

Catalytic Reforming of n-Heptane on Pt-Ti Supported on gamma-Alumina

Mehdi Vadi^{*1}, Ali Hoseinzadeh²

1-Department of Chemistry Engineering Islamic Azad University Fasa Branch , Fasa,Iran

2- Department of Chemistry Engineering Islamic Azad University Firozabad Branch, Firozabad,
Iran

*Corresponding author: E-mail: mahdi_vadi@iaufasa.ac.ir

Abstract. The catalyst Pt-Ti supported by Gamma-alumina was prepared by impregnation with solution containing compounds of H_2PtCl_6 and $TiCl_4$. The Pt concentration was kept constant at 0.4wt% while the concentration of the titanium was 0.2wt%. The activity and selectivity of catalyst were determined under conditions at 450-500 °C and 15-30 atm. Molar ratio $H_2/C_7H_{16}=5$ and $VVH=1.5mL/h$ for converted n-heptane. The results showed that when Ti is present, the catalyst is stable and have much higher selectivity for isomerization and aromatization reactions. It was shown that Ti modifies the acidity of support, resulting to higher selectivity for aromatization, and modifies the properties of the Pt.

Keywords: Activity; Selectivity; Reforming; n-heptane; Pt; Ti; Gamma- alumina

1. INTRODUCTION

The reforming of naphtha is a process in which the naphtha octane number increases by increasing the concentration of branched paraffin isomers and mainly of aromatics [1]. The overall process involves several reactions which are promoted by a bifunctional catalyst [2]. Catalytic reforming reactions proceed by bi-functional 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 1955 in oil industries [4]. Later Pt was promoted with other metals called bi or multimetallic catalysts which are Pt-Re [5-11], Pt-Sn [12-18], Pt-Pb [13], Pt-Ge [19], Pt-Ir [20], Pt-Nd [21-22], Pt-WO₃ [23] and Pt-Nb [24]. The most interesting feature of bimetallic catalysts, which distinguishes them from the monometallic $Pt/\gamma-Al_2O_3$ systems, is the improvement in reforming stability. One of the theories put forward is to explain the improvement in stability of the alloy model which attributes the alloy to a modification of catalyst properties of Platinum when Platinum is mixed with a second metal [7]. The role of the second metal has been the focus of much attention. Jassens and Petersen [9] suggest that Re interacts with Pt to reduce the activity of 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 favor coking have also been suggested to reduce deactivation [12, 15, 27, and 28]. $Pt-Ti/\gamma-Al_2O_3$ has not been the subject of sufficient researches. 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.

2. EXPERIMENTAL METHOD

2.1. Catalyst preparation

The catalyst studied was 0.4 wt% Pt and 0.2wt% Ti 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 titanium chloride(IV) . 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.

2.2. 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.

3. RESULTS AND DISCUSSION

3.1. Effect of reaction temperature on activity and selectivity

3.1.1. Activity

Activity generally means how well a catalyst does its job with respect to reaction rate, temperature and space velocity. When this fact is taken into account, a specific reaction activity may be related to reaction rate. The higher the reaction rate, the higher the activity of the catalyst. For example, Gates identifies the activity of a copper-nickel alloy catalyst for the dehydrogenation of cyclohexane by plotting reaction rate vs. the percent of copper atoms in the catalyst. Refinery engineers almost always refer to the activity in a relative sense i.e. one catalyst may be more or less active than another catalyst. In addition, a catalyst may be less active after six months and less operative than when it was fresh. For motor fuels, reforming activity is generally represented by the temperature required to produce a given octane number reformat. The lower the temperature, the more active the catalyst. One of the activity factors related to the catalyst is its percent of the change in n-heptane; the activity may be related to the reaction rate. For engines, full activity is usually defined based on temperature degree that is needed. If lower temperature degree is a requisite, the catalyst is more active. Therefore, we can say that the circumstance of reaction progress until it reaches the balance which expresses the catalyst activity. Here the catalyst activity is calculated as follows:

$$\text{Catalyst activity} = 100 - \text{unconsumed normal heptane} \quad (1)$$

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.

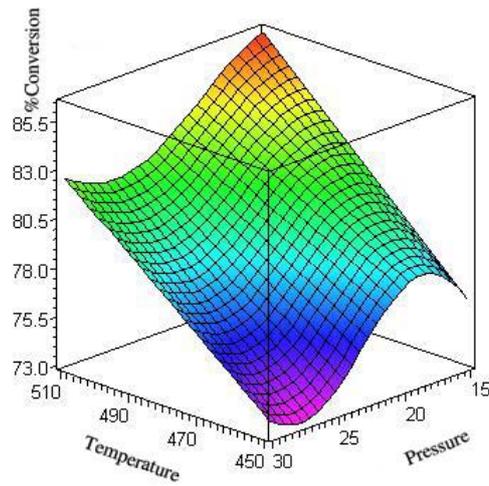


Fig 1: Effect of temperature on conversion % at different pressure.

