



Science and Engineering Symposium
4th International Science, Social Science, Engineering and Energy Conference 2012

n-Hexane Isomerization over Pt, Pd on Mixed Carrier HY+ γ - Al_2O_3 Catalysts

Dao Thi Kim Thoa^{a,*}, Luu Cam Loc^b, Nguyen Thanh Tung^b,
Nguyen Tri^b, Nguyen Dien Trung^b, Ho Si Thoang^b

^aHoChiMinh City University of Technology, HoChiMinh City, Vietnam

^bInstitute of Chemical Technology, Vietnamese Academy of Science and Technology, HoChiMinh City, Vietnam

Abstract

In this study a decationized form of faujasite zeolite HY and mixes of this zeolite with γ - Al_2O_3 of various ratios have been used as carriers for catalysts 0.35 wt.% Pt and 0.80 wt.% Pd. Physico-chemical characteristics of the obtained catalysts were determined by methods of BET-N₂ adsorption, SEM, TEM, XRD, TPR, H₂ pulse chemisorption (HPC), and NH₃ adsorption-desorption. The activity of the catalysts for n-hexane isomerization was tested at the temperature range 225 – 450 oC and two values of pressure 0.1 and 0.7 MPa. In feed flow the mol ratio hydrogen: hydrocarbon was 5.92 with the concentration of n-hexane as 9.2 mol%. It has been found that the value of optimal ratio γ - Al_2O_3 : HY was 2.5:1. The effect of the mixed carriers is included in the reduction of cluster size of noble metal, the increase of metal dispersity and the improvement of catalyst stability. At 0.7 MPa the activity, selectivity, and stability of catalysts have been shown to be significantly higher than those obtained at 0.1 MPa.

© 2013 The Authors. Published by Kasem Bundit University.

Selection and/or peer-review under responsibility of Faculty of Science and Technology, Kasem Bundit University, Bangkok.

Keywords: n-hexane isomerization, Pt, Pd, mixed carriers HY + Al_2O_3

1. Introduction

In recent three decades the petroleum refining industry is developing under the control of strict standardized criteria in fuel quality relatively not only the aspect of utilization value but relatively the aspect of environmental impact. According standards Euro-4 and Euro-5, the concentration of aromatic hydrocarbons must be reduced strongly and content of benzene in gasoline should not exceed 1 vol.%. The United States and Europe define the limit of aromatic hydrocarbons in gasoline not exceed 25 vol.%, and from the beginning of 2011, when the standard Mobile Source Air Toxics (MSAT II) is effective, the concentration of benzene must be limited to 0.62 vol.%. [1].

* Corresponding author. E-mail address: lclloc@vast-hcm.ac.vn

The problem becomes more trouble when lead containing additives, the most effective and cheap ones, have been completely eliminated, and MTBE and other oxygenated compounds also have been shown to belong to poisoning substrates and their utilization either is forbidden or must be reduced significantly. Thus in the present petroleum refinery the task of increasing octane number of gasoline lies on catalytic processes, such as cracking, reforming, alkylation, isomerization. However to reduce the content of aromatic hydrocarbons, reaction of light paraffins isomerization process must play important role because by this way one can increase octane number of gasoline without raising up the concentration of aromatic hydrocarbons. In this aspect, the isomerization process should be considered as a modern and progressive industrial one.

Various generations of isomerization catalysts have been developed. The first generation were liquid Lewis acids; the following generation was included in solid acids (amorphous and crystalline silica-alumina), and at present time in utilization one have mainly bi-functional catalysts containing noble metals supported on various acidized (chlorinated) carriers, including zeolites. The advantage of the last kind of catalysts is included in the balance between acidic and re-dox functions. Pt/zeolites catalysts able to operate at high temperatures (525 ± 575 K) with good stability and long lifetime [2]. Catalysts Pt on chlorinated alumina express high activity at low temperatures (400 ± 450 K), but very sensitive to impurities (poisons) [3]. Pt is a very expensive and scarce metal. Therefore, more and more current studies have been taken in order either to decrease Pt content or to replace it in industrial catalysts.

Palladium is an interesting alternative to platinum. Palladium is cheaper than platinum and the choice of Pd as active component is determined on the basis of its performance and stability. Pd- $H_4SiW_{12}O_{40}$ supported on SiO_2 and Pd- WO_3/ZrO_2 were found to be active in skeletal isomerization of alkanes [4].

