

New Development in Catalytic Reforming Process to Produce High Octane Gasoline

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Abstract

In this work, improved catalytic reforming reaction was carried out through using reaction promoters Sn, In and Ge. Four types of catalysts were prepared: Pt/HY, Pt-Sn/HY, and Pt-Sn-In/HY, and Pt-Sn-Ge/HY. The weight percentage of metals were 0.5 % for Pt and 0.1% for each of Sn, In and Ge.

The performances of catalysts (activity, selectivity and catalyst stability) were studied using Iraqi heavy naphtha of Al-Dura refinery (Baghdad) as feedstock. The catalytic reforming unit consisted of a vertical tubular stainless steel reactor of 20mm internal diameter, 30 mm external diameter and 680 mm height. The operating pressure was atmospheric, and the operating temperatures varied between 425 to 525 °C. For all experimental runs: the weight hourly space velocity WHSV =2, the catalyst amount = 50 g, and H₂/HC ratio =3.

The results showed that the best reforming temperature over all four types of prepared catalysts was 475 °C which gave the highest conversion of heavy naphtha to high octane products (aromatics and branched isomers). It was concluded that the trimetallic catalyst Pt-Sn-In/HY and Pt-Sn-Ge/HY show high selectivity to

desired reforming products with 91.5% and 85% respectively. On the other hand, the Pt-Sn/HY and Pt/HY, catalysts show selectivities of 79% and 74% respectively.

The results indicated a clear increase in catalyst stability with high resistance to coke formation for catalysts promoted with In and Ge as a third metal. Also, it was noted that the production of aromatics and isomers are increased for both types of trimetallic catalysts Pt-Sn-In/HY, and Pt-Sn-Ge/HY under the same operating conditions.

Keywords: Heavy naphtha reforming; Pt/HY; Pt-Sn/HY; Pt-Sn-In/HY; and Pt-Sn-Ge/HY catalysts.

الخلاصة

في هذا البحث تم اعداد دراسة لغرض تطوير عملية التهذيب بالعامل المساعد باستخدام مرقيات للعوامل المساعدة المستخدمة في العملية (Sn, In and Ge)، حيث تم تحضير اربعة انواع من العوامل المساعدة المحملة على الزيولايت نوع Y

Pt/HY, Pt-Sn/HY, and Pt-Sn-In/HY, and Pt-Sn-Ge/HY بنسب معادن 0.5% للبلاتين و 0.1% لكل من Sn و In و Ge. تم دراسة اداء العوامل المساعدة المحضرة باستخدام مادة النفثا العراقية الثقيلة (مصفى الدورة) كمادة اولية للعملية. تم الدراسة في منظومة مصنعة من الحديد المقاوم للصدى بأبعاد 20 و 30 ملم للقطر الداخلي والخارجي للمفاعل وبطول 680 ملم. الضغط المستخدم كان ضغط جوي واحد ودراسة التفاعل بمدى حرارة تتراوح بين (425-525 م°)، و WHSV=2 و 50 غم من وزن العامل المساعد، ونسبة $H_2/HC=3$.

أظهرت النتائج أن أفضل حرارة للعوامل المساعدة المستخدمة كانت 475 م° والتي أعطت أعلى نسبة تحول من النفثا الثقيلة للمركبات العطرية والايزومرات المتفرعة التي تمتلك عدد اوكتاني عالي. أثبتت النتائج ان العوامل المساعدة ثلاثية المعدن نوع Pt-Sn-In/HY, and Pt-Sn-Ge/HY أعطت انتقائية عالية بأتجاه المركبات ذات العدد الاوكتاني، وبنسبة 91.5% و 85% على التوالي. كما اظهرت العوامل المساعدة نوع Pt/HY و Pt-Sn/HY انتقائية بمقدار 74% و 79% على التوالي.

ومن جانب اخر اثبتت النتائج ان اضافة المعدن الثالث نوع الجرمانيوم والانيديوم نتج عنة استقرار عالي للعوامل المساعدة مع مقاومة لتكون الكربون وقد الفعالية. كما تم ملاحظة زيادة أنتاج المواد عالية العدد الاوكتاني عند استخدام العوامل المساعدة ثلاثية المعدن Pt-Sn-In/HY, and Pt-Sn-Ge/HY عند نفس الظروف التشغيلية.