3.1.2. Selectivity

In catalytic reforming, selectivity of catalyst means the percent of the desired product yielded from the feedstock. In motor fuel reforming, a high yield of reformat at the desired octane number is a good selectivity. In BTX reforming a high yield of total aromatics or of a desired specific aromatic is also a good selectivity. Selectivity of a catalyst means producing desirable products that are often middle compounds. They are, in turn, used to yield some products that have less energy. Because in the process of catalytic reforming different reactions occurs. Some of them are desirable and some are undesirable. Selectivity of catalyst means conducting a reaction toward the considered reaction. Selectivity can be defined as the proportion of the desired product shown as W_i to the total rate of the transformation of the primary substance shown as W :

$$S = \frac{W_i}{W} \quad (2) \quad \text{So that: } W = \sum_i r_j - \sum_i r'_j \quad \& \quad W = \sum_i r_j \quad (3)$$

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:

$$\text{Selectivity percent} = \frac{\text{Requisite product}}{\text{Changing percent}} \times 100 \quad (4)$$

The selectivity percent of aromatization and isomerization have been shown in figures 2 and 3

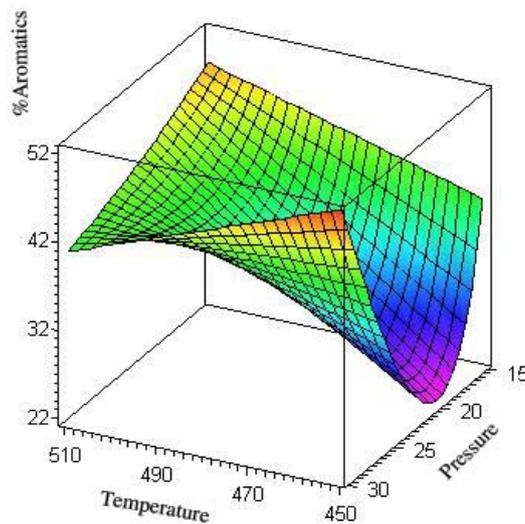


Fig 2. Effect of temperature on selectivity percent of aromatization, at different pressure

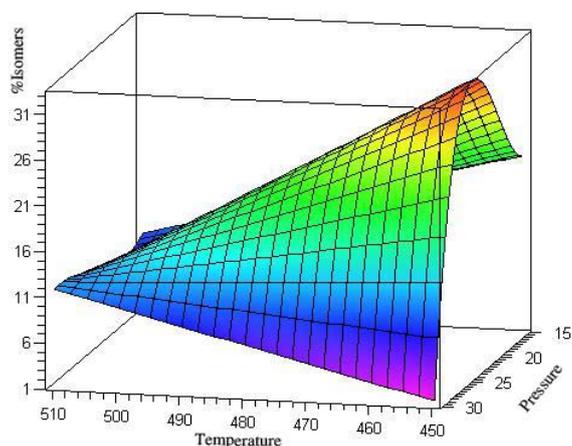


Fig 3. Effect of temperature on selectivity percent of isomerization, at different pressure

4. REFERENCES

- [1] J.M. Parera, et.al., *Prod. Res. Dev.* 19 (1980) 545.
- [2] F.G. Ciapetta, R.M. Dobres, R.W. Baker, *Catalysis.* 6 (1958) 495.
- [3] B.C. Gates, J.B. Katzer, G.C.A. Schmit, *Chemistry Of Catalytic Processes.* Mc Graw Hill, Tokyo (1979).
- [4] W.P. Hettinger, C.D. Keith, G.L. Gring, G.W. Tetr, *Ind. Eng. Chem.* 47 (1955) 716.
- [5] H.E. Klusksdahl, U.S. Patents 3,415,437, 1968.
- [6] R.J. Bertolaccini, R.J. Pellet, *Catalyst Deactivation.* (1980) 73.
- [7] P. Biloen, J.H. Helle, H.Verbeek, F.M. Dautzenburg, W.M.H. Sachtler, *J. Catal.* 63 (1980) 112.
- [8] R. Bacaud, J. Barbier, G. Balanchard, H.Charcosset, *J. Chem. Phys.* 77 (1980) 387.
- [9] L.W. Jassens and E.E. Petersen, *J. Catal.* 76 (1982) 256.
- [10] W.M.H. Sachtler, *Catal. Rev.* 14 (1976) 193.
- [11] VA. Mazzieri, J.M. Grau, J.C. Yori, C.R. Vera, C.L. Pieck, *Appl. Catal. A* 354 (2009) 161.
- [12] J. Beltramini, D.L. Trimm, *Appl. Catal.* 31 (1987) 113.
- [13] J. Volter, G. Lietz, M. Uhlemann, M. Hermann, *J. Catal.* 68 (1981) 142.
- [14] F.M. Dautzenburg, J.H. Helle, P.Biloen, W.M.H. Sachtler, *J. Catal.* 63 (1980) 119.
- [15] R. Burch, L.C. Garia, *J. Catal.* 71 (1981) 360.
- [16] B. Coq, F. Figueras, *J. Molec. Catal.* 25 (1984) 87.
- [17] H. Lieske, J. Volter, *J. Catal.* 90 (1984) 96.
- [18] B.A. sexton, A.E. Hughes, k. Foger, *J. Catal.* 88 (1984) 466.
- [19] S. Yuhan, C. Songying, Pengshaoyi, *React. Kinet. Catal.* 45 (1991) 101.
- [20] R.L Carter, J. H. Sinfelt, *J. Catal.* 62 (1984) 127.
- [21] G.J. Anots, U.S. Patents 3,915,845 (1975), 4,003,826 (1977), 4,148,715 (1979), 4,107,172(1980).
- [22] J.M. Farbotko, F. Garin, P. Girord, G. Maire, *J. Catal.* 139 (1993) 256.
- [23] W.M.H. Sachtler, *Catal. Rev.* 14 (1976) 193.
- [24] M. Vadi, G. Farmani, H. Seyyedjafari, H. Alipour, *Inter. J. Chem.* 16 (2006) 109.
- [25] R.J. Bertolaccini, R.J. Pellet, *Stud. Surf. Sci. Catal.* 6 (1980) 73.
- [26] R. Bacaud, P. Bussiere, F. Figueras, *J. Catal.* 69 (1981) 399.
- [27] J. Beltramini, D.L. Trimm, *Appl. Catal.* 32 (1987) 79.
- [28] J.M. Parera, C.A. Querini, J. Beltramini, N.S. Figoli, *Appl. Catal.* 32 (1987) 126.