Asian Journal of Chemistry Vol. 22, No. 9 (2010), 6915-6921

Catalytic Reforming of *n*-Heptane by Pt-Cu Supported on γ-Alumina

MEHDI VADI* and M. AMIN MOZAFARIPOOR†
Department of Chemistry, Islamic Azad University, Fasa Branch, Fasa, Fars, Iran
E-mail: mahdi_vadi@iaufasa.ac.ir

A two-metal catalyst was prepared by means of impregnation from the solutions which have $Cu(NO_3)_2 \cdot 3H_2O$ and $H_2PtCl_6 \cdot xH_2O$ and 1 mL of HCl (0.1 M). The activity and selectivity of this catalyst to examine on the *n*-heptane with the following experimental conditions; temperature: 450-510 ºC, pressure: 15-30 atmosphere and the ratio of the reagents under laboratory circumstances. The *n*-heptane is converted to the branched aliphatic isomers and aromatics. This catalyst has high selectivity and ability to do the aromatic reactions and in converting the *n*-heptane by using this catalyst, a little amount of cracking interaction products have been produced. According to the tests copper can improve the acidic feature of which itself increases the selectivity to aromatics and decreases the cracking.

Key Words: Platinum, Copper, Reforming catalytic, *n*-Heptane, γ-Al_2O_3.

INTRODUCTION

Catalytic reforming is a process which increases the octane number of naphtha by increasing the density of paraffin and the branched isomers and especially different kinds of aromatics[1] and this process has several reactions which are done by the two-factor catalysts[2].

The reforming reactions are done on two-factor catalysts so as the platinum does the hydrogenation and dehydrogenation reactions and the acidic and basic active places which have been produced on the basic surface (the surface of active alumina) are used for the isomerization, cracking and cyclization reactions[3]. Before 1950, in oil industries, to increase the octane number of petrol the mono metal catalyst of Pt/Al_2O_3 was used instead of the two-factor reforming catalyst[4]. Then platinum was improved by other metals which was used 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] as the catalyst of two or multi metals. The most important characteristic of two-metal catalysts to mono-metal catalyst of platinum is their stability.

Two-metal model: One reason which has been the basis of this theory is increasing the stability and improving the catalytic characteristics of platinum which is attributed to the second metal[7-24] and this increases the role of the second metal.

---

†Department of Chemistry, Islamic Azad University Firouzabad Branch, Firouzabad, Fars, Iran.

Baccaud *et al.*[8] showed that the basic acidic characteristics by using tin as the second metal must be kept fixed because of fixing the acidic sites. Betrolaccini and Pellet[6] improved the rhenium of in coke hydrogenolysis and in this way they had decreased the formation of coke. Jossen and Peterson[9] observed that rhenium increase to platinum causes the decrease of the activity of metal factor although according to them that Pt-Sn is effective on the lack of the production of the coke on the metal surface but in general had a little effect on the production of coke and the decrease of the inactivation of the catalyst[12-15, 18-27]. The recommended catalyst Pt-Cu on γ-alumina in this research paper is studied for the catalytic reforming of *n*-heptane in the case of action and selectivity.

EXPERIMENTAL

Catalyst specification: This catalyst has 0.7 weight per cent of metal that consists of 27 % Pt-43 % Cu/γ-Al_2O_3 and for specifying the correctness of metals weight per cent in catalyst by XRF apparatus in accompaniment with related standards analyzed (Table-1).

TABLE-1
EXPLORED COMPONENTS IN CATALYST BY XRF ANALYSIS

Element	Concentration (%)
Al_2O_3	96.90
SiO_2	1.11
Na_2O	0.62
Cu	0.43
Pt	0.27
Cl	0.50
CaO	0.14

The gases used in the project are hydrogen (99.95 % purity) and nitrogen (99.95 % purity), *n*-heptane (99 % purity). $H_2PtCl_6·xH_2O$ salt with 99.99 % purity and $Cu(NO_3)_2·3H_2O$ (96.8 % purity) were selected on γ-alumina base by surface area equal 270 m^2/g, porosity volume is 0.71 mL/g and the density equals 0.58 g/mL for decreasing penetrating constraint rate of pores on catalyst granuligation between 0.9-1.6 mm extrude.