Pore size of zeolite contributes part to defining the selectivity of catalysts on reaction products. For zeolite HY its pore size is favorable for forming two-branched molecules of isohexane from n-hexane [5]. Nevertheless, with high acidity, zeolite HY also enhances the cracking process leading to reduction of reaction efficiency.

Aluminum oxide is a good carrier for isomerization reaction, but it expresses relatively weak acidity. It is hopeful that the combination of two types of the mentioned above carriers could create good carriers characterized by appropriate properties for the reaction. Mixed carriers should be characterized by mild acidity, high value of specific surface area and appropriate pore size for isomerization of low n-paraffins to branched isoparaffins with high octane number.

The purpose of this work is to study the influence of mixed carriers HY + Al_2O_3 on physico-chemical properties and activity of Pt and Pd-supported catalysts in order to create highly active contacts for n-hexane isomerization at normal pressure and at 0.7 MPa.

2. Experimental

Aluminium oxide was prepared by coprecipitating 5%-solution of ammonia with solution of $Al(NO_3)_3 \cdot 9H_2O$ up to pH = 8 – 9. The precipitate was aged 12 h and the product $Al(OH)_3$ then was washed by distilled water, dried and calcined at 500 °C for receiving $\gamma-Al_2O_3$. Mixed carriers were obtained by mechanical mixing of $Al(OH)_3$ with HY, then calcined at 500 °C for 6 h. Active phases 0.35 wt.%Pt and 0.80 wt.% Pd were supported on the carriers by impregnation method, then dried, calcined at 400 °C for palladium and 500 °C for platinum catalysts during 3 h. Before reaction, the platinum catalysts were reduced at 500 °C, and palladium catalysts were reduced at 400 °C during 2 h in a hydrogen flow.

Catalysts were assigned as follows: Pd/Al-HY(3:1) means 0.8 wt.% Pd on mixed carrier $\gamma-Al_2O_3 + HY$ with ratio $Al_2O_3 : HY = 3:1$. By the same way Pt/Al-HY(2.5:1) means 0.35 wt.% Pt on mixed carrier $\gamma-Al_2O_3 + HY$ with ratio $Al_2O_3 : HY = 2.5:1$.

Physico-chemical properties of the catalysts were characterized by methods of BET- N_2 adsorption (BET), Scanning Electron Microscopy (SEM), Transferring Electron Microscopy (TEM), X-ray Diffraction (XRD), Temperature-Programmed Reduction (TPR), H_2 pulse chemisorption (HPC), and NH_3 adsorption-desorption. Activity of the studied catalysts was tested in a micro-flow reactor at following conditions: temperature range 225 ÷ 450 °C; pressure 0.1 MPa and 0.7 MPa; mol ratio of $H_2:n$ -hexane 5.92; n-hexane concentration in feed 9.2 mol%; feed flow 7.5 L/h; catalyst weight 1.5 g. The mixture of reaction products was analyzed on the GC

Agilent Technologies 6890 Plus with a FID detector, and HP-PLOT Molecular Sieve 5A column with 30 m of length and 0.32 mm of outer diameter were used.

3. Result and discussion

a) Physico-chemical properties of catalysts

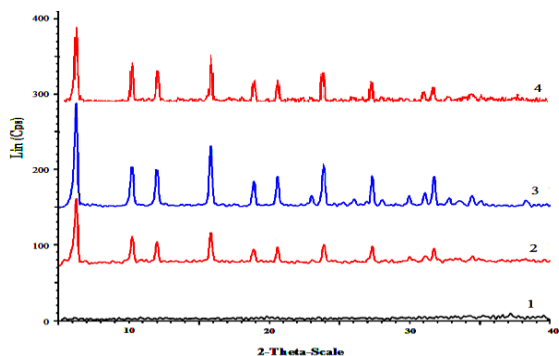


Fig. 1a. XRD patterns of catalysts: 1) Pd/Al, 2) Pd/Al-HY(2.5:1); 3) Pd/HY, and 4) Pt/Al-HY(2.5:1)

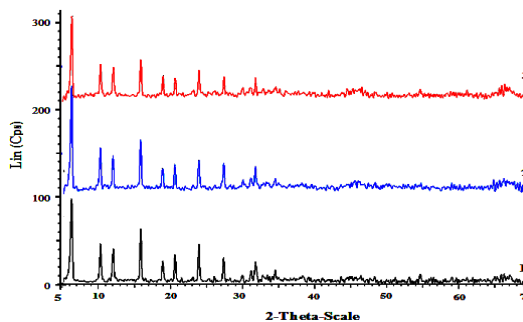


Fig. 1b. XRD patterns of catalysts: 1) Pd/Al-HY(1:1), 2) Pd/Al-HY(2.5:1), and 3) Pt/Al-HY(3:1)

