

COMPARISON OF Pt-Sn/ γ -Al₂O₃, Pt-Pb/ γ -Al₂O₃ AND Pt/ γ -Al₂O₃ CATALYSTS IN DEHYDROCYCLIZATION OF n-HEPTANE AT ATMOSPHERIC PRESSURE

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Abstract

Twelve catalysts on the basis of Pt/ γ -Al₂O₃ without and with Sn and Pb additives have been obtained and investigated. The content of Pt varied in the range of 0.15 ÷ 0.46 wt.% and the weight ratio of Pt:Sn (Pb) was changed in intervals of 0.75÷2.33 (weight ratio). Physicochemical characteristics of the catalysts were determined by several techniques, including nitrogen physisorption measurements, X-ray powder diffraction (XRD), hydrogen temperature-programmed reduction (H₂-TPR), hydrogen pulse chemisorption, transmission electron microscopy (TEM) and ammonia thermodesorption). Activity of the catalysts in the dehydrocyclization of n-heptane was studied at the temperature range of 400 ÷ 550°C. Addition of Sn and Pb led to changes in physico-chemical properties of the catalysts that increased the activity of platinum catalysts. It was found that optimal contents of Pt was 0.35 wt.% and optimal weight ratio Pt: Sn(Pb) was 2.33. The activity of the sample 0.35 wt.%Pt-0.15 wt.%Sn/ γ -Al₂O₃ and 0.35 wt.%Pt-0.15 wt.%Pb/ γ -Al₂O₃ was found to be higher than that of the non-promoted catalyst more than 1.5 times.

Keywords: Additives Sn and Pb, Dehydrocyclization, N-heptane, Pt/Al₂O₃ Catalysts

Introduction

Since fuel demand is continuously increasing and fossil fuel is being exhausted, liquid fuel synthesis from synthesis gas through Fischer-Tropsch reaction has been attracting many scientists. However, these liquid fuels are n-paraffins having low octane number. Hence, n-paraffin dehydrocyclization is gathering more interest in boosting RON for gasoline. The catalysts with the best performance are composed of Pt-based supported on Al₂O₃, promoted by another metal such as Re, Pd, Rh... The addition of small amounts of the second metal enable to increase the activity of platinum catalysts in the dehydrocyclization of n-paraffins [1, 2]. Although Sn and Pb are unactive or even poisonous in dehydrocyclization but their positive effect when they are present in the Pt/ γ Al₂O₃ are demonstrated.

The purpose of this study is to prepare promoted platinum catalysts and study the influence of Sn and Pb additives on properties and activity of the catalyst Pt/ γ -Al₂O₃ in dehydrocyclization of n-heptane.

Experimental

Firstly, the γ -Al₂O₃ support was prepared in laboratory using simultaneous drip (SD) method. 500 ml solution containing 100 grams of Al(NO₃)₃·9H₂O and 500 ml of solution of NH₃ 5% were used in this preparation. After that, the monometallic catalysts were prepared by impregnating method as following: Al₂O₃ (Merck and γ -Al₂O₃ prepared by SD method) was dried at 60, 110, 130°C for 2h at each temperature. After drying, the samples were calcined in 2h at 500°C. The treated Al₂O₃ was impregnated with solution of H₂PtCl₆·2H₂O 1,9.10⁻⁶M to obtain needed content of Pt. After stage of impregnation, the mixture was dried to remove water and dried at 110, 130°C in 2h at each temperature, calcined at 500°C in 4h in air stream. The bimetallic catalysts were prepared by a consecutive impregnation technique of the support with solutions in water, the first stage of SnCl₂, Pb(NO₃)₂ and the second stage of H₂PtCl₆·2H₂O. Before reaction the catalysts were activated in a flow of hydrogen with the volume velocity of 2 L/hrs. during 2 hours at 450°C.