Catalyst synthesis method: The catalyst synthesis has been made by impregnation method. That is placed on γ-alumina base in $H_2PtCl_6·xH_2O$, $Cu(NO_3)_2·3H_2O$ solution and 1 mL of HCl (0.1 M) then this process was continued by catalyst desiccating in 120 ºC for a 24 h period.

Then calcination is done on catalyst by following way: at first by passing specific flow of air and catalyst bed reactor temperature reaches 450 ºC and the temperature gradient is 2 ºC, that during this action metals that are placed on this base will transform to oxide formation and choler concentration become constant in 0.05 w % and continues this process for 8 h. Then catalyst bed was cleaned by N_2 gas in room temperature within a period of 0.5 h.

In next step and after gaining reactor temperature by passing specific flow of H_2 gas on catalyst bed we increase reactor temperature by temperature gradient of 2 ºC/min till 500 ºC that continue this process for 8 h and during this step catalyst metal compounds is reduced and is absorbed on catalyst bed and have catalytic property.

Catalyst test: Put 57 mL (32 g) of catalyst in reactor (Geomecaninqe, Catates Unit, Model BL 2) with volume of 220 cc in this reactor by hydrogen evaporation constant flow and increase the temperature up to 500 ºC then catalyst in gaseous flow has 600 ppm of H_2S in H_2 gas in temperature of 500 ºC and one atmosphere pressure within 0.5 h will turns into sulphide.

After that for more than 8 h in 500 ºC of H_2 gas passed over catalyst bed. In this way all the sulphur that were absorbed on catalyst were separated from catalyst bed. Experimental condition is according to these factor: 450-510 ºC 15-30 atmosphere H_2/C_7H_{16} = 7 LHSV = 2 mL/h were similar to industrial unit and each sampling was done in 3 h sampling order and experimental condition and efficiency of each sampling in time and during reactor test is according to Table-2. The order of sampling and experimental condition and the rate of qualified efficiency of each sample is show in Table-2.

TABLE-2

Case	Temp. (ºC)	Pressure atm (Bar)	Feed rate (L/H)	Gas rate (L/H)	Product (cc)	Gas product (L/H)	Yield (%)
2	450	30	114	112	110	84	38
4	480	30	114	112	45	86	20
6	510	30	114	112	50	91	22
8	510	25	114	112	23	102	10
10	480	25	114	112	67	115	28
12	480	20	114	112	107	129	47
14	510	20	114	112	50	140	29
16	510	15	114	112	40	143	23
18	480	15	114	112	80	145	47

RESULTS AND DISCUSSION

Under transformation condition of *n*-heptane under normal reaction especially at high temperature is done by metal catalytic process two factor mechanisms that include two metal and acidic sites are available on the base. Process that are important in transformation of *n*-heptane are dependent on these factor *i.e.*, acidic state metal and base and the condition that sampling was done. Total hydrocarbon conversion was determined by catalytic activity that the role of catalytic activity is gained on the basis of grams of food which are transformed in to the product on 100 g of total food and selectivity for each type of products of converted *n*-heptane is determined in this way.

For example selectivity (S) toward aromatics is as follows:

$$\text{Aromatic (S\%)} = \frac{\text{Sum of aromatic per cent}}{\text{Conversion}} \times 100$$

According to experimental condition that were mentioned maximum. Conversion and selectivity per cent compared with each of the explored group components have following volume (Table-3): maximum conversion per cent is equal 86.38 % in 15 atmosphere pressure and 510 ºC. Maximum selectivity per cent toward the aromatic is 59.54 % in 30 atmosphere pressure at 450 ºC. Maximum selectivity per cent toward the isomers is 11.79 % in 30 atmosphere pressure at 510 ºC. For parafines and naphthas this per cent is 33.25 % in 25 atmosphere pressure at 480 ºC and 30.36 % in 25 atmosphere pressure at 480 ºC, respectively.

