RESEARCH PAPER
Chemistry
Volume : 4 | Issue : 8 | August 2014 | ISSN - 2249-555X

Determination of Activity and Selectivity of Catalytic Reforming of N-Heptane by Pt-Ir Supported on Gamma-Alumina

KEYWORDS
Catalytic; Reforming; n-heptane; Pt; Ir; Gamma-alumina

Mehdi Vadi
Department of Chemistry , Sarvestan Branch, Islamic Azad University , Sarvestan, Fars, Iran

Davood Wadi
Department of Chemistry , Sarvestan Branch, Islamic Azad University , Sarvestan, Fars, Iran

ABSTRACT *Bimetallic catalyst platinum-iridium supported by Gamma-alumina was prepared by impregnation with solution containing compounds of H2PtCl6 and IrBr3. The Platinum concentration was kept constant at 0.3wt% while the concentration of the iridium was 0.3wt%. The activity and selectivity of catalyst were determined under conditions at 450-500 °C and 15-30 atm. Molar ratio H2/C7H6=5 and VVH=1.5mL/h for converted n-heptane. The results showed that when Ir is present, the catalyst is stable and have much higher selectivity for isomerization reaction. It was shown that Ir modifies the acidity of support, resulting to higher selectivity for isomerization, and modifies the properties of the Pt.*

Introduction

The reforming of naphta is a process in which the naphta octane number increases by increasing the concentration of branched paraffin isomers and mainly of aromatics (Parera. et al., 1980). The overall process involves several reactions which are promoted by a bi-functional catalyst (Ciapetta.et al., 1958) The Pt/Al2O3 as a bifunctional reforming catalyst has been used since1955 in oil industries (Hettinger.et al .,1955). Later Pt was promoted with other metals called bi or multimetalic catalysts which are Pt-Re (Bertolaccini. et al.1980; Biloen. et al .1980; Bacaud. et al .1980; Jassens .et al.1982; Sachtler.1976; Mazzieri. et al. 2009). Pt-Sn(Beltramini. et al..1987; Volter.et al. 1981; Dautzenburg. et al. 1980; Sexton. et al.1984) , Pt-Ga (Yuhan. et al,1991), Pt-Ti(Vadi. et al 2011),Pt-W (Vadi . et al .2010), Pt-Cu(Vadi and Mozafaripour.2010), Pt-Ta(Vadiand Hosseinzadeh Postchi.2010). The purpose of this research, since the element platinum is an expensive alternative for many years, researchers followed the conversion of low octane gasoline with high octane number gasoline. With different metals to replace platinum or platinum studied the metal will be used should be cheap and have good selectivity for the aromatization and isomerization reactions .Pt-Ir/γ-Al2O3 has not been the subject of sufficient researches. In this study we decided to study whether this property has element iridium. The present research reports the study of the performance i.e. the activity and selectivity of this catalyst for the catalytic reforming of n-heptane.

EXPERIMENTAL METHOD

Materials and Instrument

1) Hexachloroplatinic acid, $H_2PtCl_6{\cdot}(H_2O)_6$: Merck 98%
2) Iridium(III) Bromide Hydrate, $IrBr_3 \cdot xH_2O$: Merck 99%
3) Hydrochloric acid, HCl : 0.1 M
4) Gamma-Alumina, γ-Al_2O_3: Merck 99.99%, surface area 270 m2/g.
5) Reactor : Geomecanique, Catatest Unit, and model BL-2, France

Catalyst preparation

The catalyst studied was 0.3 wt%. Platinum and 0.3 wt%. Iridium on γ-alumina. The Chlorine content of catalyst was adjusted to 1 wt% by addition of HCl (0.1M). This was prepared by depositing the active materials in appropriate content rations on to gamma-alumina (surface area 270 m2/g and pore volume of 0.65 cm3/g) by impregnation method. Impregnation solution contained chloroplatinic acid and iridium (III) bromide. In order to insure uniform dispersion of metallic components on support (γ-alumina), the impregnation mixture was maintained in contact with the support for a period of about 7 hours at a temperature of about 60 °C. Then the catalyst sample was dried for 24 hours at 120 °C followed by calcinations in air at 400 °C for 7 hours. The calcined catalyst was purged with N2 and finally reduced with flowing H2 at 500 °C for 7 hours.

