Korean J. of Chem. Eng., **13**(4), 351-355 (1996)

DECANE REFORMING REACTION OVER Pt, Ir, Pt-Ir AND Pt-Ni BIMETALLIC CATALYSTS SUPPORTED ON Y-ZEOLITE

Yong Wan Jin, O Bong Yang* and Seong Ihl Woo†

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, Taejon 305-701, Korea
*School of Chemical Engineering and Technology, Chonbuk National University, Chonju 561-756, Korea

(Received 16 September 1995 • accepted 3 April 1996)

Abstract – Pt, Ir, Pt-Ir and Pt-Ni bimetallic catalysts supported on NaY- and HY-zeolite were examined as a catalyst for producing gasoline from n-decane via simultaneous reforming and cracking. The catalysts were prepared by calcining and reducing metal-ion-exchanged Y-zeolite with O_2 and H_2 at 300°C, respectively. Thus prepared catalysts were characterized by hydrogen chemisorption and temperature programmed desorption of ammonia. Pt-Ni/NaY and Pt-Ir/NaY bimetallic catalysts offered the improved activity maintenance compared to Pt/NaY monometallic catalyst. The catalysts supported on HY-zeolite showed higher selectivity toward C_5-C_7 and skeletal isomers of C_5-C_7 and C_8-C_{10} than those of the catalysts supported on NaY-zeolite, which is a desired characteristic for increasing octane value of gasoline these days. However, deactivation with reaction time was much more pronounced on HY-zeolite-supported catalyst. When the catalyst was presulfided with H_2S, the stability with time on stream was enhanced and the selectivity was quite different from that of the catalyst before presulfiding. The acidity of Y-zeolite and presulfiding of catalyst greatly influenced the activity, selectivity and stability of Pt, Ir, Pt-Ir and Pt-Ni bimetallic catalysts supported on Y-zeolite in n-decane reforming reaction.

Key words: Pt-Ir and Pt-Ni Bimetallic Catalyst, Y-Zeolite, n-Decane Reforming Reaction

INTRODUCTION

Catalytic reforming and cracking are principal processes to obtain the desired petrochemicals or valuable products from crude oil. As the content of heavy oil from crude oil increases, conversion of heavy hydrocarbon to gasoline is more desirable than before. In order to fulfill this purpose cracking process is required before reforming reaction. Faujasite zeolites especially Y-type and alumina-based bimetallic catalysts such as Pt-Re/Al_2O_3, Pt-Ir/Al_2O_3 and Pt-Sn/Al_2O_3 are used for cracking and reforming catalysts, respectively, in the practical industry because of their stability.

Finding a new catalyst for simultaneous reaction of partial cracking and reforming of heavy hydrocarbon to gasoline in one step was pursued for long time because of its economic advantage. The catalyst which is consist of Y-zeolite for cracking and Pt-Re, -Ir or -Sn bimetal for reforming such as Pt-Re or Pt-Ir bimetallic catalyst supported on Y-zeolite may be one of the good catalyst for producing gasoline from heavy hydrocarbon via simultaneous cracking and reforming. Yang et al. [1992, 1993, 1994] recently reported that very small (about 1 nm) Pt-Ir bimetallic clusters on NaY showed a specific characteristics different from those of Pt and Ir monometallic cluster and exhibited a high activity and improved activity maintenance in the n-C_6 and n-C_7 reforming reaction.

In this work, Pt, Ir, Pt-Ir and Pt-Ni bimetallic catalysts supported on NaY- and HY-zeolite were tested as a catalyst for producing gasoline from n-decane via simultaneous reforming and cracking in n-decane reforming reaction under atmospheric pressure. The effects of reaction condition, acidity of support and presulfiding on the catalytic activity, selectivity and stability were studied. Hydrogen chemisorption and temperature programmed desorption (TPD) of NH_3 were used for characterization of the catalysts.

EXPERIMENTAL

Monometallic Pt and Ir catalysts supported on NaY [abbreviated as Pt(x)/NaY and Ir(x)/NaY and x indicates weight %] were prepared by calcining and reducing $Pt(NH_3)_4^{2+}$-exchanged NaY and $Ir(NH_3)_5Cl^{2+}$-exchanged NaY with O_2 and H_2 at 300°C, respectively. Pt-Ir bimetallic catalysts supported on NaY [Pt(x) Ir(x)/NaY] were prepared by calcining and reducing co-ion-exchanged NaY with O_2 and H_2 at 300°C, respectively. Pt-Ni bimetallic catalyst supported on NaY was prepared in the same manner to prepare Pt-Ir bimetallic catalyst except for using Ni $(NO_3)_2 6H_2O$ as a nickel source. HY-zeolite-supported catalysts were prepared in the same manner to prepare NaY-zeolite-supported catalyst using HY (Strem Chemical Co.) instead of NaY (Strem Chemical Co.).

