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

Conversion of n-heptane at atmospheric pressure over promoted aluminaplatinum catalysts

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Abstract

In order to improve our atmosphere and reduce air pollution caused by the usage of fossil fuels, the concept of reformulated gasoline was introduced in 1990s. The aromatics content in this gasoline is quite low, below 25%, in which benzene content is restricted about 1wt.% due to its cancerous character. Meanwhile, xylenes and other aromatics C_9-C_{10} are also reduced significantly because of their photochemical activity. On the contrary, toluene does not have these negative characters and, due to its high octane number, it could be used to substitute other aromatics in reformulated gasoline. Hence, world's demand for toluene exceeds its output in conventional catalytic reforming of naphtha fraction. In some refinery plants, the isomerization and reforming units are combined in a unified system in order to produce gasoline of high octane number. In this system, initial distillate fraction with boiling temperature < 85°C has been hydroisomerized, while distillate fraction with boiling point being higher than 85°C has been reformed. Most researches on isomerization have been concentrated on light distillate fraction containing mainly pentane and hexane whereas n-heptane has been converted in dehydrocyclization unit.
In this paper, a series of catalysts on the basis of Pt/γ-Al_2O_3 with and without additives (Sn, Sb, Pb, Cu) have been obtained and investigated. The content of Pt was varied in the range of 0.35 – 0.46 wt.% and the weight ratio of Pt : additives was changed in the intervals of 0.5 – 2.33 (wt.). Physico-chemical characteristics of the catalysts were determined by BET Adsorption, TEM, XRD, TPR and NH_3-TPD methods. The activity of the catalysts in dehydrocyclization of n-heptane was studied at the temperature range of 400–550°C and at atmospheric pressure. The study found that the optimal content of Pt was 0.35 wt.%, of Sn, Sb, Cu were 0.15; 0.35 and 0.7 wt.%, respectively.
As it follows from the study results, Cu additive showed geometric effect, Cu strongly interacts with Al_2O_3 to form copper-aluminate spinel, while Pb, Sb and Sn additives expressed electronic effect on Pt. An addition of these additives to Pt/γ-Al_2O_3 catalyst led to a reduction of catalyst acidity and an increase of reduction degree of Pt^{2+}. As a result, the activity and stability of catalyst are improved. On the promoted catalysts, conversion of n-heptane increased from 0.68 to 0.84 – 0.97 and the yield of toluene went up from 0.25 to 0.45; 0.68 and 0.70, correspondingly in addition to 0.7wt.%Cu; 0.15wt.%Sn and 0.35wt.%Sb.

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1. Introduction

Toluene does not represent cancerous character as benzene or produce photochemical activity like xylene and other aromatics C_9–C_{10} [1]. In addition, it expressed a high octane number. Hence, it could replace the other aromatics in the reformulated gasoline. However, the world's demand for toluene exceed it's output in conventional catalytic reforming of naphtha fraction. Therefore, it is necessary to find out and develop new producing methods that create more toluene than the previous one [2]. A choice with a good prospect is the dehydrocyclization of n-heptane on alumina-supported platinum catalyst. Moreover, the addition of small amounts of the second metal, thus producing so-called bimetallic catalysts, enable to increase the activity of platinum catalysts in dehydrocyclization of n-paraffins [3, 4]. Although Sn, Pb, Sb and Cu are unactive or even poisonous for dehydrocyclization but their positive effect when they are present in the Pt/γ-Al$_2$O$_3$ have been demonstrated.

The purpose of this study is to prepare promoted platinum catalysts and study the influence of Sn, Pb, Sb and Cu additives on physico-chemical properties and activity of the catalyst Pt/γ-Al$_2$O$_3$ in dehydrocyclization of n-heptane.

2. Experimental

The bimetallic catalysts were prepared by a consecutive impregnation method of the support with aqueous solutions of SnCl$_2$, Pb(NO$_3$)$_2$, SbCl$_3$ or Cu(NO$_3$)$_2$, in the first stage and of H$_2$PtCl$_6$.2H$_2$O in the second stage. Before running reaction the catalysts were activated in 2 hours at 450°C in an hydrogen flow with velocity of 2 l/hrs.