1. Introduction

Catalytic naphtha reforming plays a major role in satisfying the demand for unleaded, high octane gasoline. Catalytic reforming generally is applied to a feedstock rich in paraffinic and naphthenic hydrocarbons and is effected through diverse reactions: dehydrogenation of naphthenes to aromatics, dehydrocyclization of paraffins, isomerization of paraffins and naphthenes, dealkylation of alkylaromatics and hydrocracking of paraffins to light hydrocarbons [1, 2]. The high octane gasoline is achieved through a continuous improvement of the catalytic reforming process to formation of aromatics and branched chain paraffins [3, 4, and 5].

The reforming process is carried out over bifunctional catalysts which consist mainly of a metal phase (Pt, Re, and Ru) dispersed on an acidic support such as Al_2O_3 . Usually, reforming reactions are accompanied by the formation of undesired carbonaceous compounds that deactivate the catalyst. This coke can have different crystalline structures, morphologies, and reactivities, depending on the specific reaction taking place and the reaction conditions [1, 6]. Therefore, many types of metals are used as promoters to modify the catalysts and then to improve the process activity, selectivity and catalyst stability [2, 7, 8].

Most of the catalysts that have been investigated in literature [7, 8, 9, and 10] were focused on improvement of activity and selectivity of reforming catalysts supported on Al_2O_3 . Mazzieri et al. [7] performed experimental study on the Pt-Re-Sn trimetallic catalysts for naphtha reforming. Moreover, Mazzieri et al. [12]

investigated the deactivation and regeneration of the metal function of Pt-Re-Sn/Al₂O₃-Cl and Pt-Re-Ge/Al₂O₃-Cl for catalytic naphtha reforming. On the other hand, Carlos et al. [13] studied the chemisorption of CO over mono-, bi- and trimetallic naphtha reforming catalysts containing Pt, Re and Sn in the metallic function using (TPR). The CO chemisorption results indicate that it is possible to determine in an easy way the metallic dispersion of Pt/Al₂O₃ monometallic catalysts and that the same method can be applied to measure the exposed Pt on bimetallic Pt-Re and Pt-Sn catalysts and trimetallic Pt-Re-Sn catalysts.

Maria et al. [14] studied the influence of gallium on the properties of Pt-Re/Al₂O₃ catalysts in naphtha reforming. They were found that the addition of Ga to the Pt-Re/Al₂O₃ catalyst diminishes its acidity (Brønsted and Lewis). Also, they concluded that for the n-heptane reforming reaction the addition of Ga increases both catalyst stability and selectivity to aromatics, and with low light gases. Shahrazad et al. [15] developed a comprehensive experimental and a mathematical model for the reaction of catalytic reforming process. Two types of tri-metal catalysts supported on Al₂O₃ were prepared (Pt-Re-Sn/Al₂O₃ and Pt-Ir-Sn/Al₂O₃). The dehydrogenation, dehydrocyclization, and hydrocracking reaction were investigated with Iraqi heavy naphtha as a feedstock. The results showed that the conversion of paraffin's and naphthenes increases with increasing of reaction temperature and decreases with increasing of WHSV. María et al. [16] investigated the influence of the addition of Pb to Pt-Re/Al₂O₃ naphtha reforming catalysts. It was found that Pb interacts strongly with the (Pt-Re) active phase producing decay in the metal function activity. They concluded that the hydrogenolysis is more affected than dehydrogenation. They found that a part of the Pb is deposited over the support decreasing the acidity and the strength of the most acidic sites.

It is important to mention here that many previous studies on catalytic reforming process have focused on the use of n-hexane, n-heptane, and n-octane as feedstocks [2, 4, 5, 6, and 10]. Also, it is clear that there is a little investigations about the use of trimetallic catalysts (Ge or In) supported on zeolite in catalytic reforming of heavy naphtha. On the other hand, the design, modification, and performance of reforming catalysts are required a detailed understanding of the reaction mechanism, and catalyst deactivation. Such information will lead to prepare a catalyst with reduced deactivation. Therefore, the present investigation aims to prepare and modify reforming catalysts using different types of promoters and investigate their performance using Iraqi-heavy as a feedstock. Then study the catalyst stability at different operating parameters of reforming process.

