

N-HEXANE ISOMERIZATION OVER Pt, Pd CATALYSTS SUPPORTED ON MIXES of HY+ γ -Al₂O₃

Dao Thi Kim Thoa², Huynh Ky Phuong Ha², Luu Cam Loc^{1*}, Nguyen Tuan Anh²

² Ho Chi Minh City University of Technology, Ho Chi Minh City, Vietnam

¹Institute of Chemical Technology, Vietnam Academy of Science and Technology
Ho Chi Minh City, Vietnam

e-mail: luucamloc@hcmut.edu.vn

Received Date: July 22, 2014

Abstract

In this study, a decationized form of faujasite zeolite HY and mixes of this zeolite with alumina γ -Al₂O₃ 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, SEM, EDS, TEM, XRD, TPR, H₂ pulse chemisorption (HPC), and TPD. Activity of the catalysts for n-hexane isomerization was tested at the temperature range 225-450°C and two values of pressure 0.1 and 0.7 MPa. In feed flows the molar 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 -Al₂O₃: HY was 2.5:1. The effect of the mixed carriers is included in the reduction of acidity and metal crystallites, increase of metal dispersity and reducibility of catalyst 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.

Keywords: HY, Mixed carrier, N-hexane isomerization, Pd, Pt, γ -Al₂O₃+HY

Introduction

Currently, the standardized criteria play an important role in the orientation of the petroleum refining toward not only the product usages but also the environmental impacts. The Euro-4 and Euro-5 standards require the significant reduction of aromatics and the maximum benzene concentration of 1 vol. % in gasoline. The United States and Europe define the limit of aromatic hydrocarbons in gasoline not to 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].

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, and isomerization. However, to reduce the content of aromatic hydrocarbons, reaction of light paraffin isomerization process must play an important role because by this way octane number of gasoline can be increased without rising 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 was liquid Lewis acid; 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 red-ox functions. Pt/zeolites catalysts are able to be operated 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-H₄SiW₁₂O₄₀ supported on SiO₂ and Pd-WO₃/ZrO₂ was 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 iso-hexane from n-hexane [5]. Nevertheless, with high acidity, zeolite HY also enhances the cracking process leading to the 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-paraffin to branched iso-paraffins with high octane number.

The purpose of this work is to study the influence of mixed carriers γ -Al₂O₃+HY on physico-chemical properties and activity of Pt, Pd-supported catalysts in order to create highly active contacts for n-hexane isomerization at normal pressure and at 0.7 MPa.

Experimental

Aluminium oxide was prepared by precipitating 5% solution of ammonia with solution of Al(NO₃)₃.9H₂O 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 to receive γ -Al₂O₃. 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. The procedure of catalyst preparation was described in detail in articles [6, 7]. 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 γ -Al₂O₃+HY with ratio Al₂O₃: HY = 3:1. By the same way Pt/Al-HY(2.5:1) means 0.35 wt.% Pt on mixed carrier γ -Al₂O₃+HY with ratio Al₂O₃: HY = 2.5:1.

Physico-chemical properties of the catalysts were characterized by some modern methods. Specific surface area of catalyst was obtained by Brunauer, Emmett, and Teller (BET) using Nova Station A with the lower limit is 0.01 m²/g, N₂ as the adsorption gas, saturated vapor pressure of 765 mmHg, temperature of the chamber is 77.35K, and volume of cylinder is 0.07645 cm³. The morphology and elementary distribution on the catalyst's surface were discovered by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) using FE-SEM Jeol 7401. Transmission Electron Microscopy (TEM) was utilized not only to analyze the morphology but also to measure the metal cluster on the surface and inside the pores with high resolution. The X-ray Diffraction (XRD) patterns of the catalysts were carried out using a Bruker D8 Advance at 35 kV, 30 mA, and CuK_α radiation. The XRD measurements were carried out at 2θ from 5° to 40°. The red-ox property was investigated by Temperature-Programmed Reduction (TPR). The dispersity and metal cluster size were studied by Hydrogen pulse chemisorption (HPC). Both TPR and HPC were conducted using Altamira Ami-200. The Temperature

Programmed Desorption (TPD) of adsorbed ammonia on the acid sites was carried out using nitrogen as a purge gas.

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 H₂:n-hexane 5.92; n-hexane concentration in feed 9.2 mol%; feed flow 7.5 l/h; catalyst weight 1.5 g. The reaction mixture was analyzed on the GC Agilent Technologies 6890⁺ with a FID detector, and DB 624 column with 30 m of length and 0.32 mm of outer diameter were used.