Physico-chemical characteristics of catalyst samples were investigated and determined by methods of adsorption (BET), X-ray diffraction (XRD), Temperature-Programmed Reduction (TPR), H$_2$ pulse chemisorption (HPC), Transmission Electron Microscopy (TEM) and Ammonia Thermodesorption. Activity of the catalysts was determined in a microflow reactor under atmospheric pressure at the temperature range of 400 ÷ 550°C. The volume velocity of reaction gas flow was 3 l/hrs; molar ratio H$_2$:nC7 = 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 μm thickness).

The catalysts are symbolized as follows: 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-Al$_2$O$_3$ Merck; b) 035PtAl* is the catalyst containing 0.35 wt.% Pt and carried on prepared γ-Al$_2$O$_3$.

3. Results and discussion

XRD spectrum (Fig.1) of all samples comprise characteristic peaks of γ-Al$_2$O$_3$ at rotation angles 2θ = 37.2, 45.6 and 66.9^o, but the diffraction peaks are very fuzzy. In the XRD spectrum of modified samples Pt-Sn/Al, Pt-Pb/Al, Pt-Cu/Al and Pt-Sb/Al, no new peak have been found. This fact indicates that in these catalyst samples, γ-Al$_2$O$_3$ exists in the amorphous phase and Pt, Sn, Pb, Cu, Sb with very small content and strongly interacting with alumina, exist in quite dispersed states. Particle size of Al$_2$O$_3$ in the promoted catalysts as well as monometallic platinum catalyst are represented in table 1 and calculated with the following equation [5]:

$$d = 6/\rho.S_{BET} \qquad\qquad\qquad\qquad (1)$$

where: ρ is specific density of the support (ρ of γ-Al$_2$O$_3$ is 3.60 g/cm^3) and S$_{BET}$ – specific surface area.
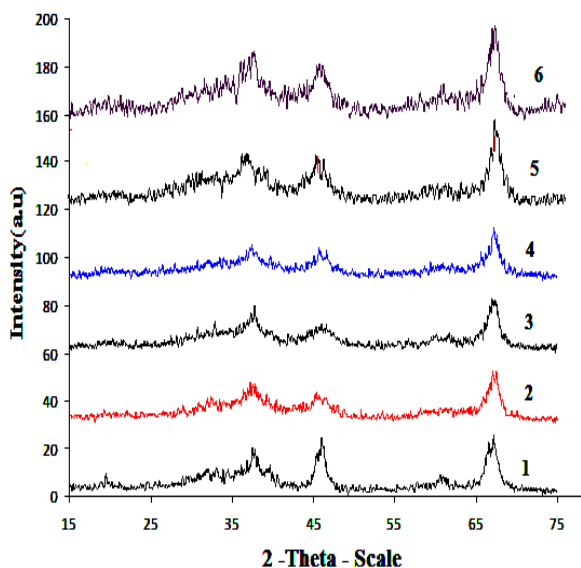
Fig. 1. XRD spectrum of catalysts:
1- 035PtAl*, 2- 035PtAl, 3- 035Pt07CuAl, 4 -035Pt035SbAl;
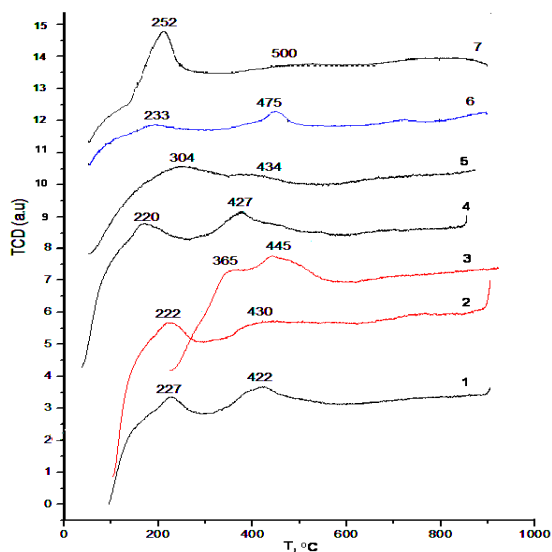5- 035Pt015PbAl, 6- 035Pt015SbAl