The XRD pattern of sample Pd/ γ -Al₂O₃ (line 1, Fig. 1a) contains very weak peaks indicating the existence of amorphous state of γ -Al₂O₃. XRD patterns of Pd- and Pt-containing catalysts on zeolite HY and on mixed carriers are similar; they contain characteristic peaks of zeolite HY at $2\theta = 6.5; 10.5; 12; 16; 19; 21; 24; 27.5; 32$ degrees. Compared to catalyst Pd/HY, characteristic peaks of HY in mixed carriers are weaker. As seen in Table 1, the value of HY crystals size calculated according Scherrer formulae [6] at peak at $2\theta = 6.5^\circ$ varied in interval 28 – 34 nm. It is interesting to notice that in XRD patterns of all the samples one does not observe any characteristic peaks of Pt, Pd or other phases.

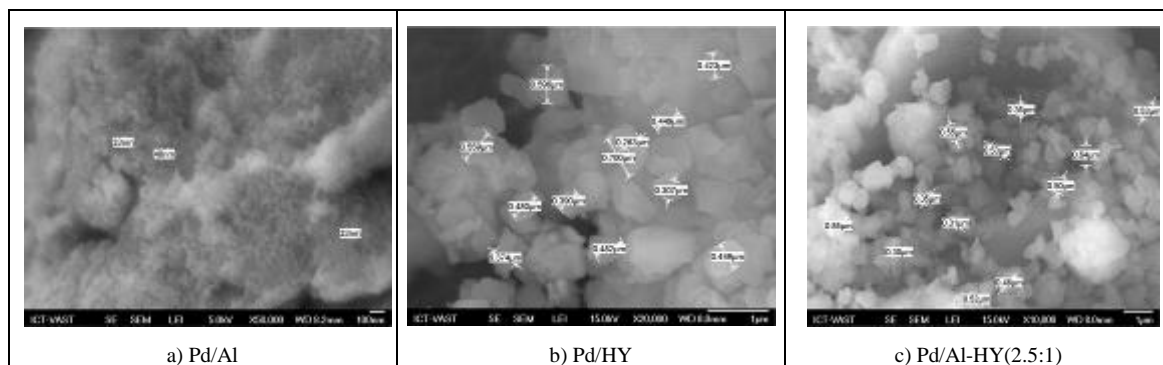


Fig. 2. SEM of catalysts

SEM images (Fig. 2a) indicates that aluminium oxide in catalyst Pd/Al exists in form of fine porous cotton with particle size in range 200 – 460 nm. In catalyst Pd on HY (Fig. 2b) and on mixed carrier (Fig. 2c) zeolite crystallites are seen in the form of rectangular cube with dimension of 350 nm x (500 – 700) nm and 300 x (550 – 850) nm. In mixed carriers HY crystallites are distributed on surface of aluminium oxide with dimension of 300 x (350 – 550) nm and small particles (54 – 80 nm).

On TEM images (Fig. 3) one can observe disperse particles Pd and Pt on surface of the catalysts. The values of agglomerates size of Pd and Pt determined by measuring on TEM images and by hydrogen pulse chemisorption are identical. As seen in Table 1, the dispersity of Pd on mixed carriers is better than that on

zeolite HY and particle dimension of Pd reduced and Pd dispersion improved with zeolite content. On Pd/HY the values of Pd agglomerates size and Pd dispersity are 7.3 nm and 16 % correspondingly, but on Pd/Al-HY these values are 4.2 – 6 nm and 18.69 – 27.57 % respectively. Also on mixed carriers agglomerates size and dispersity of Pt have been determined as 2 nm and 70 % correspondingly.