Physico-chemical characteristics of catalyst samples were investigated and determined by methods of adsorption (BET), X-ray diffraction (XRD), Temperature-Programmed Reduction (TPR), H₂ pulse chemisorption (HPC), Transmission Electron Microscopy (TEM) and Ammonia Thermodesorption. Activity of the catalysts was determined in a microflow reactor under atmospheric pressure in the temperature range of 400 ÷ 550°C. The volume velocity of reaction gas flow was 3 L/hrs.; molar ratio H₂ : n-C7 = 6.2; the concentration of n-heptane was 5.3 mol.% and the weight of catalyst sample was 3 g. The reaction mixture was analyzed on the Gas Chromatograph Agilent Technologies 6890 Plus with a FID detector and capillary column HP-1 with methyl siloxane (30 m length; 0.32 mm outer diameter; 0.25 μ m thickness).

Octan number determined by research method (RON) of liquid fraction obtained in dehydrocyclization of n-heptane was calculated as following:

$$RON = \sum RON_i \cdot X_i \% \quad (1)$$

Where: RON_i: value of RON of component "i" in the liquid product.

X_i %: molar percentage of component "i" in the liquid product.

The particle size of Al₂O₃ ($d_{Al_2O_3}$) was calculated using the following equation [3]:

$$d_{Al_2O_3} = 6/\rho \cdot S_{BET} \quad (2)$$

where: ρ is specific density of the support (ρ of γ -Al₂O₃ is 3.60 g/cm³).

The catalysts are symbolized as followings: the figures in front of element symbols indicate the percentage of the corresponding element. Examples: a) 035Pt015SnAl is the catalyst containing 0.35 wt.% Pt and 0.15 wt.% Sn on γ -Al₂O₃ Merck; b) 035PtAl* is the catalyst containing 0.35 wt.% Pt and carried on prepared γ -Al₂O₃.

Results and Discussion

Comparing to Al₂O₃ (Merck), prepared Al₂O₃ had smaller particle size and higher specific surface area. Addition of Sn, Pb made the particle size of carrier to be bigger and specific surface area of catalyst is reduced, as seen in Table 1.

XRD results (Figure 1) of all samples comprise characteristic peaks of γ -Al₂O₃ at rotation angles $2\theta = 37.2, 45.6$ and 66.9° , but the diffraction peaks are very fuzzy. In the XRD spectrum of modified samples PtSnAl and PtPbAl no new peak have been found. These facts indicated that in these catalyst samples, γ -Al₂O₃ exists in the amorphous phase

and Pt, Sn and Pb with very small content and strongly interacting with alumina, exist in quite dispersed states.

