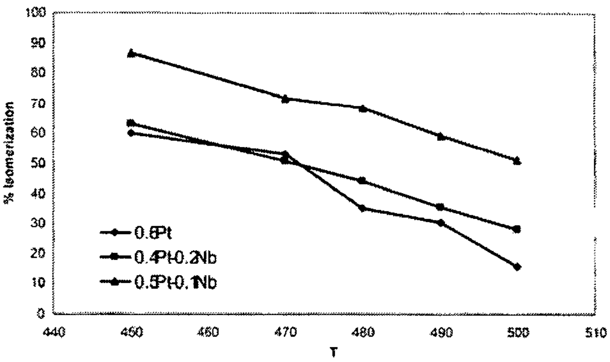

Figure 3 : Effect of Temperature on selectivity isomerization %(p=20atm)

3- Effect of pressure on activity and selectivity

3-1- Activity

The conversion of n-heptane at a pressure of 15-30 atm is clearly influenced by the second metal. This can be seen from the activity – pressure curve (Fig.4) for Pt/Al_2O_3, $Pt–Nb/Al_2O_3$ catalysts. When pressure increases the total conversion is approximately constant.

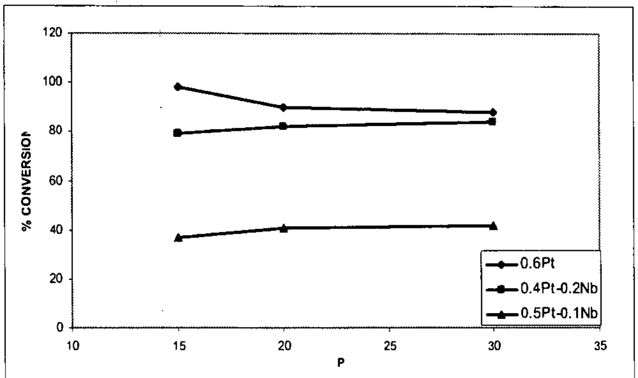

Figure 4 : Effect of pressure on conversion% (T=480)

3-2- Selectivity

Figures 5,6 show the conversion of n-heptane to each group of products as a function of pressure. When the pressure increases the percentage of total aromatics usually decreases. The selectivity for isomerization increases when the pressures increases.

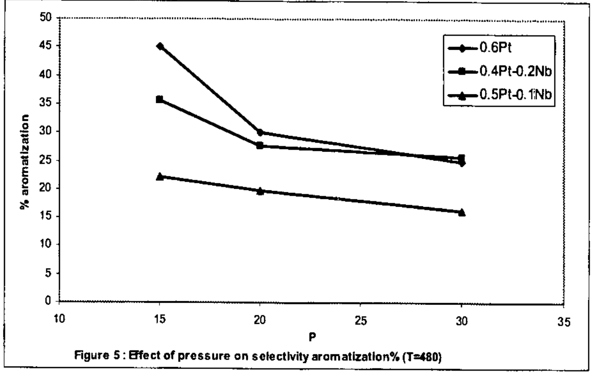

Figure 5 : Effect of pressure on selectivity aromatization% (T=480)

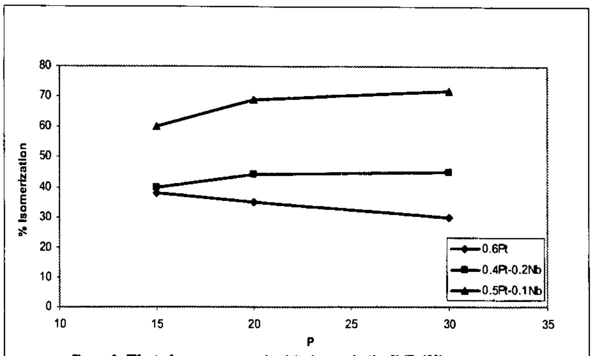

Figure 6 : Effect of pressure on selectivity isomerization% (T=480)

4- Effect of niobium on platinum

The reduction in the amount of self–poisoning by adding niobium to Pt is one of the main advantages of these bimetallic catalysts.

Poisoning occurs when dehydrogenated hydrocarbons on residues are adsorbed very strongly on metal sites. Therefore any changes in the surface properties of the Pt, which decrease the binding energy of Pt and carbon, should increase the stability. It is generally accepted that self-poisoning parallels deep hydrogenolysis in requiring several continuous metal sites for reaction to proceed (29-31). In Ni-Cu alloys (32,33) for example, the rate of hydrogenolysis of ethane decreases by several orders of magnitude when Cu is added and this is explained on the basis of a reduction in the number of Ni ensembles which are large enough to catalyze this reaction. A similar explanation has been proposed to account for the greater stability of bimetallic catalysts (7). In a number of other bimetallic systems such as Ru-Cu (34),Ir-Re and Ir-Cu(35), it has been necessary to invoke on electronic effect to account for the loss of hydrogenolysis activity since the degree of surface dilution by inactive atom is much less than that required for a geometric model. If we assume that a small amount of niobium is present as a solid solution in Pt,the niobium will either donate electrons to the Pt or cause the Pt to redistribute its electrons so as to reduce the density of states at the Fermi Level. A lower density of states localized on the surface of Pt atoms would be expected to result in a weaker bond joining carbon and so self-poisoning (and hydrogenolysis) would be reduced. Since niobium had valence electrons available a small amount of niobium will be sufficient to modify the Pt. It seems clear that the role of niobium is electronic rather than geometric. Indeed it is possible that there is a common explanation for the establising effects of many other second metal additives in terms of electronic modification of the active metal.

CONCLUSION

The focus of this paper is on the activity (total conversion) and the selectivity of the catalysts for different reaction. It is show that main effect resulting from addition of Nb to Pt is to reduce the hydrocracking reaction and to increase the selectivity for total aromatics especially for small amounts of niobium. Under experimental conditions it has been established that the conversion of n-heptane into branched aliphatic isomers is catalyzed by a bifunctional mechanism.

The conversion of n-heptane into total aromatics is bifunctional. When Nb is present the catalyst has a higher selectivity for aromatization reaction. Therefore, niobium 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.

We believe that the role of niobium in Pt-Nb catalysts is to alter the local density of states at surface Pt atoms and that this modifies the catalytic properties of these surface atoms. The main effect being to reduce the activity in cracking reactions.

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