Result and Discussion

The XRD pattern of sample Pd/ γ -Al₂O₃ (line 1, Figure 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, containing 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 [8] 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 any characteristic peaks of Pt, Pd, or other phases were not observed.

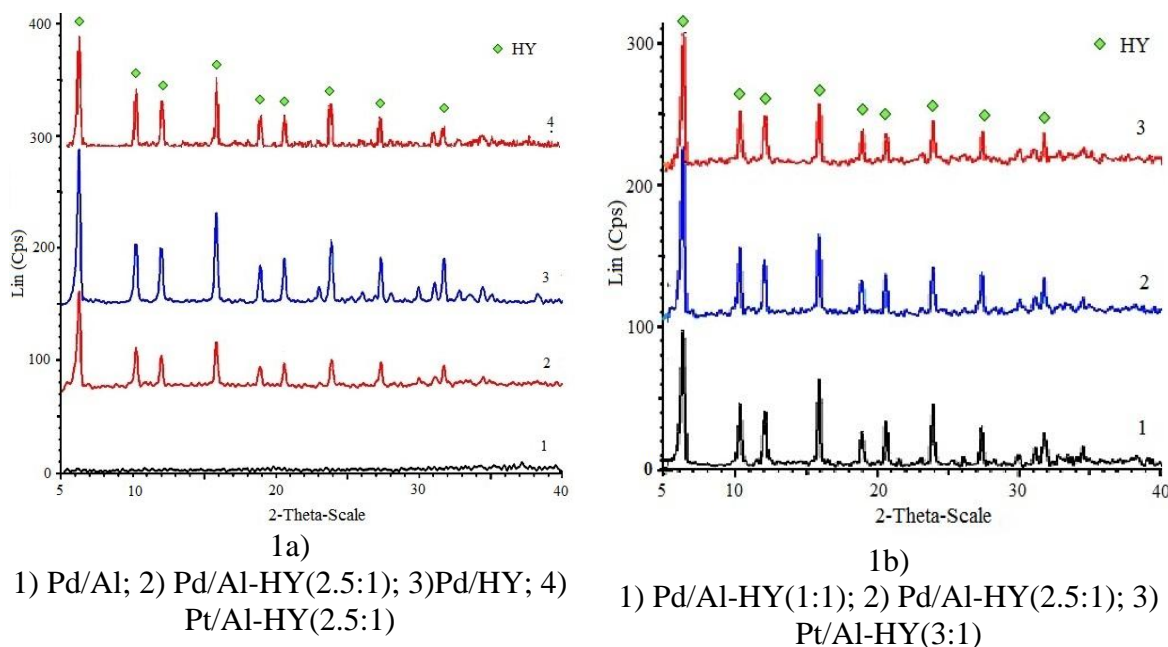


Figure 1. XRD patterns of catalysts

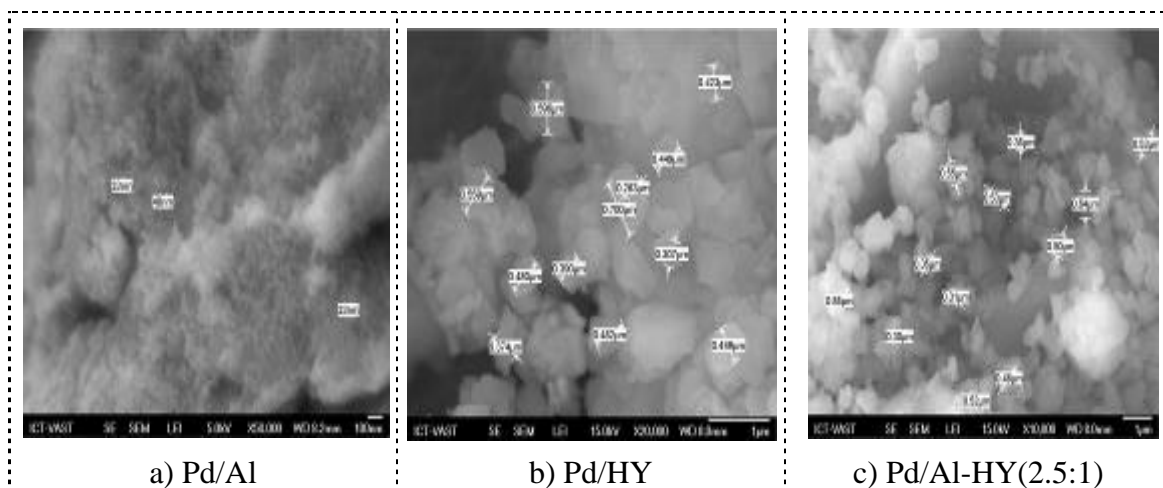


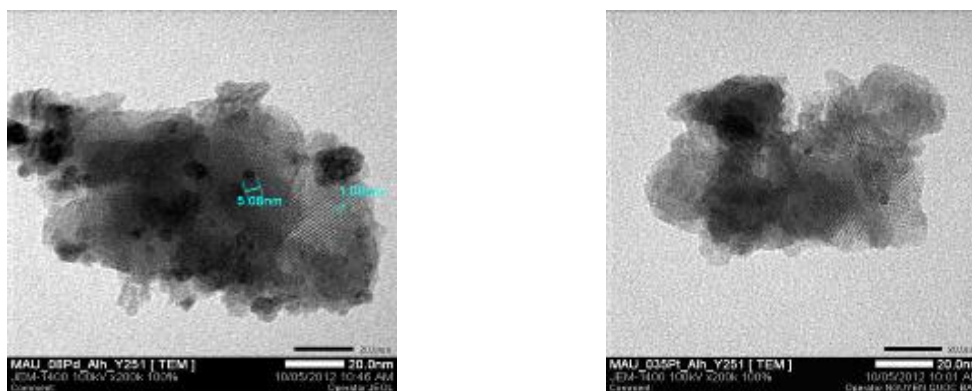
Figure 2. SEM of catalysts

SEM images (Figure 2a) indicates that aluminium oxide in catalyst Pd/Al exists in form of fine porous cotton with particle size in the range of 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 the surface of aluminium oxide with dimension of 300 x (350-550) nm and small particles (54-80 nm).

EDS pattern (not shown) indicated that on the surface of Pd/Al₂O₃ and Pd/HY catalysts the distribution of the elements is more uniform, while on Pd/Al-HY their distribution is less uniform. Elemental composition on the surface of the catalysts are presented in Table 1.

On Pd/Al sample surface concentration of Pd has been found very high (13.4 atom%), but as it seen from Table 1 the value of cluster size of Pd was the biggest and the dispersity was the lowest. On the surface of sample Pd/HY the value of ratio Si:Al = 3, closed to that in zeolite HY (the original zeolite was (Na₈₆ [(AlO₂)₅₆.