TABLE-3
CONVERSION AND GROUP SELECTIVITY PER CENT OF RECOGNIZED COMPOUNDS DETERMINATION BY GC

Case	Conversion	Aromatics	Naphthenes	Paraffins	Isomers
R_2	82.43	59.54	21.35	27.25	4.57
R_4	78.17	49.60	6.57	31.92	6.55
R_6	82.61	41.64	6.65	28.55	11.79
R_8	81.68	41.22	21.31	29.68	10.90
R_{10}	77.85	37.25	30.36	33.25	9.63
R_{12}	80.49	33.79	6.82	29.25	6.81
R_{14}	83.91	46.75	18.88	26.17	8.97
R_{16}	86.38	48.77	14.93	23.75	9.77
R_{18}	81.35	46.71	24.27	28.54	7.81

Temperature and pressure effect on conversion per cent of *n*-heptane on Pt-Cu catalyst: As is shown in Fig. 1 by temperature increase and decrease in pressure the conversion per cent shows an increase in the rate of changes of conversion per cent in lower temperature and higher pressure is less. But by increasing temperature and decreasing pressure rate of change in transformation per cent increases and because of this the maximum rate of conversion per cent is 86.38 per cent in 15 atmosphere pressure and 510 ºC.

Effect of pressure on rate of group selectivity per cent of recognized compounds on Pt-Cu catalyst: By decreasing the pressure the selectivity per cent with aromatic and parafines decrease and also increase toward naphthenes and isomers and the change of selectivity per cent rate compared with pressure decrease in constant temperature around 20 pressures has intense reducing changes and recognized compounds had proper increase by decreasing the pressure at constant temperatures.

Effect of temperature on rate of group selectivity per cent of recognized compounds on Pt-Cu catalyst: By increasing the temperature selectivity per cent toward aromatics and parafines decrease and increase toward naphthenes and isomer. This change rate in selectivity per cent compared with temperature increase in

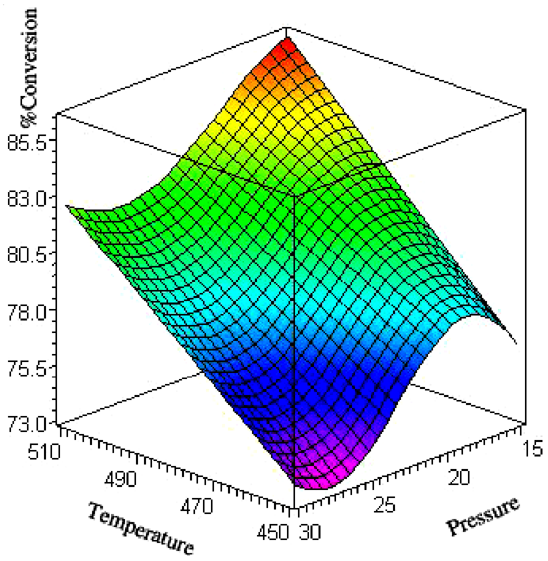

Fig. 1. Effect of temperature and pressure on the rate of conversion per cent of *n*-heptane

constant pressure for each of recognized compound group has less fluctuations compared with the changes of selectivity per cent toward pressure decrease (Figs. 2-5). The effect of temperature and pressure on selectivity per cent rate compared with aromatic, naphthenes, isomer and paraffin is also shown.

Effect of coke on reforming reaction: In this reforming reaction on catalysts and producing naphthenes is one of the most important primary materials of coke production. The rate of coke reforming reaction increase with time on catalyst surface gradually and maximum reaction velocity decrease slowly and this process continues till the maximum exit of reactors[22].