2. Experimental Work

2.1 Materials and Apparatus

Iraqi heavy petroleum naphtha delivered by Al-Dura Refinery was used as a feedstock in present investigation. The specifications and chemical analysis of Iraqi-heavy-naphtha are tabulated in tables (1) and (2) respectively. Pure hydrogen gas (99.9%) was supplied from Al-Mansour plant-Baghdad. Hexachloroplatonic acid H_2PtCl_6 (40%wt Pt) Germany, Indium nitrate $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, Tin chloride SnCl_2 , and Germanium tetra chloride GeCl_4 were supplied from Fluka.

Table (1) The specifications of Iraqi-heavy-naphtha Al-Dura Refinery (Baghdad)

NO.	Specifications	Measurement
1	API. at 15.6 °C	62.6
2	Sp.gr	0.729
3	Sulfur Content	< 7 ppm

4	Kinematic Viscosity at 25 °C	6.11x10 ⁻⁷ m ² /s
5	Octane Number	60
6	Aniline Point	48 °C
7	Distillation	
	I.B.P.	50 °C
	10 Vol.% distilled	78 °C
	20 Vol.% distilled	86 °C
	30 Vol.% distilled	96 °C
	40 Vol.% distilled	104 °C
	50 Vol.% distilled	113 °C
	60 Vol.% distilled	120 °C
	70 Vol.% distilled	128 °C
	80 Vol.% distilled	138 °C
	90 Vol.% distilled	146 °C
	E.B.P.	176 °C
	Total distillate	99 Vol.%
	Residue	0.8 Vol.%
	Loss	1 Vol.%

Table (2) The G.C. analysis of Iraqi-heavy-naphtha feedstock

NO.	Compounds	Volume %
1	iso-pentane	0.52
2	normal-pentane	3.18
3	2,2-dimehtyl butane	4.65
4	2,3-dimehtyl butane	3.88
5	2-mehtylpentane	3.78
6	3-mehtylpentane	1.12
7	normal-hexane	7.62
8	2,2-dimehtyl pentane	8.47
9	2,3-dimehtyl pentane	1.01
10	Benzene	5.50
11	Cyclohexane	4.41
12	normal-heptane	17.8
13	Toluene	4.42
14	normal-octane	15.3
15	+C8	18.34
16	Total	100%

2.2 Preparation of Reforming Catalysts

In the present investigation four types of catalysts were prepared: Pt/HY, Pt-Sn/HY, Pt-Sn-In/HY, and Pt-Sn-Ge/HY. In order to modify the specification of NaY zeolite, the Na⁺ ions were exchanged for NH⁴⁺ ions to obtain the HY by ion exchanging the original NaY zeolite with (3 N) ammonium chloride solution [3]. Thus 78.75g of ammonium chloride in 500ml distillate water were contacted with 50g of NaY zeolite with stirring for 1 hr at 50 °C. Then, the exchanging process continues for 4 days at laboratory temperature of 25 °C with 87 % of exchanging rate of Na⁺ by NH₄⁺. After exchange, the sample HY was filtered, washed and dried at 110 °C for 10 hr. Then, the prepared sample was washed with deionized water to be free of chloride ions, and drying procedures were repeated twice. The obtained zeolites were calcined in air at 550 °C for 5 hours to obtain the HY form.

2.2.1 Preparation of Pt/HY Catalyst

The exchanged zeolite (HY) was loaded with Pt at concentrations of 0.5 wt % by impregnation process with aqueous solution of hexachloroplatonic acid H₂PtCl₆ with 40% Pt [3]. The prepared solution was added dropwise to the zeolite with mixing for 4 hours at 25 °C. The mixture was then left at room temperature for 24 hr, it was stirred intermediately during this time. The mixture was then slowly evaporated to dryness over a period of 8 hr at temperature of 75°C. The resulting catalysts were dried in air at 110°C for an additional 12 hr. Then, the samples were calcined in air at 550°C for 10 hours (increasing to that temperature with a rate of 0.5°C/min) and finally reduced at 450°C in flowing H₂ for 4 hr at H₂ flow of 60 cm³/min [8, 9,15]. Then, at this stage the samples are referred to as Pt/HY catalyst.

2.2.2 Preparation of Pt-Sn/HY Catalyst

The Pt-Sn/HY catalyst was prepared by co-impregnation by adding tin chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) to the prepared Pt/HY catalyst. Tin chloride was first dissolved in deionized water and heated for 30 min at 70 °C. Then, tin chloride was added to the solution containing catalyst and leaving it without stirring for 1 hr and then gently stirred for 1 hr in water bath at 70 °C. The resulting catalyst was dried at 120 °C for 12 hrs, and calcined in air at 550°C for 10 hr (increasing to that temperature with a rate of 0.5°C/min) and finally reduced at 450°C in flowing H_2 for 4 hr at H_2 flow of 60 cm^3/min , the final catalyst concentration was 0.5 wt% Pt, and 0.1 wt% Sn [15].