The metal dispersion of the catalyst was determined by hydrogen chemisorption. The adsorption isotherm of hydrogen on the catalyst was volumetrically obtained at 23°C after all the preadsorbed hydrogen during the reduction was desorbed at 400°C and 1×10^{-5} Torr for 1 h. The total number of hydrogen atoms per metal atom (H_{total}/M) was determined by extrapolating the high-pressure linear part of the isotherm to zero pressure. Second adsorption isotherm was obtained after the re-

---

†To whom all correspondences should be addressed.

versibly physisorbed hydrogen was desorbed at 23°C and 1×10^{-5} Torr for 1 h. The difference between the two isotherms was a horizontal straight line and corresponded to the number of hydrogen atoms chemisorbed irreversibly (H_{irrev}/M) at 23°C.

The experiment of temperature programmed desorption (TPD) of NH_3 on NaY- and HY-zeolite was carried out with 0.5 g samples in a conventional TPD apparatus using He as a carrier gas. The sample was heated to 500°C to remove adsorbed water and impurities by He flushing at 60 ml/min, then cooled to 100°C in the He stream for adsorption of NH_3. The adsorption of NH_3 on NaY- and HY-zeolite samples was conducted by flowing NH_3 at 60 ml/min and physically adsorbed NH_3 was desorbed by He flushing (60 ml/min) at 100°C for 1 h, respectively. For TPD of NH_3, the sample was heated from 25°C to 800°C at a rate of 2.5°C/min in the He flowing (60 ml/min). Desorbed NH_3 was measured by on-lined thermal conductivity detector (TCD) and computer interfaced mass spectrometer (VG Quadruples Model: MMPC 3000D).

n-C_{10} reforming reaction was carried out with 0.1 g of catalyst in a microflow, fixed-bed reactor made with stainless steel (SS-316) under atmospheric pressure. 0.1 g of catalyst was charged and re-reduced by 60 ml/min of hydrogen at 400°C for 2 h, the reaction was initiated by introducing the mixture of H_2 and n-C_{10} in a mole ratio of 15 to 1 and the total flow rate was 43 ml/min. H_2 and n-C_{10} reaction mixture was generated by bubbling hydrogen through a n-decane saturator kept at 91.8°C. The catalyst was presulfided by exposing to 15 ppm H_2S in H_2 (40 ml/min) at 400°C for 5 h. The catalyst presulfided was purged with H_2 (60 ml/min) at 400°C for 30 min and the reaction was started. The reaction products were analyzed by an on-line HP 5890A GC equipped with a 50 m crosslinked methyl silicon fused silica capillary column and a flame ionization detector (FID).

RESULTS AND DISCUSSION

The reaction rate was proportional to the amount of catalyst indicating the absence of external mass transfer limitations in this reaction condition. n-Decane (n-C_{10}) conversion was defined as the mole ratio of n-C_{10} disappeared to n-C_{10} fed. The selectivity to a particular product is defined as the mole ratio of n-C_{10} converted to that product to total n-C_{10} converted. The products are classified as follows: light gas (C_1-C_4); C_5-C_7 (normal and skeletal isomers of C_5-C_7); C_8-C_{10} (normal and skeletal isomers of C_8-C_{10}); BTX (benzene, toluene and xylene); C_8-C_{10} aromatic compound (such as mesitylene, cumene and propylbenzene etc.) and oligomers (C_{11}-C_{12}).

Hydrogen adsorption data are given in Table 1. The number of total hydrogen atom adsorbed per metal atom (H_{total}/M) is larger than 1 and the number of hydrogen atom adsorbed irreversibly per metal atom (H_{irrev}/M) is nearly equal to unity for all catalysts used in the reaction. The diameters of above metal clusters were about 1 nm and these nanoclusters were located inside the supercage of NaY by studying the ^{129}Xe NMR, hydrogen chemisorption and xenon adsorption in our previous work [Yang et al., 1992].