On this base we can classify reforming reactions into 2 type: one type that coke rates is effective on them and the other has less relationship with the quantity of produced cokes and the reason of this grouping is because of the following reason cokes obliterate catalyst surface in an unobvious way and this means that does not affect equally on the reforming reaction[23].

On this basis dehyrocyclization reaction and aromatization are the most important reforming reactions that need a surface on metal to be absorbed on it and from other side it seems that hydrogenazation, dehydrogenazation and isomerization and cyclo development do not need absorbent surface and remain constant toward the mentioning change of temperature and pressure in selectivity rate compared with recognized groups in Figs. 3-5 this catalyst after 30 h of sampling under experimental condition and after doing pyrolyze test and determination amount of CO_2 gas by GC NDIR detector has 9.25 weight per cent of coke.

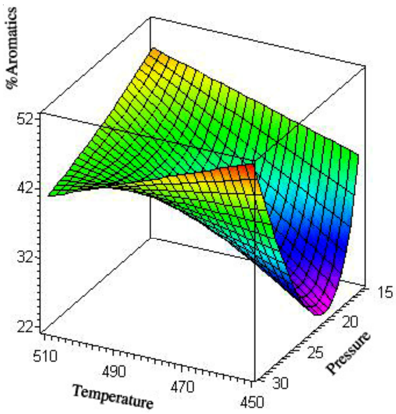

Fig. 2. Show the effect of temperature and pressure on selectivity per cent toward aromatic

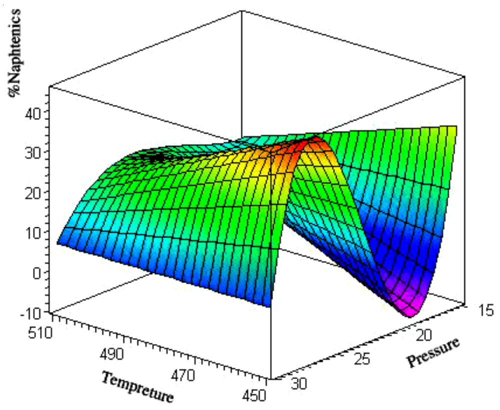

Fig. 3. Show the effect of temperature and pressure on selectivity per cent toward naphthenes

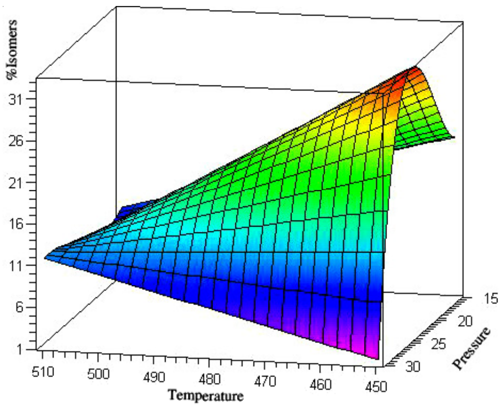

Fig. 4. Show the effect of temperature and pressure on selectivity per cent toward isomers

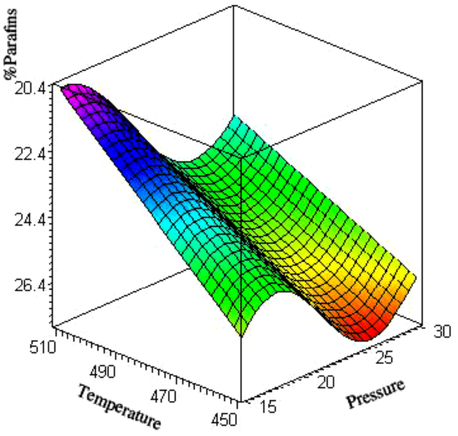

Fig. 5. Show the effect of temperature and pressure on selectivity per cent toward paraffins