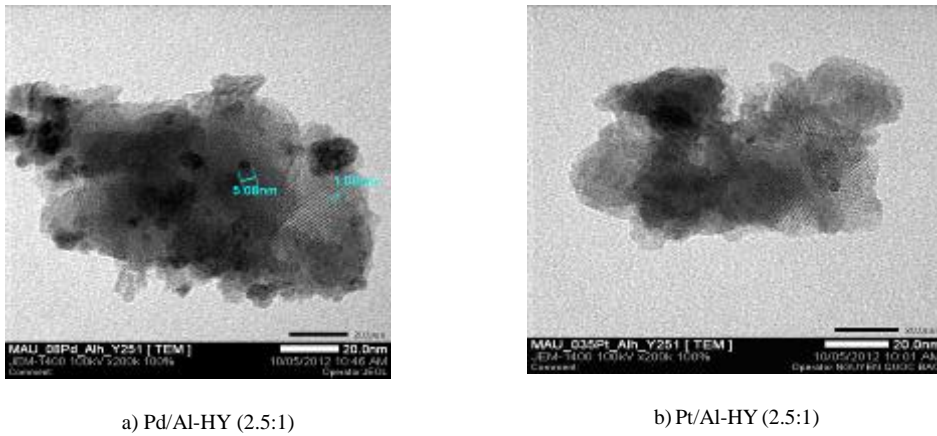


Fig. 3. TEM images of catalysts

Table 1. Surface area (S_{BET}); crystallite size of HY calculated at $2\theta = 6.5^\circ$ (d_{HY}); particle dimension of Pd or Pt determined by TEM images (d_{met}), cluster size of Pd or Pt (d_{clu}) and metal dispersity (γ) determined by HPC method and elemental composition determined by EDX

Catalyst	S_{BET} (m^2/g)	d_{HY} (nm)	d_{met} (nm)	d_{clu} (nm)	γ (%)	Elemental composition (atom%)			
						O	Si	Al	Pd
Pd/Al	218	-	-	25.0	4.46	26.00	60.60	0.00	13.40
Pd/HY	409	33.1	-	7.3	15.95	33.90	48.03	16.85	1.24
Pd/Al-HY(3:1)	-	33.6	-	6.2	18.69	-	-	-	-
Pd/Al-HY(2.5:1)	285	34.1	5.08	6.1	18.80	22.98	75.69	1.33	0.00
						25.70	59.60	14.0	0.73
						27.20	36.50	33.3	2.98
Pd/Al-HY(1:1)	322	27.8	-	4.4	26.10	-	-	-	-
Pd/Al-HY(1:2)	-	-	-	4.2	27.57	-	-	-	-
PtAl-HY(2.5:1)	245	32.7	2.00	1.7	70.05	-	-	-	-

EDS pattern (Fig. 4b) indicated that on the surface of catalyst Pd/HY elements O, Al, Si, Pd are distributed sufficiently evenly, while on catalyst Pd/Al the distribution of elements is less uniform; in several areas the density of Pd is higher than in others. The distribution of elements Pd and Si on mixed carrier Al-HY also is not uniform.

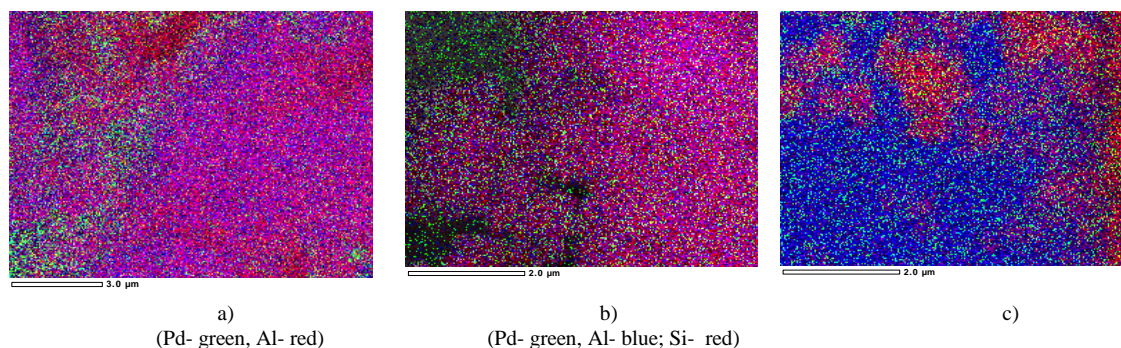


Fig. 4. EDS patterns of catalyst: a) Pd/Al, b) Pd/HY and c) Pd/Al-HY (2.5:1)