Fig. 2. TPR diagram of catalysts:
1-035PtAl, 2-035Pt015SnAl, 3- 035Pt0467SnAl,
4-035Pt015PbAl, 5- 035Pt0467PbAl, 6 -035Pt035SbAl,
7- 035Pt07CuAl

Addition of Sn, Pb, Sb or Cu made the particle size of carrier to be bigger and specific surface area of catalyst is reduced, as seen in Table 1.

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}); Maximum reducing temperature and reduction extent of the first peak and second peak and total reduction extent (K_{Red}) of catalysts

Catalyst	S_{BET} (m^2/g)	$d_{Al_2O_3}$	d_{Pt}	d'_{Pt},	γ_{Pt} (%)	$Pt^{4+} \rightarrow Pt^{2+}$		$Pt^{2+} \rightarrow Pt^{0}$		K_{red} (%)
			(nm)			T_{max1} (^oC)	K_{red1} (%)	T_{max2} (^oC)	K_{red2} (%)	
035PtAl	131.5	12.7	1.6	1.2	91.0	229	1.3	422	56.6	57.9
035Pt015SnAl	96.8	17.2	1.1	1.2	98.8	222	23.8	430	49.0	72.8
035Pt0467SnAl	-	-	-	1.1	100.0	365	0.3	445	41.7	42.0
035Pt015PbAl	113.8	14.6	1.3	1.3	92.7	220	18.2	427	51.8	70.0
035Pt0467PbAl	-	-	-	1.5	80.2	304	33.0	434	1.4	34.4
035Pt035Sb	93.9	-	1.1	-	-	233	22.3	476	68.3	90.6
035Pt07CuAl	95.6	-	1.1	-	-	252	72.0	500	7.84	79.8

Cluster size of Pt in the catalysts was determined by H_2 pulse chemisorption and TEM (Fig.3) methods is approximately the same. From the data of Table 1, the addition of Sn, Pb, Sb and Cu additive in quantities of 0.15 ÷ 0.70 wt.% is able to decrease the cluster size of Pt from 1.58 nm to 1.0÷ 1.3 nm. The Pt dispersity is increased by 1.5 times, from 67% to 100% when 0.15 wt.% Sn is added to PtAl catalyst. The positive effect of Sn additive is still remained when the amount of Sn is increased to 0.467 wt.%. Meanwhile, the addition of 0.15 wt.% Pb increases the Pt dispersity up to ~ 93%, but continued increase Pb concentration up to 0.467 wt.% led to a decrease of value of γ_{Pt} down to ~ 80% and cluster size of Pt increased up to 1.5 nm.