2.2.3 Preparation of Pt-Sn-Ge/HY and Pt-Sn-In/HY Catalysts

On the other hand, the trimetallic catalysts Pt-Sn-Ge/HY, and Pt-Sn-In/HY were prepared by follow the same procedure that was conducted for the preparation of bimetallic catalyst, but using a third metal (Ge and In) with metals Pt-Sn/HY catalyst. Thus, it was used the Germanium tetra chloride GeCl_4 (1.6 mg Ge. ml^{-1}) and Indium nitrate $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (2 mg In. ml^{-1}). These metal solutions added to the bimetallic Pt-Sn/HY catalyst. Then, each tri-metallic catalyst was dried at 120 °C for 12 hr, and calcined in air at 550°C for 10 hr (increasing to that temperature with a rate of 0.5°C/min) and then, the catalyst reduced in flowing H_2 for 4 hours at 450°C at H_2 flow of 60 cm^3/min . Then, the final tri-metallic catalyst composition was 0.5 wt% Pt, 0.1 wt% Sn, and 0.1 wt% of Ge or In.

2.3 Reaction Apparatus and Procedure

The catalysts performance of reforming process was investigated by designing and constructing an experimental pilot plant as shown in figure (1). On the other hand, figure (2) shows a schematic diagram of catalytic reforming unit. The

apparatus consisted of a vertical tubular stainless steel reactor of 20 mm internal diameter, 30mm external diameter and 680mm height. The reactor was heated uniformly using an electrical furnace. The reactor fitted with accurate means for control of pressure, gas and liquid flow rates. The temperature at the reactor center of the catalyst bed was determined and controlled by a temperature control system, which have a calibrated thermocouple sensor type K (iron-constantan).



Fig. (1) General view of experimental catalytic reforming unit

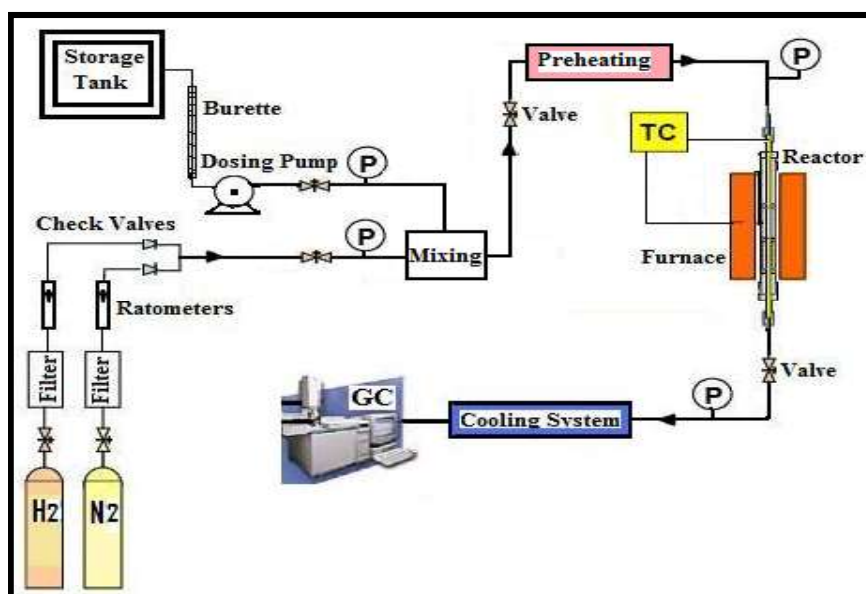


Fig. (2) Schematic diagram of catalytic reforming apparatus

The prepared catalyst was dried at 110 °C in N₂ flow for 1 hr and reduced at 450 °C in hydrogen flow for 4 hours. In each run 50 g of catalyst was charged into the reactor. The WHSV= 2, H₂ /HC molar ratio=3, were used for all experimental runs. The feed mixture of hydrogen and hydrocarbon was preheated to reactor temperature before entering the catalytic bed. The reaction was carried out at a temperatures varied between 425 to 525 °C with atmospheric pressure.