(SiO₂)₁₃₆].260 H₂O). On this catalyst the surface concentration of Pd was found sufficiently low (1.24 atom%). 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). In this region Pd has very low concentration, only about 0.73 atom%. In the third region the values of concentrations of Al and Si were found identical, approximately 33-36 atom%, and concentration of Pd in this region is about 3 atom%. From the above analysis shows that, on the mixed carrier, Pd seems to be concentrated on the Si-rich surface, means on zeolite. It can be assumed that, in the mixed carrier, zeolite located on the surface of alumina, as confirmed by SEM data.

On TEM images (Figure 3) the Pd and Pt dispersed particles on the surface of catalysts could be observed. 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.



a) Pd/Al-HY (2.5:1)

b)Pt/Al-HY(2.5:1)

Figure 3. TEM images of catalysts

Table 1. Surface Area (S_{BET}); Crystallite Size of HY Calculated at $2\theta = 6.5^\circ$ (d_{HY}); Cluster Size of Pd, Pt (d_{clu}) and Metal Dispersity (γ) Determined by HPC, and Elemental Composition Determined by EDS

Catalyst	S_{BET} (m^2/g)	d_{HY} (nm)	d_{clu} (nm)	γ (%)	Elemental Composition(atom%)			
					O	Al	Si	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	16.85	48.03	1.24
Pd/Al-HY(3:1)	-	33.6	6.2	18.69	-	-	-	-
Pd/Al-HY(2.5:1)	285	34.1	6.1 5.08*	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	-	-	-	-
Pt/Al-HY(2.5:1)	245	32.7	1.7 2.0*	70.05	-	-	-	-