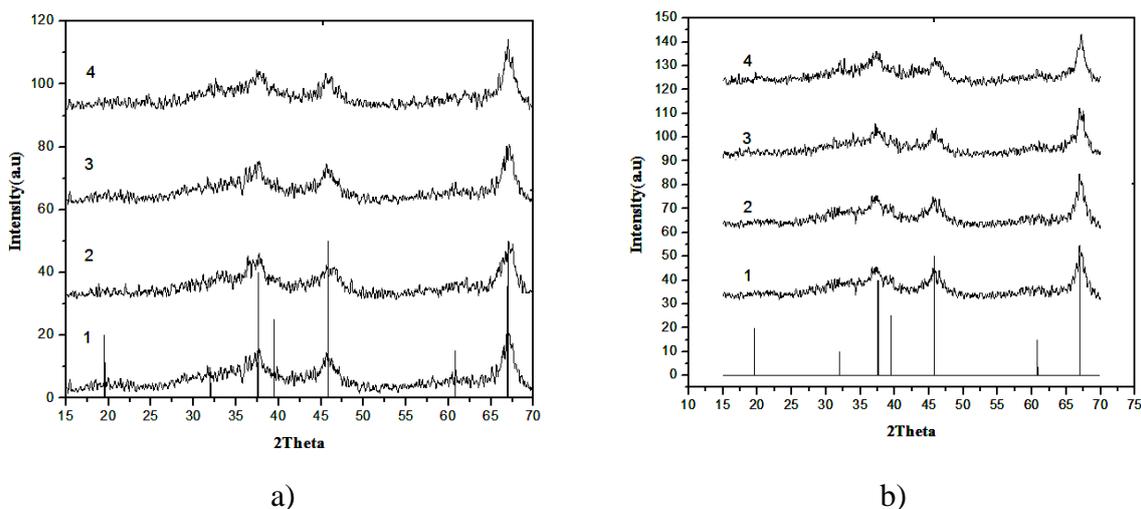


Figure 1. XRD spectra of PtSn/Al catalysts (a) and Pt-Pb/Al catalysts (b)
a) 1- 035Pt015SnAl, 2- 035Pt0233SnAl, 3-035Pt035SnAl, 4-035Pt0467SnAl
b) 1-035Pt015PbAl, 2-035Pt0233PbAl, 3-035Pt035PbAl, 4-035Pt0467PbAl

Table 1. Surface Specific Area (S_{BET}), Particle Size of Al_2O_3 ($d_{Al_2O_3}$), Dimension of Platinum Cluster Determined by TEM Image (d_{Pt}) and by H_2 Pulse Chemisorption (d'_{Pt}) and Pt Dispersity (γ_{Pt})

Catalyst	S_{BET} , m^2/g	$d_{Al_2O_3}$ nm	d_{Pt} , nm	d'_{Pt} , nm	γ_{Pt} , %
035PtAl*	176.6	9.4	-	-	-
035PtAl	131.5	12.7	1.58	1.2	91.0
046PtAl	-	-	-	1.3	96.8
035Pt015SnAl	96.8	17.2	1.1	1.2	98.8
035Pt0467SnAl	-	-	-	1.1	100
035Pt015PbAl	113.8	14.6	1.3	1.3	92.7
035Pt0467PbAl	-	-	-	1.5	80.2

Size of Pt clusters in the catalysts, which was determined by two methods is approximately the same. From the data of Table 1 and Figure 2, it follows that the addition of Sn additive in quantities of 0.15 ÷ 0.467 wt.% is able to decrease the cluster size of Pt from 1.6 nm to 1.1÷1.3 nm, leads to the increase of Pt dispersity from 91% to 100%. Meanwhile, the addition of 0.35% Pb increases the Pt dispersity up to ~ 93%, but if Pb concentration was still increased to 0.467%, a decrease of γ_{Pt} down to ~ 80% and an increase of cluster size of Pt to 1.5 nm were observed.