For each run, the reformat products were analyzed in a Gas Chromatograph type Shimadzu GC-2014 with FID using capillary column type S.G.E., length=25 mm, I.D.= 0.22 mm, film=0.2µm, and using nitrogen gas as a carrier gas.

3. Results and Discussions

The main aim of the present investigation is to prepare modified catalysts through promoting their specifications using some types of promoters such as Sn, In, and Ge. The advantage of the third metal is to inhibit or enhance the reactions bath ways of chemisorption, hydrogenolysis, and hydrogenation.

In operation of catalytic reforming, the compositional information of the feedstock and catalysts are required for monitoring, control, and selection of optimal process conditions. Therefore, in the present work, the chemical composition of the reformat is studied to ensure the control of the reforming process.

It is important to mention here that the catalysts investigated in the present work were dependent on the zeolite Y support. Zeolites are the alumina silicate (molecular sieve) in which has the capacity to selective adsorption of molecules based on pore diameter. Table (3) summarizes the general characterization and properties of prepared catalysts. The specific surface area of the catalysts BET, and the pore volume has been evaluated by N₂ adsorption at -196 °C. It is clear that all

the general properties of the four catalysts are the same with slightly variation. Obviously, the relatively high surface area of the Y-zeolite support ($420 \text{ m}^2/\text{g}$) favors the dispersion of metallic particles on the external surface of the catalyst in comparison with classical Al_2O_3 that posses a surface area of about $200 \text{ m}^2/\text{g}$.

Table (3) The specifications of the four prepared catalysts

No.	Property	Pt/HY	Pt-Sn/HY	Pt-Sn-In/HY	Pt-Sn-Ge/HY
1	Platinum content (wt%)	0.5 wt% Pt	0.5 wt% Pt and 0.1% Sn	0.5 wt% Pt, 0.1% Sn, and 0.1% In	0.5 wt% Pt, 0.1% Sn, and 0.1% In
2	Surface Area (m^2/g)	425	423	420	420
3	Pore Volume (cm^3/g)	0.6	0.6	0.56	0.55
4	Average Pore Size (\AA)	25	25	25	25
5	Chlorine Content (wt%)	0.3	0.3	0.3	0.3
6	Internal (Si/Al)	1.6	1.6	1.6	1.6

3.1 Effect of Reaction Temperature

The mole percentage of produced reformat from the conversion of heavy naphtha over the four types of prepared catalysts (Pt/HY, Pt-Sn/HY, Pt-Sn-Ge/HY, and Pt-Sn-In/HY) are shown in figures (3) to (6) as a function of reaction temperatures. The produced reformat come from aromatization, isomerization, and cracking reactions. Therefore, the results in the present work are shown in the

form of overall compounds of aromatics: (benzene, toluene, xylenes), branched isomers: (iso-C4, to iso-C9), n-paraffins: (n-C5 to n-C10), and naphthenes: (C6 to C9). Then figures (3) to (6) demonstrated that the reaction temperature is very dominated factor in controlling of the reformate products distribution.

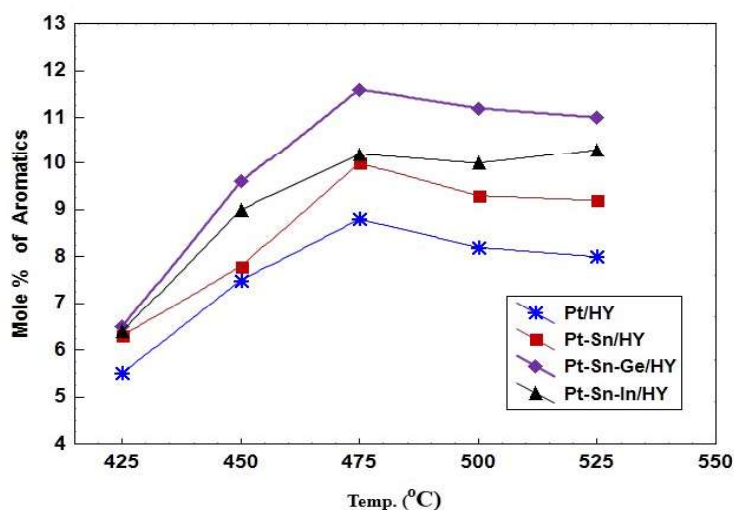


Fig. (3) The mole % of produced aromatics for each catalyst as a function of temperature