Table 1. Hydrogen adsorption data

Catalyst	(H_{total}/M)	(H_{irrev}/M)
Pt(4)/NaY	1.3	0.95
Pt(3)Ir(1)/NaY	1.2	0.93
Pt(2)Ir(2)/NaY	1.2	0.93
Pt(1)Ir(3)/NaY	1.5	0.97
Ir(4)/NaY	1.6	0.99

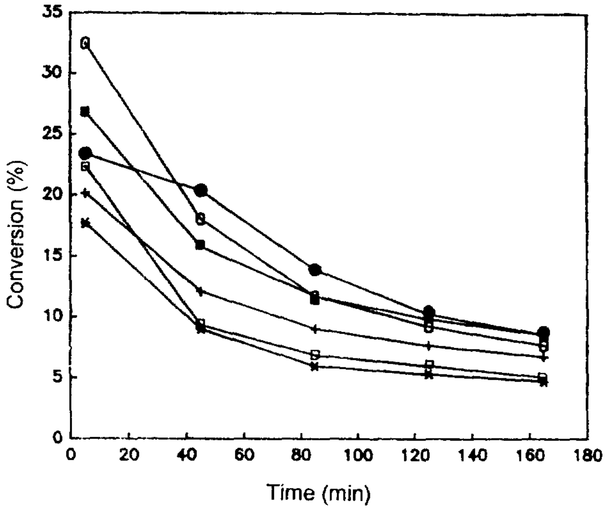

Fig. 1. n-C_{10} conversion as a function of reaction time over the catalysts supported on NaY-zeolite at 350°C.
Pt(4)/NaY (*), Pt(3)Ir(1)/NaY (□), Pt(2)Ir(2)/NaY (+), Pt(1)Ir(3)/NaY (■), Ir(4)/NaY (○) and Pt(2)Ni(2)/NaY (●).

Fig. 1 shows n-C_{10} conversion as a function of reaction time over the catalysts supported on NaY-zeolite at 350°C. Pt(4)/NaY catalyst exhibited the lowest activity. Ir(4)/NaY catalyst started at the highest conversion level but steadily decreased with time on stream. At steady state (165 min), the activity of Ir(4)/NaY was lower than that of Pt(1)Ir(3)/NaY bimetallic catalyst. As increasing the Ir content the activities of Pt-Ir bimetallic catalysts increased. Pt-Ir/NaY bimetallic catalysts showed a higher activity and improved activity maintenance than Pt(4)/NaY catalyst. Especially Pt(2)Ni(2)/NaY bimetallic catalyst was most stable compared to other Pt-Ir/NaY bimetallic and Pt/NaY catalyst. In our previous work, the improvement of activity and activity maintenance of Pt-Ir/NaY bimetallic catalysts could be explained by less amount of coke formation and the nature of graphitic coke in n-C_6 reforming reaction [Yang et al., 1993]. The enhanced stability of Pt(2)Ni(2)/NaY bimetallic catalyst as well as Pt(2)Ir(2)/NaY is not fully understood but interesting result to be studied further.

Fig. 2 shows n-C_{10} conversion as a function of reaction temperature over the catalysts supported on NaY-zeolite at 165 min. The catalytic activities of Pt-Ir/NaY were higher than that of Pt/NaY at reaction temperature of 300-500°C. The catalytic activities were increased as increasing the reaction temperature and reached the maximum value at 400°C. However, the catalytic activities were decreased above 400°C, which might be due to the sintering of metal clusters reported by our previous study [Yang et al., 1993]. The Pt, Ir and Pt-Ir bimetallic clusters thus prepared in this work were remained stably inside the zeolite supercage after re-oxidation below 400°C. However,