Elemental composition on surface of the catalysts are presented in Table 1. Although the low common content of Pd in catalyst Pd/Al (0.8 wt.%), its surface concentration has been found very high (13.4 atom%). On surface of sample Pd/HY the value of ratio Si:Al = 3, closed to that in zeolite HY (the original zeolite was $(\text{Na}_{86}[(\text{AlO}_2)_{56}(\text{SiO}_2)_{136}]\cdot 260 \text{H}_2\text{O})$). On this catalyst the surface concentration of Pd was found sufficiently low (1.24 atom%) and the value of particle size was biggest and the dispersity was the lowest. It is possible to distinguish three regions of the surface for sample Pd/Al-HY. In the first region the concentration of aluminium reaches 75.69 atom% and the concentration of silicon only 1.33 atom%. No palladium was seen in this region. In the second region the values of Al and Si concentrations were found 60 and 14 atom% respectively (ratio Al:Si > 4) and the concentration of oxygen is similar to that on catalyst Pd/Al (about 26 atom%). In this region Pd has very low concentration, only about 0.73 atom%. In the third region the concentration of Al is lower than on Pd/Al but higher than on Pd/HY, while the concentration of Si is in reverse order. The values of concentrations of Al and Si were found identical, approximately 33 – 36 atom%, that means the value of Si:Al ratio ~ 1. The value of oxygen concentration in this region is higher than on sample Pd/Al but lower than on Pd/HY. The concentration of Pd in this region is about 3 atom%, higher than in the second region but much lower than on sample Pd/Al. Based on this analysis one should consider that on the surface of this kind carriers $\text{Al}_2\text{O}_3 + \text{HY}$ combined mixes with different compositions have been formed but, as confirmed by XRD data, the structure of the decationized zeolite was not changed.

Table 2. Maximum reduction temperatures (T_{max}), reduction extents (K_{Red}) and acidity of the studied catalysts (mmol NH_3 /100g catalyst)

Catalyst	T_{max} (°C)	K_{Red} (%)	Acidity (mmol/100g catalyst)			
			Weak	Medium	Strong	Total
Pd/Al	75	34.21	0.964	0.445	0.751	2.160
Pd/HY	65	29.84	9.369	8.872	7.160	25.401
Pd/Al-HY(3:1)	80	41.57	5.950	1.844	1.301	9.095
Pd/Al-HY (2.5:1)	70	41.20	5.832	1.290	1.080	8.202
Pd/Al-HY (2:1)	80	37.64	7.044	4.156	3.057	14.257
Pd/Al-HY (1:1)	70	41.89	6.922	2.264	2.397	11.583
Pd/Al-HY (1:2)	75	33.84	7.301	2.800	6.591	16.692
Pt/Al-HY(2.5:1)	202	24.02	0.6351	1.367	2.140	4.142
	373	13.14 37.16				

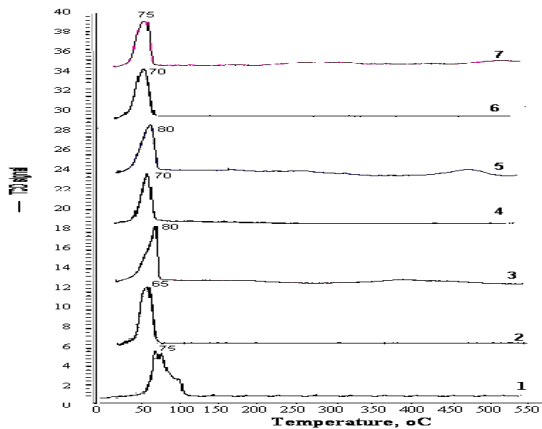


Fig. 5. TPR diagrams of Pd catalysts: 1)Pd/Al (1); 2)Pd/HY; 3) Pd/Al-HY(3:1); 4) Pd/Al-HY(2.5:1); 5) Pd/Al-HY(2:1); 6) Pd/Al-HY(1:1); 7) Pd/Al-HY(1:2)

TPR diagrams (Fig. 5) of all Pd/Al, Pd/HY and Pd/Al+HY catalysts had only one negative peak with $T_{max} = 65 - 80^{\circ}\text{C}$ (the plots in Fig. 5 were inverted). According authors [7] for both Pd/Al and Au-Pd/Al samples, the presence of TPR peaks at about 81°C indicates the reduction of PdO species interacting with the alumina surface. In addition, the TPR profile of the Au-Pd/Al sample shows a peak at 31°C , indicative the reduction of bulk PdO. The negative peak of H_2 consumption at 84°C is attributed to H_2 - desorption from the decomposition of a bulk palladium hydride formed through H-diffusion within the Pd crystallites [8]. So, the reduction peak on TPR diagrams of all Palladium catalysts ($T_{max} = 65 - 80^{\circ}\text{C}$) characterizes the reduction of PdO species interacting with the carrier surface. It should be noted that, mixing of aluminum oxide to zeolite HY made the reduction extent of catalyst to be increased from 30% up to $\sim 34 - 42\%$, depended on ratio $\text{Al}_2\text{O}_3:\text{HY}$. This should be understandable, because on the mixed carriers the Pd dispersion improved with zeolite content (Tab.1).