*) particle dimension of Pd, Pt determined by TEM

TPR diagrams (Figure 4) of Pd/Al, Pd/HY, and Pd/Al+HY (3 ratios of $Al_2O_3:HY$) catalysts had only one negative peak of H_2 desorption with $T_{max} = 65 - 80^\circ C$ (the plots in Figure 4 were inverted). According to Pawelec[9] for both Pd/Al and Au-Pd/Al samples, the presence of TPR peaks at about $81^\circ C$ 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 $31^\circ C$, indicative the reduction of bulk PdO. The negative peak of H_2 desorption at $84^\circ C$ is attributed to H_2 -desorption from the decomposition of a bulk palladium hydride formed through H-diffusion within the Pd crystallites [10]. So, the reduction peak on TPR diagrams of all palladium catalysts ($T_{max} = 65 - 80^\circ C$) characterizes H_2 -desorption from the decomposition of a bulk palladium hydride. 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 of $Al_2O_3:HY$. This should be understandable, because on the mixed carriers the Pd dispersion improved with zeolite content (Table 1).

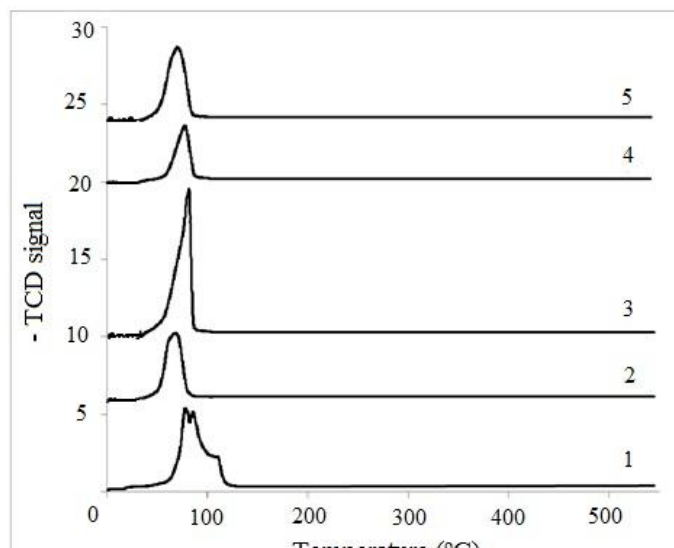


Figure 4. TPR diagrams of Pd catalysts: 1)Pd/Al; 2)Pd/HY; 3) Pd/Al-HY(3:1); 4) Pd/Al-HY(2.5:1); 5) Pd/Al-HY(2:1)

TPR diagram of catalyst Pt/Al-HY(2.5:1) (Figure 5) 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 the first kind reduced sites is two times higher than that of the second one. Jordao[5] showed two reduction peaks at 270 and 400 °C for catalyst sample 1.0 wt.% Pt/HUSY calcined at 500 °C. The first peak characterizes the reduction of Pt^{2+} located in sodalite cages and the second peak characterizes the reduction of Pt^{2+} located in hexagonal prisms. At this time, according to Fortunato [11], on catalysts Pt/YSZ the peak consuming hydrogen at 355-400°C is related to the hydrogen spillover from reduced particles of Pt to surface of YSZ.

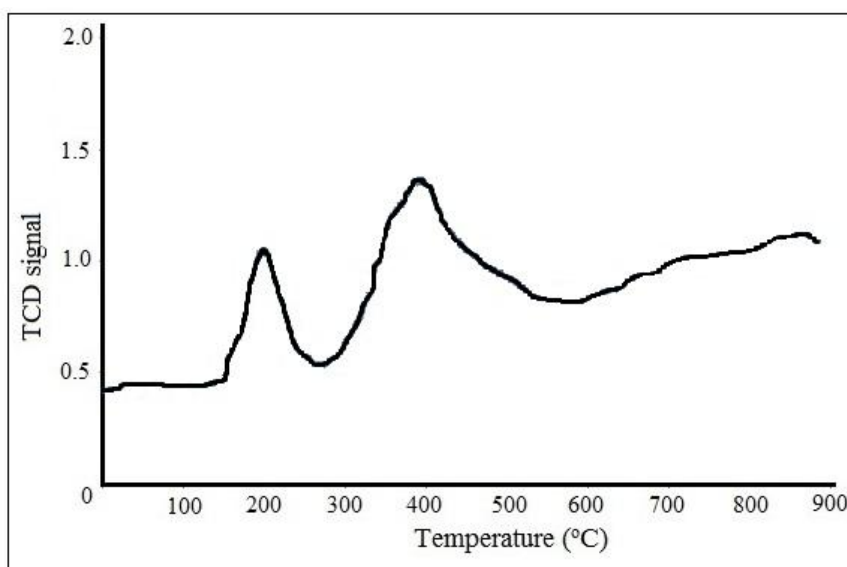


Figure 5. TPR diagrams of Pt/Al-HY(2.5:1) catalyst

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 Taimoor [12], 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.