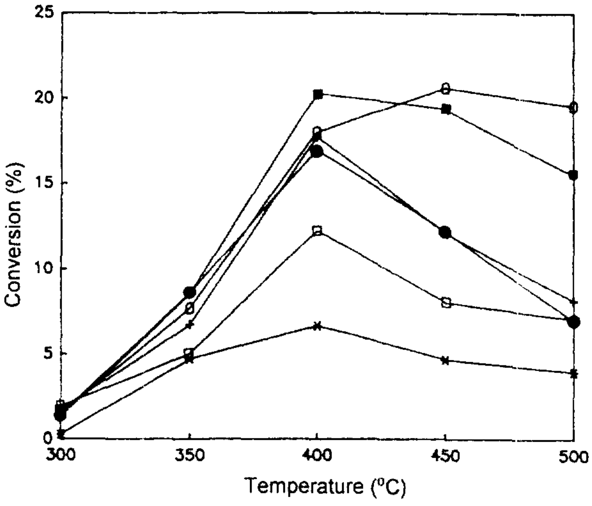

Fig. 2. n-C_{10} conversion as a function of reaction temperature over the catalysts supported on NaY-zeolite at 165 min. Pt(4)/NaY (*), Pt(3)Ir(1)/NaY (□), Pt(2)Ir(2)/NaY (+), Pt(1)Ir(3)/NaY (■), Ir(4)/NaY (○) and Pt(2)Ni(2)/NaY (●).

Table 2. Product distributions of the catalysts supported on NaY- and HY-zeolite at 400°C

	Products (%)					
	C_1-C_4	C_5-C_7	C_8-C_{10}*	BTX	C_8-C_{10} aromatics	C_{11}-C_{12}
Pt(4)/NaY	15.5	3.4(23.4)	26.5(96.5)	6.1	31.8	12.9
Pt(3)Ir(1)/NaY	16.1	2.0(47.1)	27.8(96.5)	2.9	33.0	15.8
Pt(2)Ir(2)/NaY	9.3	3.9(50.0)	22.3(95.0)	3.0	48.9	9.0
Pt(1)Ir(3)/NaY	16.9	6.3(54.7)	18.2(85.4)	5.0	41.9	7.0
Ir(4)/NaY	35.7	18.0(58.5)	10.8(89.7)	5.5	19.4	5.9
Pt(2)Ni(2)/NaY	13.9	10.7(57.3)	21.7(96.4)	3.3	31.8	14.4
Pt(4)/HY	18.5	27.6(69.0)	15.8(99.1)	3.6	31.9	2.6
Pt(2)Ir(2)/HY	22.3	37.2(68.0)	12.3(99.0)	4.0	22.1	2.1
Pt(2)Ni(2)/HY	16.2	26.0(68.2)	18.4(99.5)	1.3	33.0	4.1

*Numbers in parenthesis denote the percentage of skeletal isomers.

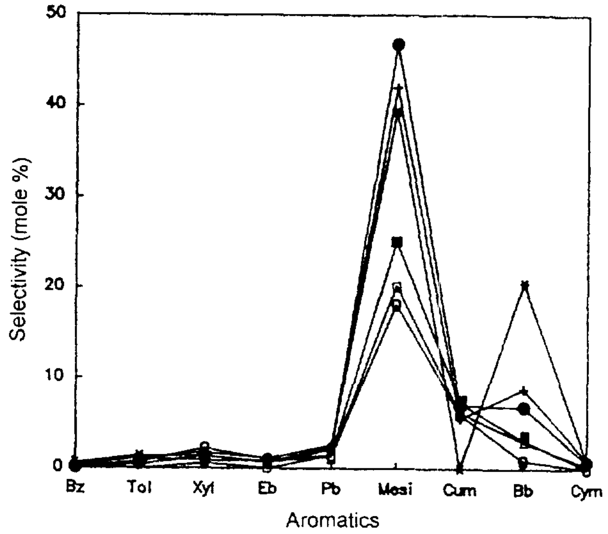

Fig. 3. Distributions of aromatic compounds at 400°C. Pt(4)/NaY (*), Pt(4)/HY (□), Pt(2)Ir(2)/NaY (+), Ir(4)/NaY (○), Pt(2)Ni(2)/NaY (●) and Pt(2)Ni(2)/HY (■). Bz: Benzene, Tol: Toluene, Xyl: Xylene, Eb: Ethylbenzene, Pb: Propylbenzene, Mesi: Mesitylene, Cum: Cumene, Bb: butylbenzene, Cym: Cymene.

these small clusters were migrated and agglomerated to large metallic crystallites on the exterior surface of NaY after re-oxidation above 400°C evidenced by the ^{129}Xe NMR and hydrogen chemisorption. Also, Jacobs et al. [1977] reported the migration and agglomeration of Ni metal clusters above 400°C.