TPR diagram of catalyst Pt/Al-HY(2.5:1) is characterized by 2 reduction peaks at $T_{max,1} = 202^{\circ}\text{C}$ và $T_{max,2} = 373^{\circ}\text{C}$, and the value of first kind reduced sites is two times higher than that of second ones. Authors [9] showed two reduction peaks at 270 and 400°C for catalyst sample 1.0 wt.% Pt/HUSY calcined at 500°C . First peak characterizes the reduction of Pt^{2+} located in sodalite cages and second peak characterizes the reduction of Pt^{2+} located in hexagonal prisms. At this time, according to Fortunato et al [10], on catalysts Pt/YSZ the peak consuming hydrogen at $355 - 400^{\circ}\text{C}$ is related to the hydrogen spillover from reduced particles of Pt to surface of YSZ.

Compared to catalyst Pd on Al-HY(2.5:1) catalyst Pt supported on the same carrier is characterized by higher reduction temperatures and lower reduction extent. This fact once again confirms that Pt is associated with carrier stronger than Pd. According to [11], a preliminary reduction of Pt catalyst at 500°C , on the one hand, makes platinum oxide to be reduced completely and, on the another hand, eliminates completely newly formed carbonyl compounds able to poison Pt sites. Consequently, before running reaction, catalyst Pt/Al-HY was reduced at 500°C .

Results in Table 2 indicate that for Pd-based catalysts the value of total acidity of sample Pd on $\gamma\text{-Al}_2\text{O}_3$ is lowest, much lower compared to that of catalyst on zeolite HY. Acidity of the catalyst on mixed carrier lies between those of catalyst Pd/Al and catalyst Pd/HY. Among catalysts supported on $\text{Al}_2\text{O}_3 + \text{HY}$, sample Pd/Al-HY(2.5:1) has the lowest acidity, but its value is 4 time higher than the acidity of sample Pd/Al and equal one third of Pd/HY acidity. On this sample the value of medium acidity is 3 times higher than on sample Pd/Al, while in strong acidity the first sample exceeds the second one only 1.5 time. In both types strong and medium acidity catalyst Pd/Al-HY(2.5:1) points for only 1/8 of Pd/HY acidity. Thus on the basis of obtained results one can conclude that the creation of carrier by mechanical mixing of components not only should lead to having appropriate acidity, but makes the ability to regulate particle size and dispersity of Pd to be possible

Catalyst 0.35%Pt/Al-HY(2.5:1) is characterized by the acidity equal to half of the acidity of catalyst 0.80%Pd/Al-HY(2.5:1). Nevertheless, in strong acidity the Pt-based catalyst two times exceeds the Pd-based one, while two the catalysts have the same medium acidity and for weak acidity the Pt catalyst has the value in 10 times less compared to the Pd catalyst.

Table 3 shows the values of activity, selectivity and stability of catalysts at optimal temperatures and two values of pressure. The reaction products are unreacted n-hexane, isomers of n-hexane, such as 2,3- DMB, 2-MP, 3-MP, and products of cracking. Optimal temperatures of the reaction were in the range of $300^{\circ}\text{C} - 400^{\circ}\text{C}$.

Table 3. Conversion (X), selectivity on isohexane (S_{i-C_6}), i-C₆ yield (Y_{i-C_6}), 2,3-DMB:2-MP:3-MP ratio, cracked species ratio (C₃:C₄:C₅), octane number of liquid product (RON) and stability (τ) of catalyst at optimal temperatures (T_{opt}) at pressure (P) of 0.1 MPa and 0.7 MPa

Catalyst	P, MPa	T_{opt} , °C	X, %	S_{i-C_6} , %	Y_{i-C_6} , %	2,3DMB: 2-MP : 3-MP	S_{cr} , %	C ₃ : C ₄ : C ₅	τ , hour
Pd/Al	1	400	18	92	16.7	1:100:57	8	1:4:7	
Pd/HY	1	350	32	59	18.9	1:12:7	41	2:1:1	1.25
	7	300	82	85	66.0	1:3:1.7	7	1:3:2	14
Pd/Al-HY(1:2)	1	325	34	72	24.5	1:12:7	28	2:1:1	-
Pd/Al-HY(1:1)	1	325	23	77	17.7	1:14:8	23	1:1:1	-
Pd/Al-HY (2:1)	1	300	19	90	17.1	1:8:24	10	1:2:2	-
Pd/Al-HY (2.5:1)	1	350	39	90	35.1	1:11:6	10	2:1:1	3
	7	325	79	84	66.4	1:4:2	16	3:2:1	>34
Pd/Al-HY (3:1)	1	325	29	92	26.7	1:11:7	8	2:1:1	-
Pt/Al-HY(2.5:1)	1	350	76	85	65	1:5:3	15	2:1:1	23.7
	7	325	82	81	69.7	1:3:2	19	2:1:1	>34