Table 2. Maximum Reduction Temperatures (T_{max} , °C), Reduction Extents (K_{Red} , %), and Acidity of The Studied Catalysts

Catalyst	T_{max}	K_{Red}	Acidity (mmol NH ₃ /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				

Results in Table 2 indicate that for Pd-based catalysts the value of total acidity of sample Pd on γ -Al₂O₃ is the lowest, much lower compared to that of catalyst on zeolite HY. Acidity of the catalyst on mixed carrier lies between those of Pd/Al and Pd/HY. Among catalysts supported on Al₂O₃+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. N-hexane Conversion (X), Selectivity on Iso-Hexane (S_{i-C_6}), I-C₆ Yield (Y_{i-C_6}), 2,3-DMB:2-MP:3-MP Ratio, Cracking Selectivity (S_{cr}), and Stability (τ) of Catalyst at Optimal Temperature (T_{opt}) at Pressure of 0.1 and 0.7MPa (P)

Catalyst	P (MPa)	T_{opt} (°C)	X (%)	S_{i-C_6} (%)	Y_{i-C_6} (%)	2,3DMB: 2MP: 3-MP	S_{cr} (%)	τ (h)
Pd/Al	0.1	400	18	92	16.7	1:100:57	8	-
Pd/HY	0.1	350	32	59	18.9	1:12:7	41	1.25
	0.7	300	82	85	66.0	1:3:1.7	7	14
Pd/Al-HY(1:2)	0.1	325	34	72	24.5	1:12:7	28	-
Pd/Al-HY(1:1)	0.1	325	23	77	17.7	1:14:8	23	-
Pd/Al-HY (2:1)	0.1	300	19	90	17.1	1:8:24	10	-

Pd/Al-HY (2.5:1)	0.1	325	39	90	35.1	1:11:6	10	3
	0.7	325	79	84	66.4	1:4:2	16	>34
Pd/Al-HY (3:1)	0.1	325	29	92	26.7	1:11:7	8	-
Pt/Al-HY(2.5:1)	0.1	350	76	85	65	1:5:3	15	23.7
	0.7	325	82	81	69.7	1:3:2	19	>34

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 – 400 °C.

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 $Y_{iC6} = 16.7\%$, while catalyst Pd/HY started to appear activity at 250 °C and reached the maximum of activity at 350 °C with isohexane yield $Y_{iso} = 18.9\%$. 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 the content of zeolite in carrier, reaching a maximal value at some ratio of $Al_2O_3 : HY$ and after that decreases with zeolite content (Figure 6). As seen in Table 3, the optimal composition of carrier is $Al_2O_3 : HY = 2.5:1$. 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 Pd/HY. These factors should lead to the increase in activity and stability of the considered catalyst. Indeed, catalyst Pd/Al-HY(2.5:1) can be operated with good stability about 3 hours, while catalyst Pd/HY can keep stable activity only more than one hour.

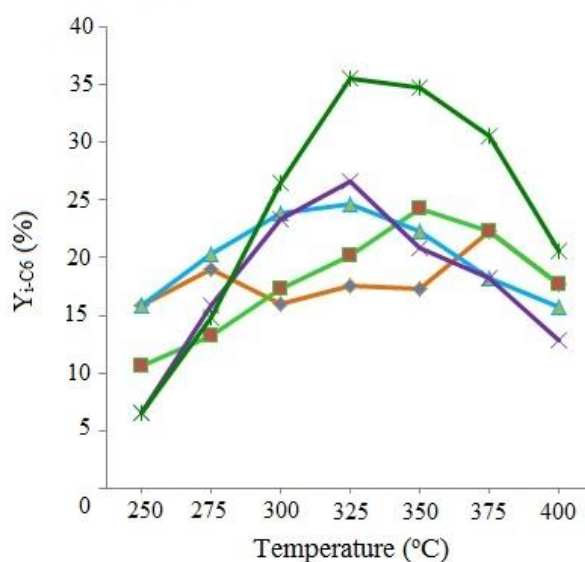


Figure 6. Activity of Pd/Al-HY catalysts

▲ Pd/Al-HY(1:2); ◆ Pd/Al-HY(1:1); ■ Pd/Al-HY(2:1);
✱ Pd/Al-HY(2.5:1); ✳ Pd/Al-HY(3:1)