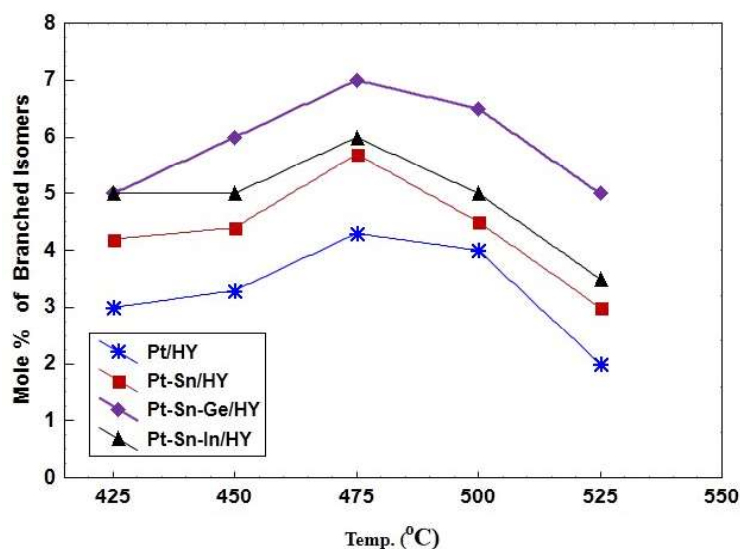


Fig. (4) The mole % of branched isomers produced for each catalyst as a function of temperature

From figures (3) to (4) it was noted that the best reaction temperature of all catalyst types was 475°C in which give the highest conversion of heavy naphtha to desired products of aromatics and branched isomers. Also, according to these figures, it can be clearly noted that when trimetallic catalysts (Ge and In) a high concentration of aromatics and branched compounds are produced and then high RON gasoline. This approach is in agreement with the conclusion of Moljord et al. [10] who's found that the RON has a direct dependence on the existing aromatic in reformate content.

On the other hand, from the same figures it can note that the concentration of branched isomers is increased in comparison with aromatics products. This behavior is agree with the more recently formulations to increase of the branched isomers to aromatics ratio in order to reduce the content of aromatic hydrocarbons in the fuel due to environmental regulations [1, 7].

It important to mention here that the cracking reaction be more effected at temperatures greater than 475°C Therefore, the results pointed to formation of low value products (C1-C4 gases) with temperature increasing than 475°C. On the other hand, the same figures pointed to that the addition of Ge and In (trimetallic catalysts: Pt-Sn-In/HY and Pt-Sn-Ge/HY) decrease the formation of low value products such as methane, ethane and propane. This conclusion is in agreement with the work of Maria et al. [14] and Shahrazad et al. [15].

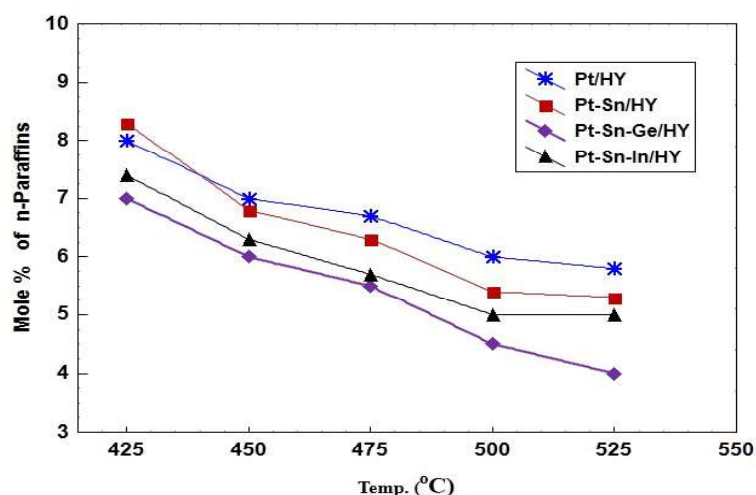


Fig. (5) The mole % of n-Paraffin's produced for each catalyst as a function of temperature