From the results in Table 3 it follows that catalyst Pd/Al expresses the lowest quantities of activity (conversion and yield in isohexane formation) and the highest optimal temperature compared to catalysts Pd/HY và Pd/Al-HY. Catalyst Pd/Al started to appear its activity at 350 °C and reached the maximum of activity at 400 °C with isohexane yield Y_{i-C_6} = 16.54%, while catalyst Pd/HY started to appear activity at 250 °C and reached the maximum of activity at 350 °C with isohexane yield Y_{iso} = 17.76%. Nevertheless, catalyst Pd/Al expresses the lowest selectivity on products of cracking thanks to the weakest acidity, while catalyst Pd/HY expresses the highest selectivity on products of cracking.

Activity of Pd-based catalysts expresses a common trend including in that it increases with content of zeolite in carrier, reaching a maximal value at some ratio of Al₂O₃ : HY and after that decreases with zeolite content. As seen in Table 3, the optimal composition of carrier is Al₂O₃ : HY = 2.5:1. This can be explained by high reducibility of the catalyst supported on this carrier. The cracking selectivity of catalysts decreased with reduction of zeolite proportion in carrier. Also on catalyst Pd/Al-HY(2.5:1) one obtained values of conversion, isohexane selectivity and yield higher than on catalyst Pd/HY. This observation can be understood because all catalysts supported on mixed carriers are characterized by smaller particle size, higher palladium dispersity and lower acidity compared to those on catalyst Pd/HY. These factors should lead to increasing activity and stability of the considered catalyst. Indeed, catalyst Pd/Al-HY(2.5:1) could operate with good stability about 3 hours, while catalyst Pd/HY could keep stable activity only more than one hour.

At pressure 0.1 MPa compared to sample Pd/Al-HY(2.5:1), on catalyst Pt/Al-HY(2.5:1) values of conversion and isohexane yield are higher, value of isohexane is a little lower and value of stability is higher (24 hours compared to 3 hours). The reason of this difference is included in higher dispersity, smaller particle size and lower acidity of the Pt-based catalyst. Also it has been found that on catalyst Pt/Al-HY the value of ratio two-branched isomers:one-branched isomers was higher than on Pd-based catalyst.

The common feature of catalysts Pd and Pt supported on HY and mixed carrier is that the values of proportion of two-branched isomers on these catalysts are higher than that on catalyst Pd/Al. This fact should be understood from the mentioned above considerations of structure and properties of the carriers. The another feature is included in products distribution. In composition of cracking reaction on catalyst Pd/Al hydrocarbons C₄ and C₅ dominate, while the values of proportion C₃: C₄: C₅ obtained on catalysts supported on zeolite and mixed carrier are similar.

In order to increase activity, especially selectivity of catalysts, the pressure 0.7 MPa has been applied to the reaction conditions. As understood, although for the given reaction pressure does not influence its efficiency, but side reactions, such as cracking and coke formation, should be affected by values of applied pressure. It is clear that pressure should depress side reactions and therefore lead to increase of selectivity in isohexane as well as increase of catalyst stability. As shown in Table 3, when pressure increased from 0.1 MPa to 0.7 MPa, the values of conversion, selectivity and isohexane yield on catalysts increased, while the values of optimal temperatures decreased. On all the catalysts the conversion reached about 80 % and the selectivity – higher than 80 %.

Operating at 0.7 MPa at optimal reaction temperatures catalyst Pd/HY improved its stability from 1.25 to 14 hours and two catalysts Pd/Al-HY(2.5:1) and Pt/Al-HY(2.5:1) improved their stability up to more than 34 hours. At 0.7 MPa on catalysts Pd/HY và Pd/Al-HY values of ratio two-branched isomers:one-branched isomers increased from 1:(17-19) to 1:(5-6), and on Pt-based catalyst – from 1:8 to 1: 5. On the three mentioned catalysts the proportion between products of cracking also changed with creasing of pressure; the quantity of C₄ and C₅ fraction increased. This fraction should be used as LPG or a component of light gasoline. As seen from experimental data, at 0.1 MPa the Pt-based catalyst was better than the Pd-based compared catalyst, but at 0.7 MPa both the catalysts expressed similar activity and stability. That means, at high pressures, palladium can entirely replace platinum in preparation of catalysts for the reaction of n-hexane isomerization.