At 0.1 MPa, compared to sample Pd/Al-HY(2.5:1), on catalyst Pt/Al-HY(2.5:1) the values of conversion and iso-hexane yield are higher, value of iso-hexane selectivity is a little lower and value of stability is higher (24 hours compared to 3 hours). The reason of this difference is included in the higher dispersity, the smaller particle size, and the 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 of 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 iso-hexane 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 iso-hexane yield on catalysts increased, while the values of optimal temperatures decreased. On all catalysts the conversion reached about 80 % and the selectivity is 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 and 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. 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.

Conclusions

Mixed carriers for n-hexane isomerization catalysts containing gamma-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.

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 iso-hexane selectivity with good stability during several dozen 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

Research group acknowledge the financial support from The Materials Science Council, Vietnam Academy of Science and Technology.

References

- [1] T.G. Kaufmann, A. Kaldor, G.F. Stuntz, M.C Kerby, and L.L. Ansell, "Catalysis science and technology for cleaner transportation fuels," *Catalysis Today*, Vol. 62, No. 1, pp. 77-90, 2000.
- [2] A. Corma, J. Frontela, J. Lazaro, and M. Perez, "Alkylation, aromatization, oligomerization and isomerization of short chain hydrocarbons over heterogeneous catalysts," *ACS Symposium Series*, New York, pp. 833, 1991.
- [3] P.J. Mangnus, and A. Jacobs, "Hydroprocessing," *Akzo Chemical Division*, Amersfort, Netherlands, p. 163, 1991.
- [4] A. Miyaji, R. Ohnishi, and T. Okuhara, "Skeletal isomerization of n-heptane over Pd-H₄SiW₁₂O₄₀ supported on SiO₂: Comparative study with typical bifunctional catalysts," *Applied Catalysis A: General*, Vol. 262, pp. 143-148, 2004.
- [5] M.H. Jordão, V. Simões, and D. Cardoso, "Zeolite supported Pt-Ni catalysts in n-hexane isomerization," *Applied Catalysis A: General*, Vol. 319, pp. 1-6, 2007.
- [6] L.C. Loc, D.T.K. Thoa, B.V. Tuong, N. Tri, and G.T. Hung, "Investigation into n-hexane isomerization over Pt/HZSM-5 catalysts," *Journal of Chemistry*, Vol. 50, No. 4A, pp. 324-328, 2012.
- [7] L.C. Loc, D.T.K. Thoa, P.N. Thuan, B.T. Huong, and H.S. Thoang, "Effect of treatment temperature of NH₄ZSM-5 and HZSM-5+ γ -Al₂O₃ on physico-chemical properties and activity of Pd in n-hexane isomerisation," *Journal of Chemistry*, Vol. 50, No. 4A, pp. 329-332, 2012.
- [8] K.Y. Jung, and S.B. Park, "Effect of calcination temperature and addition of silica, zirconia, alumina on the photocatalytic activity of titania," *Korean Journal of Chemical Engineering*, Vol. 18, No. 6, pp. 879-888, 2001.
- [9] B. Pawelec, E. Cano- Serrano, J.M. Campos-Martin, R.M. Navarro, S. Thomas, and J.L.G. Fierro, "Deep aromatics hydrogenation in the presence of DBT over Au-Pd/ γ -alumina catalysts," *Applied Catalysis A: General*, Vol. 275, pp. 127-139, 2004.
- [10] T.C. Chang, J.J. Chen, and C.T. Yeh, "Temperature-programmed reduction and temperature-resolved sorption studies of strong metal-support interaction in supported palladium catalysts," *Journal of Catalysis*, Vol. 96, pp.51-57, 1985.
- [11] M.A. Fortunato, D. Aubert, C. Capdeillayre, C. Daniel, A. Hadjar, A. Princiville, C. Guizard, and P. Vernoux, "Dispersion measurement of platinum supported on Ytria-Stabilised Zirconia by pulse H₂ chemisorption," *Applied Catalysis A: General*, Vol. 403, No. 1, pp. 18-24, 2011.
- [12] A.A. Taimoor, I. Pitault, and F.C. Meunier, "Correlation between deactivation and Pt-carbonyl formation during toluene hydrogenation using a H₂/CO₂ mixture," *Journal of Catalysis*, Vol. 278, pp. 153-161, 2011.