a) 035PtAl

b) 035Pt015SnAl

c) 035Pt015PbAl

d) 035Pt035SbAl

e) 035Pt07CuAl
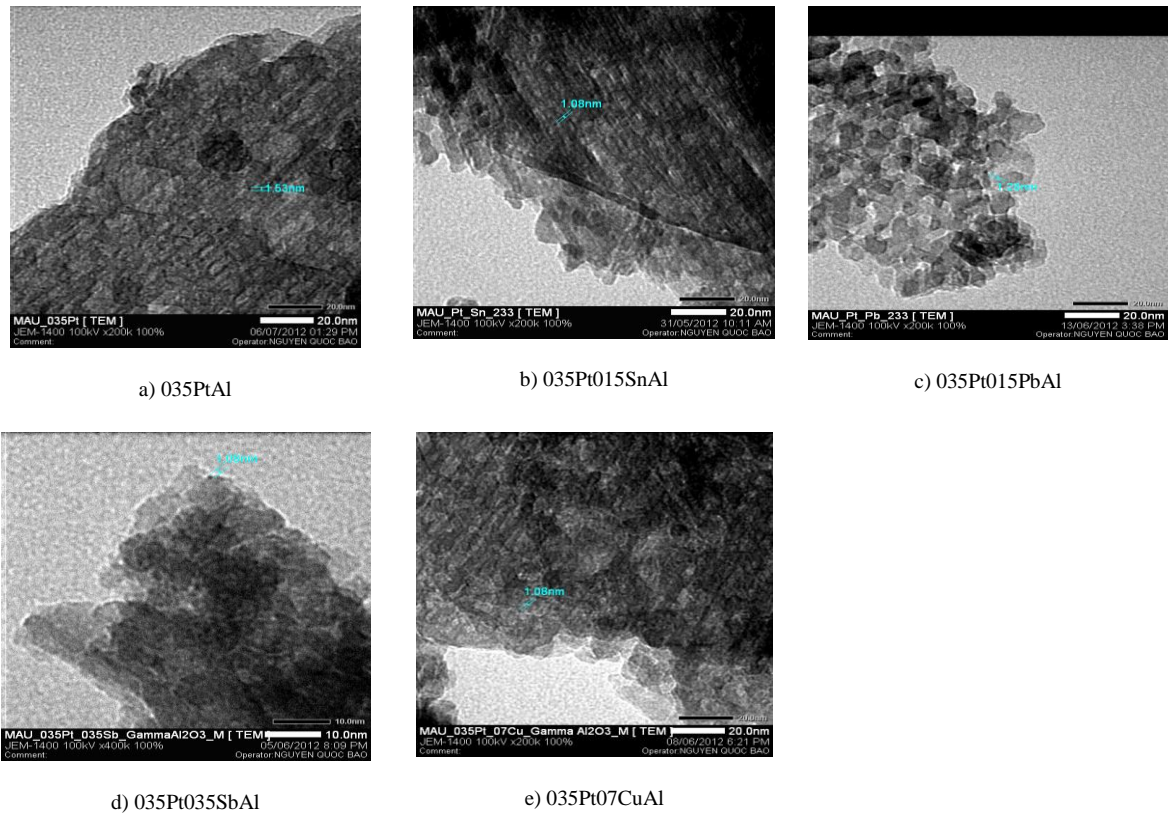
Fig. 3. TEM images of catalysts

On TPR diagram of the samples (Fig. 2) one can observe two peaks: The first peak at $T_{max}= 230 \div 250^{o}C$ and the other one at $T_{max}= 420 \div 430^{o}C$. According to [6], in the hydrogen reduction process takes place in the temperature range of $250 \div 400^{o}C$, platinum existed in state of high dispersity. The author [7] demonstrated that, in the system Pt/SiO_2, at temperature range of about $300 \div 400^{o}C$, Pt^{4+} is transformed into Pt^{2+} and partly converted into Pt^{o}. In Pt/Al_2O_3 system, a similar phenomenon also is observed, but due to the stronger interaction between Pt and alumina the maximum reduction temperature was shifted to higher temperature region (above $300^{o}C$). This might be explained by the fact that platinum cations are inserted into the surface layer of support. 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^{o}.

The addition of 0.15 wt.% of Sn or Pb into PtAl catalyst leads to a remarkable increase of reduction extent of catalyst from 57.9% to 72.8% and 70%, respectively (table 1), and on promoted catalysts, Pt^{2+} centers are predominant. Besides, the reduction extent is drastically increased from 57.9% to 90.6% when 0.35 wt.% Sb is added to 035PtAl catalyst. As it known [8], CuO in $CuO/\gamma-Al_2O_3$ catalyst is reduced at $300^{o}C$ and $375^{o}C$. So, two reduction peaks in TPR diagram of PtCu/Al (pattern 7) characterirized for reduction of platinum. As is follows from Table1, addition of 0.7 wt.% Cu also leads to an increase of K_{red} to 79.8%. This can be explained that in the promoted by Sn, Pb, Cu or Sb catalysts, platinum is divided into cluster of small dimension (~1nm) as TEM analysis shows. 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.