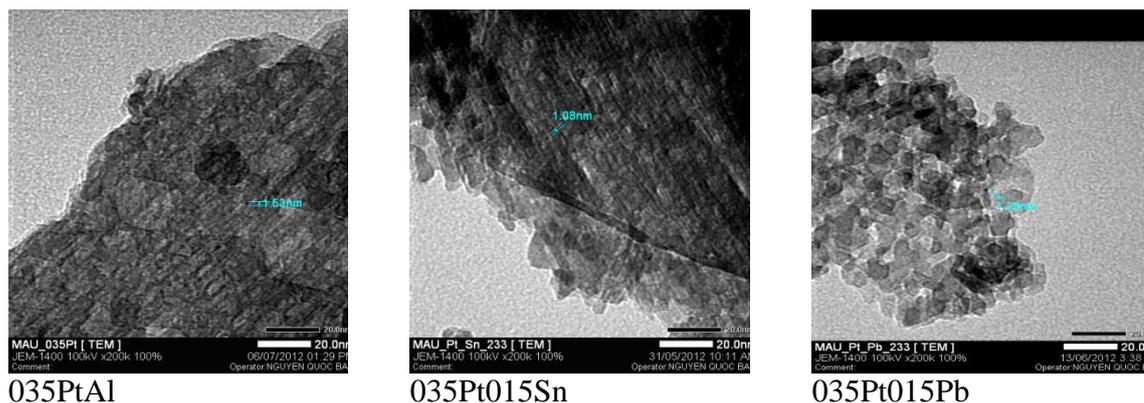


Figure 2. TEM images of given catalysts

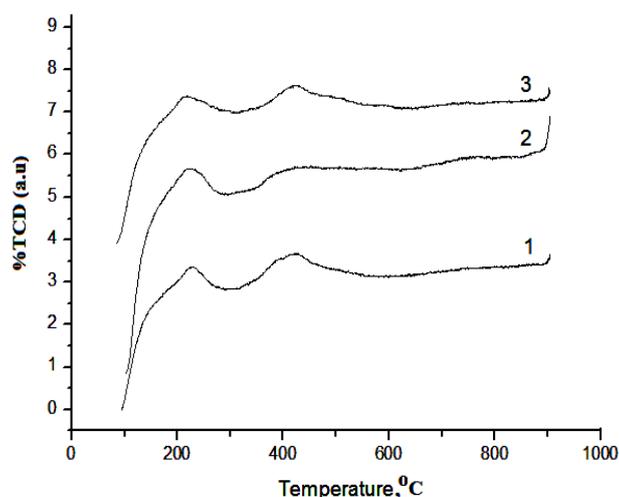


Figure 3. TPR diagrams of catalysts:1-035PtAl; 2-035Pt015SnAl; 3-035Pt015PbAl

Table 2. Maximum Reducing Temperature and Reduction Extent of the First Peak and Second Peak and Total Reduction Extent (K_{red}) of Catalysts

Catalyst	$Pt^{4+} \rightarrow Pt^{2+}$		$Pt^{2+} \rightarrow Pt^0$		K_{red} (%)
	T_{max1} (°C)	K_{red1} (%)	T_{max2} (°C)	K_{red2} (%)	
035PtAl*	220	39.4	420	13.5	52.9
035PtAl	229	1.3	422	56.6	57.9
035Pt015SnAl	222	23.8	430	49.0	72.8
035Pt0467SnAl	365	0.3	445	41.7	42.0
035Pt015PbAl	220	18.2	427	51.8	70.0
035Pt0467PbAl	304	33.0	434	1.4	34.4

On TPR diagram of the samples (Figure 3), two peaks were observed: The first peak at $T_{max} = 230 \div 250^\circ C$ and the another one at $T_{max} = 420 \div 430^\circ C$. According to Subramanian [4] in the hydrogen reduction process of Pt/ Al_2O_3 system takes place in the temperature range of $300 \div 500^\circ C$, but Castro et al [5] pointed out that on TPR diagram of Pt/ Al_2O_3 a reduction peak at $240^\circ C$ due to reduction of platinum have been observed. The author [6] demonstrated that, in the system Pt/ SiO_2 at temperature range of about $300 \div 400^\circ C$, Pt^{4+} is transformed into Pt^{2+} and partly converted into Pt^0 . In Pt/ Al_2O_3 system, a similar

phenomenon also is observed. However, due to the stronger interaction between Pt and alumina, the maximum reduction temperature was shifted to higher temperature region (above 300°C). The fact that platinum cations are inserted into the surface layer of support could stand for the reason in this circumstance. Therefore, it can be suggested that the first peak on TPR diagram characterizes the reduction of Pt^{4+} in Pt^{2+} , the second one characterizes the reduction of Pt^{2+} in Pt^0 .