Catalyst testing

12 grams of the catalyst was loaded into a 220 CC reactor (Geomecanique, Catatest Unit, and model BL-2). The amount was reduced by heating it in a hydrogen stream at a constant flow rate from 25°C up to 500 °C for 7 hours. The catalyst was sulfide in a gas flow consisting of 600 ppm H2S in H2 at 500 °C and 1 atm. for 15 minutes. This was followed by cooling it for 7 hours by H2 at room temperature. The next step was to heat the catalyst at constant rate from room temperature to 500 °C by flowing hydrogen. The temperature was kept constant for 2 hours before feeding the n-heptane. Total hydrocarbon conversion after 2 hours was taken as a measure of catalyst activity, total conversion, liquid yield and selectivity. These items were calculated from gas chromatography (Varian 3 600 star) using a 60 mm capillary, 250 μ diameter L.phase DB-1, detector, FID, and integrator variant 4 400 carrier gas He.

Results and discussion

Effect of reaction temperature at different pressure on activity and selectivity

Activity

Here the catalyst activity is calculated as follows:

Catalyst activity=100- unconsumed normal heptane (1)

Measurements of catalytic activity and determination of selectivity parameters have been performed at various temperatures (400-500 °C). The conversion of n-heptane as a function of temperature at different pressures is shown in figure 1.

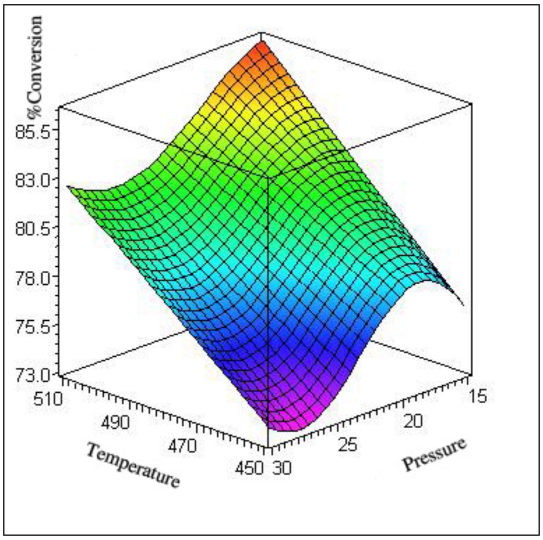

Fig 1: Effect of temperature on conversion % at different pressure.

Selectivity

Selectivity can be defined as the proportion of the desired product shown as Wi to the total rate of the transformation of the primary substance shown as W:

$$S = \frac{W_i}{W} \qquad (2)$$

So that:

$$W = \sum {}_i r_J - \sum {}_i r'_J \quad \& \quad W = \sum {}_i r_J \qquad (3)$$

Here r_J stands for the reaction rates existing in the formation of the primary desired product and r'_J stands for the transformation of the primary substance. In this piece of research selectivity is calculated by the following equation:

$$\text{Selectivit y percent} = \frac{\text{Requisite product}}{\text{Changing percent}} \times 100 \qquad (4)$$

For example the selectivity percent for isomerization have been shown in figure 2.

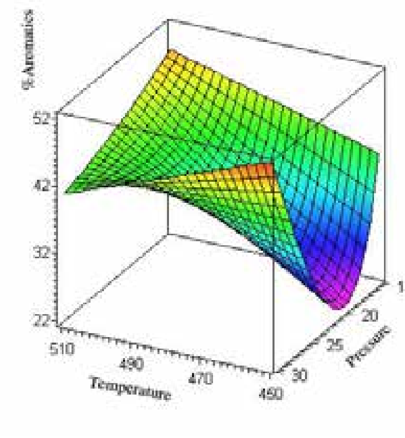

Fig 2. Effect of temperature on selectivity percent of isomerization, at different pressure

CONCLUSION

This catalyst is highly active at higher temperatures and relatively constant at different pressures. The catalyst is highly selective for n-heptane isomerization at 500 °C and 15 atm. Maximum isomerization is 40 at 450°C and 15 atm. Selectivity for isomerization of n-heptane are controlled by the acidic function of catalyst, therefore the acid function of this catalyst depends on the second metal Ir added to Pt. Cyclization and aromatization produced by a bi-functional mechanism are controlled by the acidic function.