Conclusion

This research concentrates on conversion per cent of catalyst activity and selectivity per cent rate toward different reactions in conversion of *n*-heptane to branched aliphatic isomer and at last the aromatic production by two factor mechanisms under experimental catalyst condition. The most important effect of adding copper to the platinum is hydrocracking reaction decrease and increase in selectivity per cent toward the aromatic. The conversation of *n*-heptane by two factor mechanisms when copper is available has high tendency toward implementing aromatic reaction is done. Therefore copper optimized catalytic properties of platinum in two way: One way is acidic state increase that leads to poising reduction of catalyst and increase the tendency for exerting useful reaction.

REFERENCES

1. N.S. Fígoll, M.R. Sad, J.N. Beltraminl, E.L. Jablonski and J.M. Parera, *Ind. Eng. Chem. Prod. Res. Dev.*, **19**, 545 (1980).
2. F.G. Ciapetta, R.M. Dobrs and R.W. Baker, In Catalysis, Vol. 6, (Ed.: P.H. Emmett) Reinhold, New York, 495 (1985).
3. B.C. Gates, J.B. Katzer and G.C.A. Schmuit, Chemistry of Catalytic Processes, M.C. Graw Hill, Tokyo (1979).
4. W.P. Hettinger, C.D. Keith, J.L. Gring and J.W. Teter, *Ind. Eng. Chem.*, **47**, 716 (1955).
5. H.E. Klusksdahl, US Patent, 3415437 (1968).
6. R.J. Bertolacin and R.J. Pellet, in eds.: B. Delmonand and G.F. Froment, Catalyst Deactivation, Elsevier Publ. Co. Amesterdam (1980).
7. P. Boilen, J.N. Hell, H. Verbeek, F.M. Dautzenberg and W.M.H. Schtler, *J. Catal.*, **63**, 112 (1980).
8. R. Bacaud, J. Barbier, G. Blanchard and H. Charcosset, *J. Chem. Phys.*, **77**, 387 (1980).
9. L.W. Jossens and E.E. Peterson, *J. Catal.*, **76**, 256 (1982).
10. W.M.H. Sachtler, *Catal. Rev.*, **14**, 193 (1979).
11. E. Mon and W.C. Baird, Reforming using a Pt/Re catalyst, U.S. Patent 5562817 (1996).
12. J. Beltramini and D.L. Trimm, *Appl. Catal.*, **31**, 113 (1987).
13. J. Volter, G. Lietz, M. Uhlemann and M. Hermann, *J. Catal.*, **68**, 142 (1981).
14. F.M. Dautzemberg, J.H. Helle, P. Biloen and W.M.H. Sachtler, *J. Catal.*, **63**, 119 (1980).
15. R. Burch and L.C. Garia, *J. Catal.*, **71**, 360 (1981).
16. B. Coq and F. Figueras, *J. Mole. Catal.*, **25**, 87 (1984).
17. H. Lieske and J. Volter, *J. Catal.*, **90**, 96 (1984).
18. B.A. Sexton, A.E. Hughes and K. Foger, *J. Catal.*, **88**, 466 (1984).
19. S. Yuhan, C. Songying and P. Shaoyi, *React. Kinet. Catal. Lett.*, **45**, 101 (1991).
20. R.L. Carter and J.H. Sinflet, *J. Catal.*, **62**, 127 (1984).
21. J. Anots, US Patents 3,915,845 (1975); 4,003,826 (1971); 4,148,715 (1979); 4,107,172 (1980).
22. K. Liu, S.C. Fung, T.C. Ho and D.R. Rumschitzki, *J. Catal.*, **188**, 201 (2001).
23. K. Liu, S.C. Fung, T.C. Ho and D.R. Rumschitzki, *J. Catal.*, **169**, 455 (1997).

(*Received*: 31 December 2009; *Accepted*: 10 June 2010) AJC-8780