Product distributions of the catalysts supported on NaY- and HY-zeolite at 400°C are given in Table 2. The major products over all catalysts were C_8-C_{10} aromatic compounds such as mesitylene, cumene, propylbenzene and butylbenzene. Especially mesitylene is the most predominant component among the C_8-C_{10} aromatic compounds as shown in Fig. 3. Second abundant products were C_8-C_{10} and C_5-C_7 on the catalysts supported on NaY- and HY-zeolite, respectively. The most significant difference on product distributions between the catalysts supported on NaY-zeolite and HY-zeolite is the percentage of skeletal isomers among C_5-C_7 and C_8-C_{10} compounds. The percentage of skeletal isomers over HY-zeolite-supported catalysts is much higher than that over NaY-zeolite-supported catalysts.

The normal composition of gasoline at these days is about 30-40% of BTX and 40-50% of C_5-C_7 hydrocarbon, 10-20% of heavy hydrocarbon (C_8-C_{10}), 5% of light gas and 5% of oxygenate such as methyl tert-butyl ether (MTBE). The octane values of skeletal isomers are higher than those of normal straight chain hydrocarbons. Therefore, the principal components of gasoline are skeletal isomers of C_5-C_7 and BTX. NaY-zeolite-supported catalysts may not be suitable catalyst for producing the gasoline from heavy hydrocarbon (e.g. n-C_{10}) via simultaneous cracking and reforming because of relatively low selectivities to C_5-C_7 and BTX. However, very high selectivity to C_5-C_7 and skeletal isomers of C_5-C_7 and C_8-C_{10} is a desired characteristics of HY-zeolite-supported catalysts for simultaneous cracking and reforming. It has been known that most of isomerization and cracking reaction are taken place on acid site. Therefore, acid site may be inevitably needed for simultaneous cracking and reforming in the n-decane reaction. However, a few weak acid sites at 200°C are observed on NaY-zeolite measured by the temperature programmed desorption (TPD) of NH_3 as shown in Fig. 4. On the other hand, a large number of weak acid site, quite a number of medium acid site at 300-400°C and some strong acid site at 600°C are distributed on HY-zeolite. High selectivity to skeletal isomers over the catalysts supported on HY-zeolite is ascribe to a large number of acid site on HY-zeolite.

Fig. 5 shows the comparison of activity between HY- and NaY-zeolite-supported catalysts. The initial activities of HY-zeolite-supported catalysts were much higher than those of NaY-zeolite-supported catalysts. However, the activities of HY-zeolite-supported catalysts were rapidly deactivated with time on stream and reached a lower level than those of NaY-zeolite-supported catalysts after 165 min. Severe deactivation of the catalysts supported on HY-zeolite should be improved to use as a catalyst for simultaneous cracking and reforming reaction.

Initial activities of the catalysts presulfided were quite lower than those of fresh catalysts as shown in Fig. 1 and Fig. 6.

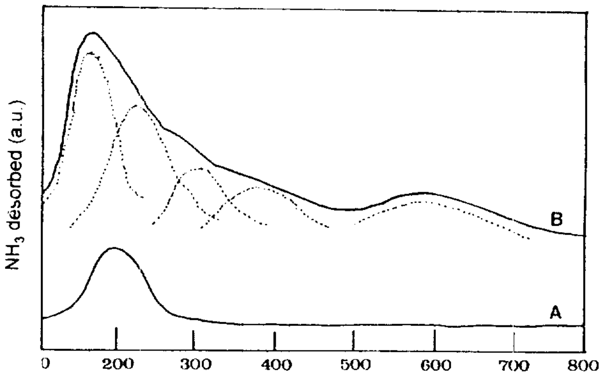

Fig. 4. NH$_3$ TPD spectra of NaY-zeolite (A) and HY-zeolite (B).

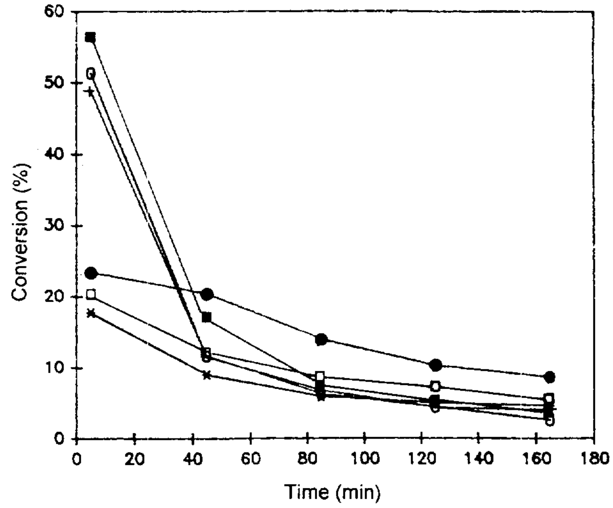

Fig. 5. Support effect on a catalytic activity at 350°C.
Pt(4)/NaY (*), Pt(4)/HY (+), Pt(2)Ir(2)/NaY (■), Pt(2)Ir(2)/HY (□), Pt(2)Ni(2)/NaY (●), Pt(2)Ni(2)/HY (○).