Comparing among Sn, Pb, Cu and Sb additives, one can assert that PtSbAl catalyst has the highest reduction extent and PtPbAl catalyst has the lowest maximum reduction temperatures T_{max1} and T_{max2}. However, in Cu promoted catalyst, the amount of Pt^{2+} ion reduced at low temperature is much more than the ones promoted by Sn, Pb and Cu. This can be correlated with the appearance of amorphous spinel $CuAl_2O_4$ in the support. In addition, it is claimed that the presence of Sn, Pb and Sb causes to PtAl catalyst electronic effect forming bimetallic clusters. The interaction appearing in these clusters impose causes platinum ions be reduced more easily in the temperature interval of $200 \div 500^{o}C$.

Table 2. Acid characteristics of catalysts (mmol/100 g catalyst)

Catalyst	Acid density (mmol NH$_3$/100g catalyst)			
	Weak	Medium	Strong	Total
035Pt/Al	2.96	0.72	0.51	4.19
035Pt015Sn/Al	2.25	0.19	0.88	3.32
035Pt0467Sn/Al	3.58	2.55	0.90	7.02
035Pt015Pb/Al	2.94	0.85	0.57	4.36
035Pt0467Pb/Al	2.94	0.85	0.37	4.16
035Pt-0233Sb/Al	2.70	0.15	0.12	2.97
035Pt-035Sb/Al	2.24	0.16	0.22	2.62
035Pt-047Sb/Al	1.91	0.20	0.26	2.37
035Pt-047Cu/Al	2.71	0.76	0.08	3.55
035Pt-07Cu/Al	1.78	0.22	0.10	2.10
035Pt-105Cu/Al	2.50	0.23	0.18	2.91

Table 2. shows 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. The adding of tin additive with content higher than 0.15 wt.% led to enhancing acidity and the more the concentration of Sn the bigger the number of acid sites. Nevertheless, the increase of Cu or Sb content in the catalyst leads to the decrease of acid density. The reason for this is that the strong interaction between Cu and Al_2O_3 forming $CuAl_2O_4$ spinel, led to decrease of Bronsted and Lewis acid sites amount while electronic effect of Sb on Pt species is used to explain the case of PtSbAl catalysts. Catalyst promoted with 0.7 wt.% Cu has the lowest number of acid sites. Added Pb in quantities of $0.15 \div 0.467$ wt.% does not influence the acidity of catalysts.

From the experimental results, increasing temperature reaction the n-heptane and toluene yield increases. The activity of Pt-based catalysts in dehydrocyclization of n-heptane at $550^{o}C$ are presented in Table 3. The reaction products included unreacted n-heptane, isomers, naphthene, toluene and cracking products. In bimetallic catalysts modified with Sn, Pb, Cu and Sb, the highest n-heptane conversion (X) and toluene yield (Y_{tol}) are obtained on the catalyst with the content of aditive being 0.15%, 0.15%, 0.7%, 0.35%, respectively. The observed positive effect of the catalyst containing optimal content of catalyst can be explained by their smallest crystal size of Pt and the best reducibility.

The addition of additives should be able to increase the dispersity of Pt, and to reduce the platinum cluster dimension and acidity of catalyst, that should lead to enhancement of catalytic stability, as seen in Table 3. Among the optimal catalysts, 035Pt015Sn showed the best catalytic performance, with X of 96.7%, Y_{tol} of 72.1%

and Y_{DHC} of 82.8, and stability of 4.5 hours. This can be a consequence of the highest Pt dispersity (γPt), smalles size of platinum cluster and relativly high reduction extent of this catalyst. Meanwhile, 035Pt07CuAl catalyst has shown a lower activity, having X of 83.1% and Y_{tol} of 45.1% in dehydrocyclization process although it contains platinum cluster with small dimension. In this case, low acidity and small value of reduction extent are expected to explain the phenomenal.