From Table 2, it can be seen that, in the 035PtAl catalyst, platinum exists primarily as Pt^{2+} (98%), meanwhile, in the 035PtAl* one, Pt^{4+} centers are predominant and accounting for 75% of platinum centers being reduced. In addition, total reduction extent of catalyst 035PtAl is higher. As shown in Table 2, adding 0.15 wt.% of Sn or Pb into 035PtAl catalyst leads to sharply increase reduction extent of catalyst from 57.9% to 72.8% and 70%, respectively, and on promoted catalysts Pt^{2+} centers are predominant. This can be explained that in the promoted by Sn and Pb catalysts, on the one hand platinum is divided into cluster of small dimension (~1nm) as TEM analysis shows and on the other hand it is probable that additives present electronic effects on Pt. When the content of Sn and Pb in the catalysts increased to 0.467 wt.%, the reduction extent decreased and the maximum reducing temperature increased. This implicates the poisonous effect of Sn and Pb when their content in the catalysts is high.

Table 3. Acid Density of Catalysts

Catalyst	Acid Density (mmol NH ₃ /100g catalyst)			
	Weak	Medium	Strong	Total
035PtAl*	3.14	0.96	0.33	4.43
015PtAl	1.43	0.25	0.04	1.72
035PtAl	2.96	0.72	0.51	4.19
046PtAl	2.45	2.91	1.23	6.59
035Pt015SnAl	2.25	0.19	0.88	3.32
035Pt0233SnAl	3.14	0.70	0.38	4.22
035Pt035SnAl	3.90	1.36	0.52	5.78
035Pt0467SnAl	3.58	2.55	0.9	7.02
035Pt015PbAl	2.94	0.85	0.57	4.36
035Pt0233PbAl	3.14	0.61	0.51	4.26
035Pt035PbAl	3.20	0.67	0.46	4.33
035Pt0467PbAl	2.94	0.85	0.37	4.16

From data in Table 3, it can be observed that all the samples are characterized by the existence of acid centers, including weak, medium and strong, but the number of weak ones are predominant. It should be noted that 046PtAl catalyst is characterized by a greater number of acid centers compared to those of the 035PtAl sample. This demonstrates the existence of chlorate complex in the prepared catalysts. The adding of tin additive with content being higher than 0.15 wt.% led to the enhancement of catalyst acidity and the more concentration of Sn was added, the bigger number of acid sites was obtained. The acid density of 035Pt015Pb catalyst was slightly improved comparing to that of 035PtAl one. Moreover, when more Pb additive was present in the catalyst, the total number of acid centers fluctuated slightly around 4.3.

From the results presented on Figure 4, it follows that when the reaction temperature went up, the n-heptane conversion and toluene yield increased. Data on activity of the

studied catalysts at 550°C are presented in Table 4. The reaction products included unreacted n-heptane, isomers, naphthene, toluene and cracking products.

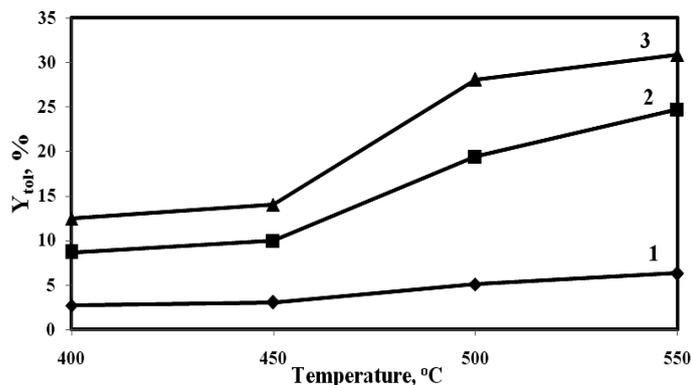


Figure 4. Toluene yield (Y_{tol}) on platinum- alumina catalysts containing different amounts of Pt: 1- 015PtAl; 2- 035PtAl; 3- 046PtAl

Table 4. n-Heptane Conversion (X), Toluene Selectivity (S_{tol}), Toluene Yield (Y_{tol}), Cracking Selectivity (S_{cr}), Naphtene Selectivity (S_{naph}), Octane Number of Liquid Product (RON) and Stability (τ) of Catalyst at 550°C