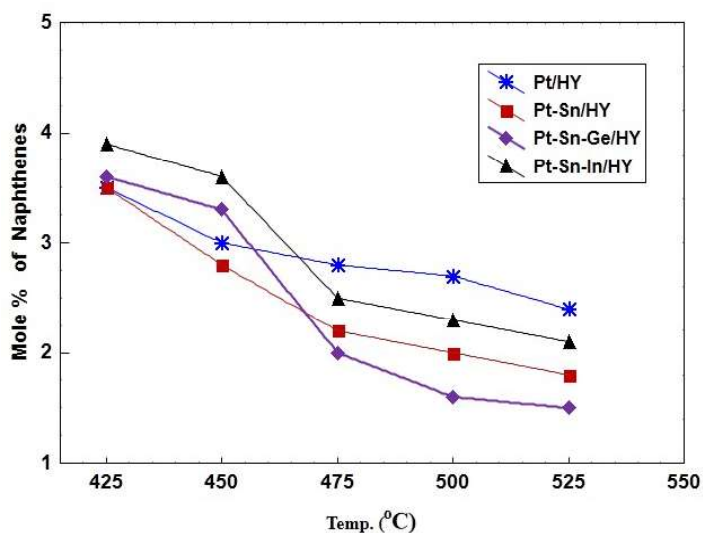


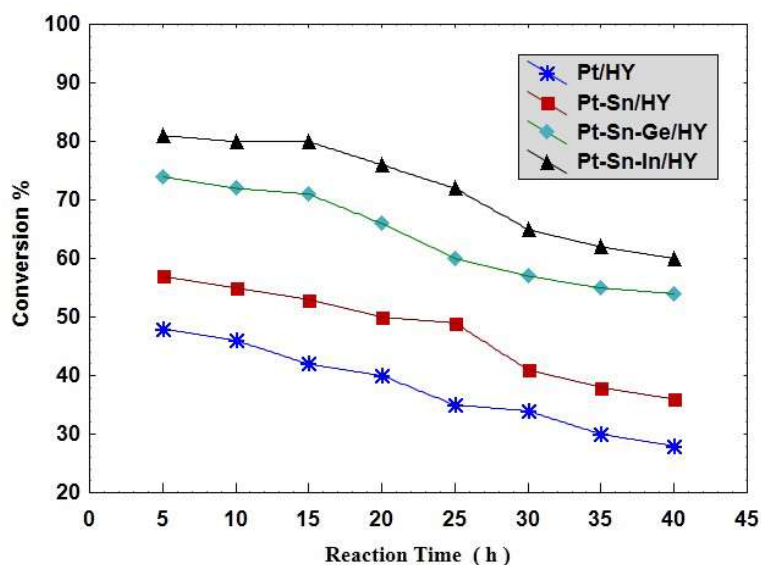
Fig. (6) The mole % of produced naphthenes for each catalyst as a function of temperature.

3.2 Effect of Reaction Time

Figure (7) presents the relationship between the conversion of heavy naphtha and reaction time over the four types of prepared catalysts. All experiments were performed at 475°C, H₂/HC=3, and WHSV=2. The catalytic activity was tested on stream over a period of 40 hr of reaction time on stream.

The results show that the fresh catalysts exhibit the highest initial heavy naphtha conversion. In this situation, the total conversion was 81% for Pt-Sn-In/HY, 74%

for Pt-Sn-Ge/HY, 57% for Pt-Sn/HY, and 48% for Pt/HY. Then, the catalysts activities decreased gradually with time due to the carbon depositions that produced during the reaction. In this case the coke formation can cover the active sites of the catalysts, thus decreasing the catalytic activity. These results are agreed with the work of Jorge et al. [8] and María et al. [16].



**Fig. (7) The percentage of total heavy naphtha conversion as a function of reaction time
Reaction conditions: 475 °C, H₂/HC=3, and WHSV=2**

It is important to mention here that the dehydrogenation and hydrogenolysis are supposed to occur over metallic sites, while isomerization occurs over acid sites. Dehydrocyclisation and aromatization reactions present a bifunctional mechanism. On the other hand, in the reforming process, there is a substantial difference in the rate between particular reactions. Thus, the hydrogenation of naphthenes to aromatic hydrocarbons runs at a rate, which is by two orders of magnitude faster than the rate with which paraffins are dehydrocyclized to naphthenes [5, 12]. Therefore, in the preparation of reforming catalysts, a careful balance must be maintained between the hydrogenation and dehydrogenation functions of the metals and the support.