REFERENCE

Bacaud.R, Arbier.J, Balanchard.G, Charcosset.H (1980). Selectivity and rate of activity decline of bimetallic catalysts.J. Chem. Phys. 77:387. | Beltramini.J, Trimm.DL (1987) .Activity and selectivity of Pt-Sn/Nb2O5 in n-heptane conversion"Appl. Catal.31:113. | Bertolaccini. RJ, Pellet.RJ (1980) .Selectivity and rate of activity decline of bimetallic catalysts. Catalyst Deactivation. 73. | Biloen.P, Helle.JH, Verbeek.H, Dautzenburg.FM, Sachtler.WMH (1980). The role of rhenium and sulfur in platinum-based hydrocarbon-conversion catalysts"J. Catal.63:112. | Ciapetta.FG, Dobres.RM, Baker.RW (1958) .Dual-functional activities in nickel acid catalysts" Catalysis.6:495. | Dautzenburg.FM, Helle.JH, Biloen.P, Sachtler.WMH(1980) .Conversion of n-hexane over monofunctional supported and unsupported Pt-Sn catalysts". J. Catal. 63:119. | Hettinger.WP, Keith.CD, Gring.GL, Tetr.GW (1955).Catalytic transformations of cyclohexane hydrocarbons on aluminosilicate catalyst. Ind. Eng. Chem. 47:716. | Jassens .LW, Petersen.EE (1982). The effect of catalyst preparation on catalytic activity: IV. The design of Ni/Al2O3catalysts prepared by incipient wetness".J. Catal.76: 25. | Mazzieri.VA, Grau.JM, Yori.JC ,Vera,CR, Pieck.CL (2009) . Effect of Ge content on the metal and acid properties of Pt-Re-Ge/Al2O3-Cl catalysts for naphtha reforming" Appl. Catal. A 354: 161. | Parera.JM, et.al (1980).The role of Re and S in the Pt-Re-S/Al2O3 catalyst. Prod. Res. Dev. 19:545. | Sachtler.WMH (1976). Characterization of a Pt-Pd combustion catalyst on an alumina washcoat, with and without prior hydrothermal treatment of the washcoat .Catal. Rev 14:193. | Sexton.BA, Hughes .AE, Foger.K (1984). Influence of alloying platinum for the hydrogenation of p-chloronitrobenzene over Pt-M/Al2O3 catalysts with M-Sn, Pb, Ge, Al, Zn. J. Catal. 88: 466. | Vadi.M, Hoseinzadeh.A (2011), "Catalytic Reforming of n-Heptane on Pt-Ti Supported on gamma-Alumina", 2011 International Conference on Food Engineering and Biotechnology. 9: 69-72 | Vadi.M, Safavi.SA (2009).Catalytic reforming of n-heptane on platinum-tungsten supported on gamma-alumina. 49(6) : 521–524 | Vadi.M, Mozafaripoor.MA (2010), "Catalytic Reforming of n-Heptane by Pt-Cu Supported on g-Alumina. Asian Journal of Chemistry . 22(9) : 6915 – 6921 | Vadi.M, HosseinzadehPostchi.A (2010).Catalytic Reforming of n-Heptane on Platinum-Palladium Supported on γ-Alumina. Asian Journal of Chemistry . 22(9) : 6640 - 6646 | Volter.J, Lietz.G, Uhlemann.M, Hermann.M (1981) .Reactions of alkanes and reforming of naphtha" J. Catal.68:142. | Yuhan.S, Songying.C (1991).Effect of Ga on Catalytic Behavior of Pt Catalyst. React. Kinet.Catal.45 :101.