Catalyst	X, %	S_{tol} , %	Y_{tol} , %	S_{cr} , %	S_{naph} , %	RON	τ , h
035PtAl*	64	22	14	74	9	37.9	2.5
015PtAl	50	13	6	87	8	18.0	-
035PtAl	68	36	25	33	13	69.1	3.5
046PtAl	90	34	31	66	5	85.0	2.0
035Pt015SnAl	97	70	68	24	7	109.7	5.5
035Pt0233SnAl	70	61	43	28	7	70.8	-
035Pt035SnAl	65	62	40	29	10	63.7	-
035Pt0467SnAl	44	60	26	25	4	43.0	-
035Pt015PbAl	94	72	67	23	6	105.7	2.7
035Pt0233PbAl	68	68	46	19	7	70.4	-
035Pt035PbAl	54	61	33	24	6	52.0	-
035Pt0467PbAl	48	53	25	29	5	44.5	-

Among monometallic catalyst, 015PtAl catalyst expresses the lowest activity, selectivity, and toluene yield. This can be explained by low content of Pt and acidity of this sample. Meanwhile, 046PtAl catalyst is less stable than 035PtAl. As noted above, this catalyst is characterized by high acid density, which is favorable for cracking reaction, leading to coke formation. At 550°C, 035PtAl gave n-heptane conversion of 68%, toluene selectivity of 36%, and toluene yield of 25%.

Comparing with 0.35 wt.% Pt supported on γ -Al₂O₃ (Merck), catalyst supported on γ -Al₂O₃ (prepared) exhibited lower activity, selectivity and toluene yield although γ -Al₂O₃ (prepared) had a higher S_{BET} . This can be explained by the higher concentration of Pt⁰ obtained in the catalyst after reduction in H₂ stream in case of catalyst supported on γ -Al₂O₃ (Merck) as TPR analysis showed. At 550°C, 035PtAl* give n-heptane conversion of 64%, toluene selectivity of 22%, and toluene yield of 14%.

It can be observed from Figures 5 that for bimetallic catalysts modified with tin, the highest n-heptane conversion and toluene yield were obtained on the catalyst with Pt/additives weight ratio of 2.33 (Sn and Pb content is 0.15 wt.% separately). The observed positive effect of the catalyst containing 0.15 wt.% additive (Sn or Pb) can be explained by its smallest cluster size of Pt and the best reducibility. The same situation has been found in case using Pb as additive. Thus, it can be concluded that both additives show their geometric and electronic effects to O35PtAl catalyst.

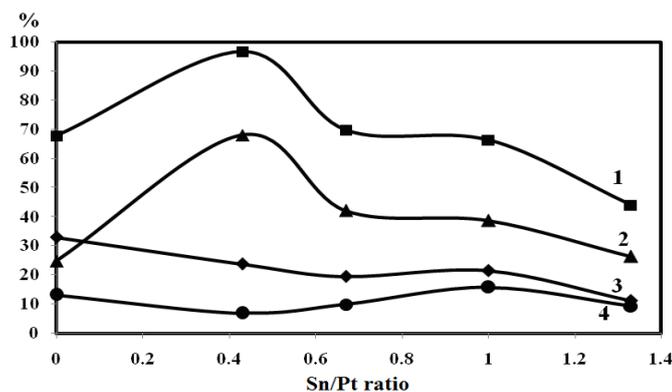


Figure 5. Influence of Sn content on catalyst activity and selectivity at 550°C: 1- n-heptane conversion; 2- conversion into cracking products; 3- conversion into toluene; 4- selectivity of naphthene

Experimental results showed that addition of 0.15 wt.% Sn should be able to increase the dispersity of Pt, and reduce the platinum cluster dimension and acidity of catalyst, that should lead to enhancement of catalytic stability, as seen in Table 4. As mentioned in Table 3, comparing with monometallic catalyst O35PtAl, addition of 0.15 wt.% Pb additive enhanced the acidity of catalyst, favors the formation of coke, that made the stability of catalyst to be reduced.