However, deactivation of the catalysts presulfided with time on stream was improved. This enhanced activity maintenance after presulfiding has not been clearly understood. A model was proposed by Shum et al. [1985], in which firmly adsorbed sulfur atoms impede the reorganization of the carbonaceous over-layer into pseudo-graphitic entities which are detrimental to the catalyst. It is well known that the activity and selectivity of Pt-Re/Al$_2$O$_3$ reforming catalyst were greatly affected by sulfiding [Biloen et al., 1980, Jossens and Petersen, 1982].

Table 3 shows the product distributions of the catalysts presulfided. The product distributions of Pt, Ir and Pt-Ir bimetallic catalyst presulfided were different from those of the catalysts before presulfiding in Table 2. After presulfiding, the selectivities to BTX and C$_8$-C$_{10}$ aromatics decrease and skeletal isomers of C$_8$-C$_{10}$ increased, which may be arising from the decrease in ensemble size needed for dehydrocyclization reaction (n-C$_{10}$ to BTX and C$_8$-C$_{10}$ aromatics) by adsorption of sulfur atoms on Ir metal atoms. On the catalysts presulfided, the percentage of mesitylene was negligible and the selectivities toward propylbenzene, cumene and butylbenzene slightly increased. However, product distribution of Pt(2)Ni(2)/NaY after presulfiding was nearly similar to those of Pt(2)Ni(2)/NaY. This result can be explained that the sulfur atom seems to more dominantly or strongly adsorbed on Ir atom than Pt or Ni atom. Especially the adsorbed sulfur atom on Ni atom may be not so many or not strong enough to alter the product distribution. In case of Pt-Re/Al$_2$O$_3$ bimetallic catalyst, Biloen et al. [1980] and Sachtler [1984] discussed that Pt-S bond was weaker than the Re-S bond and Re atoms preferentially capped by chemisorbed sulfur.

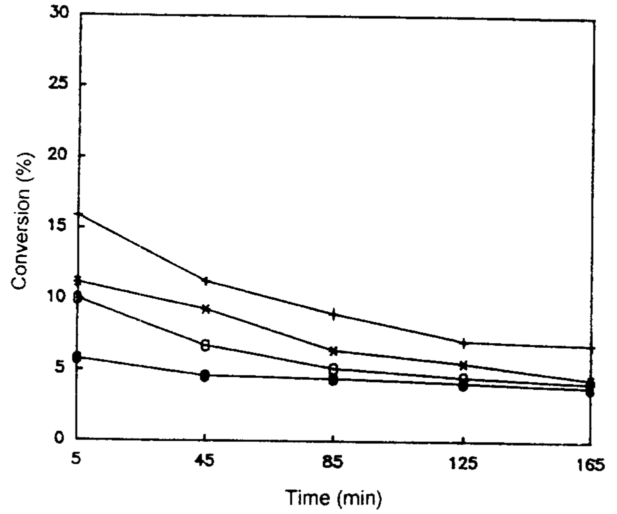

Fig. 6. n-C$_{10}$ conversion over the catalyst presulfided at 350°C.
Pt(4)/NaY (*), Pt(2)Ir(2)/NaY (+), Ir(4)/NaY (●) and Pt(2)Ni(2)/NaY (○).

Table 3. Product distributions of the catalysts presulfided with H$_2$S at 400°C for 5 h

	Products (%)					
	C$_1$-C$_4$	C$_5$-C$_7$	C$_8$-C$_{10}$*	BTX	C$_8$-C$_{10}$ aromatics	C$_{11}$-C$_{12}$
Pt(4)/NaY	4.9	0(0)	48.6(99.0)	0	29.4	17.1
Pt(2)Ir(2)/NaY	4.8	0(0)	46.2(99.1)	2.5	29.0	17.5
Ir(4)/NaY	36.2	35.6(92.0)	13.2(99.3)	2.0	6.8	6.2
Pt(2)Ni(2)/NaY	13.1	10.3(90.5)	28.5(99.5)	3.5	37.8	6.8

*Numbers in parenthesis denote the percentage of skeletal isomers.