Figure (8) shows the relationship between the total selectivity of desired products (aromatics and isomers) with reaction time (time on stream) over the four prepared catalysts. The results pointed to that the trimetallic catalysts (Pt-Sn-In/HY and Pt-Sn-Ge/HY) give the highest selectivities and stabilities with low coking formation in comparing with monometallic and bimetallic catalysts. The initial catalysts selectivities (up to 10 hr) for Pt-Sn-In/HY, Pt-Sn-Ge/HY, Pt-Sn/HY, and Pt/HY were 91.5%, 85%, 79%, and 74% respectively.

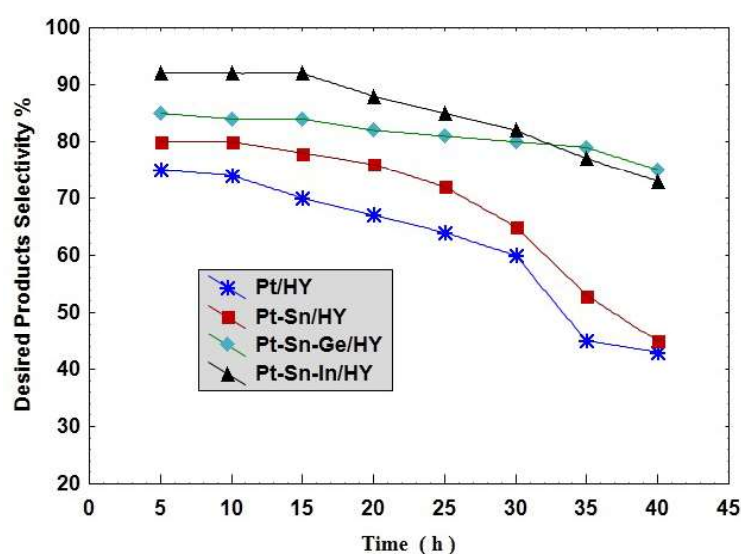


Fig. (8) The total selectivity of desired products as a function of time at reaction temperature of 475°C, H₂/HC=3, and WHSV=2

In general, the decrease in catalysts selectivity relates to a decrease in catalyst surface area due to carbon formation that block the active sites of both metals and acid site. The accumulation of the coke with time will be reducing the properties of the catalyst and then the selectivity to desired products. The same results are shown by Carlos et al. [13] and Shahrazad et al. [15]. It is important to mention here that the coke deposition regards as the more challenging problem on reforming catalysts, which leads to loss activity, selectivity, life time, and yield. The coke deposition induces a decrease of the amount of strong Lewis and

Brønsted acid sites. This decrease of the amount of strong Lewis acid sites involves an increase in the isomer yield.

On the other hand, according to explanation of Ponc and Bond [17] the introducing of a second or third metal (such as Ge, In,) would divide the metal surface into smaller islands, preventing thus polymerization of unsaturated intermediates to form a two-dimensional layer of potential coke precursors. Also, from the results of figure (8) it can be noted that the presence of In and Ge decrease the hydrogenolysis function of the catalysts with reaction time. Therefore, the In, and Ge trimetallic catalysts showed the highest selectivity and resistant against deactivation under the operational conditions. Then, the Pt-Sn-In/HY catalyst have a higher selectivity to branched isoparaffins, while, a reformat rich in aromatics can be obtained over Pt-Sn-Ge/HY catalyst as shown in figures (3) and (8).

4. Conclusions

- 1- The addition of germanium or indium as a third metal to the bimetallic catalyst Pt-Sn/HY improves the metal side and acid site of the prepared catalyst. The third metal reduces the hydrogenolytic activity of the bimetallic catalyst.
- 2- The results showed that the best reforming temperature over all prepared types of catalysts was 475 °C which gave the highest conversion of heavy naphtha to aromatization and isomerization products with low cracking products.
- 3- It was noted that the catalysts selectivities to aromatics and isomers products were improved through the addition of the Ge and In metals. The trimetallic catalyst Pt-Sn-In/HY and Pt-Sn-Ge/HY show high selectivity to desired products of 91.5% and 85% respectively. On the other hand, the Pt-Sn/HY and Pt/HY, catalysts show selectivities of 79% and 74% respectively.
- 4- The trimetallic catalysts showed higher stability than the mono and bi-metallic catalysts because of the reduction of polymerization reaction of unsaturated intermediates that converted to coke precursors.
- 5- Then, the Pt-Sn-In/HY catalyst have a higher selectivity to branched isoparaffins, while, a reformate rich in aromatics can be obtained over the and Pt-Sn-Ge/HY catalyst, with low concentration of cracking products.

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