From experimental results (Table 4), for almost all catalysts, selectivity toward naphthene exhibits a decreasing trend when the temperature goes up. This can be explained that the cracking reaction increases more rapidly than the dehydrocyclization reaction with increasing temperature because of higher activation energy of cracking reaction.

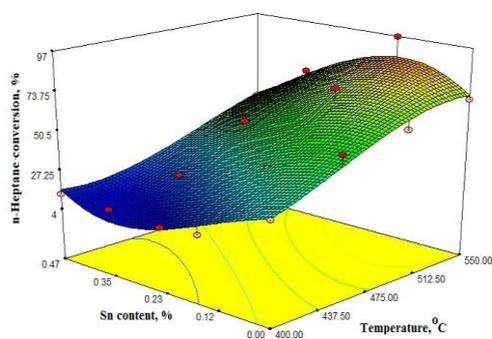


Figure 6. The variation of n-heptane conversion with reaction temperature and Sn content

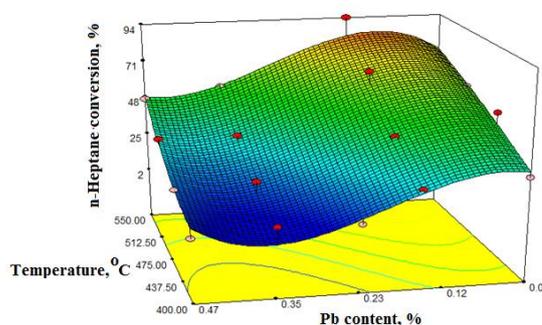


Figure 7. The variation of n-heptane conversion with reaction temperature and Pb content

Figure 6 and 7 show that, for Pt-Sn/Al₂O₃ and Pt-Pb/Al₂O₃ catalysts, n-heptane conversion increases when the reaction temperature goes up. In addition, in lower temperature interval (< 450°C), modified catalysts shown lower activity than that of non-promoted catalyst. This means Sn and Pb are poisonous to Pt/Al₂O₃ catalysts at low temperature. Nevertheless, at higher temperature interval (> 450°C), n-heptane conversion increases when Sn and Pb are added into Pt/Al₂O₃ catalyst. The highest activity of catalyst is obtained at 550°C on promoted catalysts with content of Sn and Pb of 0.15 wt.%.

Conclusions

In summary, the activity of Pt catalysts depends on the chemical and physical properties of γ -Al₂O₃. Alumina γ -Al₂O₃ (Merck) is suitable carrier for Pt catalysts in reaction dehydrocyclization.

The Pt content strongly influence Pt dispersity, reduction extent and acidity of catalyst. The more Pt content the higher activity of platinum-alumina catalysts. But catalyst containing 0.46 wt.% Pt obtained higher acidity, should have less stability than catalysts containing 0.35 wt.% Pt.

Sn and Pb additives present electronic and geometric effects on Pt/Al₂O₃ catalyst. Additives Sn and Pb should be able to increase the platinum dispersity, reduce the platinum cluster dimension and change acidity of platinum catalyst. Sn and Pb additives demonstrates the poisoning or activating Pt/Al₂O₃ catalyst depends on their concentration and reaction temperature. Sn and Pb additives act as poison for the platinum catalyst in the low temperature (< 450°C) and show promoted role in the high temperature (> 450°C). Optimum concentration of additive is 0.15 wt.% (the weight ratio Pt/additives = 2.33). Addition of 0.15 wt.% of Sn or Pb leads to enhancement of catalytic activity more than 1.5 times.

Addition of 0.15 wt.% Sn leads to increase stability of platinum catalyst, meanwhile due to enhancing the acidity of catalyst, addition of 0.15 wt.% Pb made the stability of catalyst to be reduced.

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