4. Conclusion

1. Mixed carriers for n-hexane isomerization catalysts containing gama-aluminium oxide and decationized faujasite zeolite have been prepared by method of mechanical mixing with different compositions. Mixed carriers expressed medium (between zeolite and alumina) acidity, gave better metal (Pt and Pd) dispersity (compared to zeolite and alumina) and improved reducibility of catalysts, so activity, selectivity and stability of catalysts increased. The optimal composition of mixed carriers has been observed as Al₂O₃:HY = 2.5:1.

2. At 0.1 MPa catalyst 0.35 wt.%Pt/Al₂O₃-HY(2.5:1) has been shown as the best catalyst for the given reaction. When reaction pressure increased to 0.7 MPa activity, selectivity and stability of all the studied catalysts increased. At this pressure and optimal temperatures all catalysts gave values about 80 % of conversion and isohexane selectivity with good stability during several dozens hours. It has been shown that for the given reaction at pressure 0.7 MPa catalyst 0.8%Pd/Al₂O₃:HY(2.5:1) expressed the activity, selectivity and stability similar to those of Pt-based catalyst.

Acknowledgements

The research group acknowledged the financial support from The Materials Science Council, Viet Nam cademy of Sciences and Technology.

References

- [1] T.G Kaufmann, A Kaldor, G.F Stuntz, M.C Kerby, L.L Ansell, Catalysis science and technology for cleaner transportation fuels, *Catalysis Today*, **62(1)**, 77-90 (2000).
- [2] A. Corma, J. Frontela, J. Lazaro, M. Perez, *Alkylation, Aromatization, Oligomerization and Isomerization of Short Chain Hydrocarbons over Heterogeneous Catalysts*, ACS Symposium Series, New York, 1991, p. 833.
- [3] P.J. Mangnus, A. Jacobs, *Hydroprocessing*, Akzo Chem. Div., Amersfort, Netherlands, 1991, p. 163.
- [4] A. Miyaji, R. Ohnishi, T. Okuhara, Skeletal isomerization of n-heptane over Pd-H₄SiW₁₂O₄₀ supported on SiO₂: Comparative study with typical bifunctional catalysts, *Appl. Catal. A*, **262**, 143-148(2004).
- [5] Maura H. Jordao, Vicemario Simoes, Dilson Cardoso, Zeolite supported Pt – Ni catalysts in n-hexane isomerization, 2007.
- [6] Kyeung Youl Jung and Seung Bin Park, Effect of Calcination Temperature and Addition of Silica, Zirconia, Alumina on the Photocatalytic Activity of Titania, *Korean Journal of Chemical Engineering*, **18(6)**, 879-888 (2001).
- [7] Pawelec B, Cano- Serrano E, Campos- Martin J M, Navarro R M, Thomas S, Fierro J L G, Deep aromatics hydrogenation in the presence of DBT over Au–Pd/ γ -alumina catalysts, *Appl. Catal. A: General*, **275**, 127-139 (2004).

- [8] Chang T –C, Chen J –J, Yeh C - T, Temperature-programmed reduction and temperature-resolved sorption studies of strong metal-support interaction in supported palladium catalysts. *J. Catal.* **96** 51-57 (1985).
- [9] Maura H. Jordão, Vicemario Simões, Dilson Cardoso, Zeolite supported Pt-Ni catalysts in n-hexane isomerization, *Applied Catalysis A*, **319** 1-6 (2007).
- [10] M. Alves Fortunato, D. Aubert, C. Capdeillayre, C. Daniel, A. Hadjar, A. Princivale, C. Guizard, P. Vernoux, Dispersion measurement of platinum supported on Ytria-Stabilised Zirconia by pulse H₂ chemisorption, *Applied Catalysis A*, **403(1)**, 18-24 (2011).
- [11] A. A. Taimoor, I. Pitault, F.C. Meunier, Correlation between deactivation and Pt-carbonyl formation during toluene hydrogenation using a H₂/CO₂ mixture, *J. Catal.* **278**, 153-161(2011).