Table 3. n-Heptane conversion (X), toluene selectivity (S_{tol}), other cyclic hydrocarbons selectivity (S_{cycl}), cracking selectivity (S_{cr}), toluene yield (Y_{tol}), yield of total cyclic hydrocarbon (Y_{DHC}), and stability (τ) of catalyst at 550°C

Catalysts	X, %	S_{tol}, %	$S_{cycl,}$ %	$S_{cr,}$ %	Y_{tol}, %	$Y_{cycl,}$ %	Y_{DHC}, %	τ, h
035PtAl*	63.9	21.5	7.4	74.0	13.6	4.5	17.9	2.5
015PtAl	49.6	12.7	7.7	87.4	6.3	3.5	9.8	-
035PtAl	67.7	36.5	13.1	32.9	24.7	8.8	33.5	3.5
046PtAl	89.8	34.4	5.0	65.6	30.8	4.5	35.3	2
035Pt015SnAl	96.7	74.6	11.0	14.4	72.1	10.7	82.8	5.5
035Pt0233SnAl	69.8	61.3	9.9	27.8	42.8	6.9	49.7	-
035Pt035SnAl	65.1	61.5	15.7	29.0	40.1	10.2	50.3	-
035Pt0467SnAl	44.0	60.1	9.3	25.2	26.4	4.0	30.4	-
035Pt015PbAl	93.8	71.5	6.6	23.2	67.0	6.2	73.1	2.7
035Pt0233PbAl	67.6	67.8	9.9	19.5	45.8	6.6	52.4	-
035Pt035PbAl	53.5	61.4	10.7	24.5	32.9	5.7	38.6	
035Pt0467PbAl	47.5	53.1	11.5	29.4	25.2	5.5	30.7	-
035Pt0175SbAl	74.3	73.3	5.0	17.1	54.5	3.7	58.2	
035Pt0233SbAl	78.5	81.6	5.0	11.9	64.0	3.9	67.9	
035Pt035SbAl	84.3	83.1	3.6	11.2	70.1	3.0	73.1	4.5
035Pt0467SbAl	69.4	88.5	5.2	3.0	61.5	3.6	65.1	
035Pt0175CuAl	59.8	45.8	12.8	28.3	27.3	7.6	34.9	
035Pt0233CuAl	56.2	41.4	11.6	35.3	23.3	6.5	29.8	
035Pt035CuAl	69.1	50.0	14.0	31.2	29.9	9.6	39.5	
035Pt047CuAl	81.5	40.8	10.9	51.5	33.3	8.9	42.2	
035Pt07CuAl	83.1	54.2	10.8	27.7	45.1	9.0	54.1	4.5
035Pt1.05CuAl	78.2	57.0	9.2	30.6	44.5	7.0	51.5	

* τ : the duration of time after that the catalyst activity is reduced by 30%.

As Table 2, comparing with monometallic catalyst 035PtAl, addition of 0.15 wt.% Pb additive enhanced the acidity of catalyst, favors the formation of coke, that could induce the stability of catalyst to reduce.

In comparison with 035Pt015Sn sample, the catalysts contained 0.467 wt.% of Sn or Pb additive showed the lower activity, selectivity, and toluene yield. As noted above, these catalysts are characterized by the least

reduction extent and highest maximum reducing temperature and too high acid density. In other words, the reducibility of this catalysts is worse.

4. Conclusions

From the experimental results it was concluded:

Sn, Pb and Sb additives present electronic and geometric effects on Pt/Al_2O_3 catalyst. Copper interacts strongly with Al_2O_3 forming aluminates spinel that causes the reduction of catalysts' acidity, the increase of reduction extent of platinum ion.

Additives Sn, Sb and Pb should be able to increase the reducibility and platinum dispersity, reduce the cluster size of Pt and change acidity of platinum catalyst. In addition, Sn and Pb additives demonstrates the poisoning or activating Pt/Al_2O_3 catalyst depending on the their concentration and reaction temperature. The PtAl catalyst contained 0.15 wt.% of Sn or Pb expressed the best performance, while optimum content of Sb and Cu is 0.35 and 0.7 wt.%, respectively.

On the promoted catalysts, conversion of n-heptane increased from 0.68 to 0.84÷0.97 and the yield of toluene went up from 0.25 to 0.45; 0.68 and 0.70, correspondly to addition of 0.7 wt.% Cu; 0.15 wt.% Sn and 0.35 wt.% Sb.

Catalyst promoted by 0.15%Sn has been shown to be the best one for n-hexane isomerization.

Acknowledgements

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