CONCLUSIONS

Pt-Ni/NaY as well as Pt-Ir/NaY bimetallic catalysts showed the improved activity maintenance compared to Pt/NaY monometallic catalyst in n-decane reforming reaction. C$_8$-C$_{10}$ aromatics especially mesitylene are major products of the catalysts supported on NaY- and HY-zeolite. The catalysts supported on HY-zeolite showed higher selectivity to C$_5$-C$_7$ and skeletal isomers of C$_5$-C$_7$ and C$_8$-C$_{10}$ than those of the catalysts supported on NaY-zeolite, which is a good characteristic for producing gasoline from n-C$_{10}$ via simultaneous cracking and reforming. However, the catalyst supported on HY-zeolite showed more severe deactivation than the catalyst supported on NaY-zeolite. When the catalysts were presulfided, although the initial activity decreased, the activity maintenance was enhanced. The product distributions of Pt, Ir and Pt-Ir bimetallic catalyst presulfided were significantly different from those of the catalysts before presulfiding. After presulfiding, the selectivities of BTX and C_8-C_{10} aromatics decrease and skeletal isomers of C_8-C_{10} increased, which may be arising from the decrease in ensemble size needed for dehydrocyclization reaction (n-C_{10} to BTX and C_8-C_{10} aromatics) by adsorption of sulfur atoms on Ir metal atoms. It can be concluded that the acidity of Y-zeolite and presulfiding of catalyst greatly influence the activity, selectivity and stability of Pt, Ir, Pt-Ir and Pt-Ni bimetallic catalysts supported on Y-zeolite in n-decane reforming reaction.

ACKNOWLEDGEMENT

This research was funded by KOSEF Purpose Oriented Fundamental Research Fund (1990-1993).

REFERENCES

Biloen, P., Helle, J. N., Verbeek, H., Dautgenberg, F. M. and Sachtler, W. M. H., "The Role of Rhenium and Sulfur in Platinum-Based Hydrocarbon-Conversion Catalysts", *J. Catal.*, **63**, 112 (1980).

Jacobs, P. A., Tielen, M., Linart, J. P., Nijs, H. and Uytterhoeven, J. B., "Redox Behavior of Transition Metal Ions in Zeolites-Part 5-Method of Quantitative Determination of Bidisperse Distributions of Metal Particle Sizes in Zeolites", *J. Chem. Soc. Faraday I*, **73**, 1745 (1977).

Jossens L. W. and Petersen, E. E., "Fouling of a Platinum-Rhenium Reforming Catalyst Using Model Reforming Reactions", *J. Catal.*, **76**, 265 (1982).

Sachtler, W. M. H., "Selectivity and Rate of Activity Decline of Bimetallic Catalysts", *J. of Molecular Catal.*, **25**, 1 (1984).

Shum, V. K., Butt, J. B. and Sachtler, W. M. H., *J. Catal.*, **96**, 371 (1985).

Yang, O. B., Ryoo, R. and Woo, S. I., "Formation of Small Pt-Ir Bimetallic Cluster in NaY Zeolite Probed with ^{129}Xe NMR Spectrometer and Ethane Hydrogenolysis", *J. of Catalysis*, **137**, 357 (1992).

Yang, O. B. and Woo, S. I., "Characterization and Catalytic Properties of Pt-Ir Small Bimetallic Cluster in NaY", Studies in Surface Science and Catalysis, vol. 75 (New Frontiers in Catalysis: Proceedings of 10th International Congress on Catalysis, ed. L. Guczi et al., Elsevier, Amsterdam), 671 (1993).

Yang, O. B., Woo, S. I. and Hwang, I. C., "Deactivation Characteristics in n-Heptane Reforming Reaction Catalyzed over Small Pt, Ir and Pt-Ir Bimetallic Clusters in NaY", *Catalysis Letters*, **19**, 239 (1993).

Yang, O. B. and Woo, S. I., "CO Hydrogenation over Small Pt, Ir and Pt-Ir Bimetallic Clusters Entrapped in the Supercage of NaY Zeolite", *Reaction Kinetics & Catalysis Letters*, **52**(2), 269 (1994).