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Kinetic Study of Hydroisomerization of n-Decane using Pt/SAPO-11 catalysts

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Abstract

The hydroisomerization of n-decane was studied on SAPO-11 catalyst. Catalyst of 0.25wt.%Pt/SAPO-11 was prepared locally and used in the present work. The hydroconversion performed in a continuous fixed-bed laboratory reaction unit. Experiments of n-decane isomerization were performed in a temperature range of 200 to 275°C,LHSV range of 0.5-2 h^{-1}, and hydrogen to decane mole ratio of 2.1-8.2. The results show that the n-decane conversion increases with increasing temperature and decreasing LHSV , the maximum conversion 56.77 % was achieved at temperature 275°C and LHSV of 0.5 h^{-1}. The kinetic of n-decane isomerization was also studied and the reaction was first order. The kinetic analysis also showed that the activation energy equal to 61.1137 kJ/mol.

Keywords: SAPO-11 catalyst, Isomerization, n-Decane

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1- Introduction

Isomerization, cracking and alkylation are acid-catalyzed reactions. Considering the great amount of oil consumption in the world, it can be concluded that acid catalyzed reactions of hydrocarbon are critically important and not surprisingly that many studies have been published for this reason. Nonetheless, important questions regarding the mechanism and the effect of the catalyst pore structure on the activity and selectivity remain to be answered [1].

Regardless the reaction involved in a particular process, it is of considerable importance that the catalyst exhibits not only the ability to perform its specific functions initially but also perform them satisfactorily for sufficient periods of time. The analytical terms used to measure the efficiency of a particular catalyst performance in a particular hydrocarbon conversion process are activity, selectivity and stability [2]. Isomerization of n-paraffins to branched isomers is important in petroleum refining industry for improving fuels properties such as high gasoline octane number [3] and diesel fuel with high cetane number, low pour point and high viscosity index.

To accomplish high isomerization selectivity, balance between metal and acid functions is needed [4]. In the hydroisomerization process, catalytic systems have been successfully constructed for hydroisomerization evolution [5]. These systems employ bifunctional catalysts that contain noble metal particles as hydrogenation/dehydrogenation components in association with an acidic component. Recently, among the several catalytic materials investigated for n-alkane isomerization, zeolite with large pores has been reported to produce a large yield of cracked products.

This could be due to their spatial constraints that might induce shape selectivity or excessive acid sites that would induce cracking. On the other hand [6], SAPO-11 with one-dimensional 10-membered ring channels has attracted the attention in the field of hydroisomerization due to its shape selectivity and moderate acidity [7]. SAPO-11 showed perfect conversion of hydrocarbons into isomers [8],[9]. However, the microporous structure of SAPO-11 stops multi-branched isomers formation.

It is generally observed that the active sites for isomerization are located near the pore mouths of the SAPO-11 [10]. Therefore, for satisfy the mono-branched isomers production from long chain paraffins it is important to investigate SAPO-11 with suitable pore structure [11]. For good performance, suitable catalyst is needed for the conversion of hydrocarbons. Many catalysts were used in the isomerization of long chain n-alkanes, however, SAPO-11 was found to be the most efficient catalyst in the isomerization of long chain alkanes and this is due to its medium acidities and appropriate pore structure (one dimensional 10-membered-ring channel of 0.39 nm x 0.63 nm) and AEL pore structure [12].

The present study aimed to synthesis Pt/SAPO-11 by impregnation method, then pysico-chemical properties were compared. n-decane was used to study the catalytic activity of Pt/SAPO-11for isomerization process and study the effect of pyridine adsorption on bronsted and Lewis acid site of SAPO-11 catalysts.

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2- Experimental Work

2.1. Material and Method

a. Chemicals

n-Decane 99% (BDH, England) is used as feed stock in this study. Ortho phosphorous acid (85 wt% H_3PO_4) (Panreac, Spain)**;** Aluminum isopropoxide (BDH, England); di-n-propylamine, m.wt. 101.19 (BDH, England) as template**.** Silica sol. 99.9% (Qingdaw Jiyida, China)**;** deionized water; Poly Vinyl Alcohol (PVA) 99% (Sigma) as a binder; ɤ-nano-alumina.99.99% (HWNANO,China) are used to synthesized SAPO-11.

Hexachloroplatinic acid (40wt%Pt), m.wt. 517.92 (Fluk Chemi AG)

b. Synthesis of SAPO-11

SAPO-11 was prepared by adding 46.1 g of phosphorous acid as a source of phosphor and 167.2 g of water (double the amount used in the literature[8]) were added to the gelation mixture at a temperature of 30°C, these contents were mixed until a homogeneous mixture was obtained. After 30 minutes of stirring, 81.7 g of aluminum isopropoxide was added and stirred for 2 hours. A structure-directing template of 14.7 g of di-n-propylamine was added into the gelation autoclave, this is followed by immediate addition of 13.85 g of silica sol.

The reaction mixture was prepared by stirring part of this mixture for 2 hours. The mixture was aged at room temperature for 24 hours without stirring and then was crystallized in a stainless steel crystallization autoclave at temperatures of (170,180,190 and 200) °C for 24 hour .

Following the filtration of the crystallized products, they were washed and dried at 110°C for 3 hours. Raw powders were then calcined in furnaces at 550°C for 3 hours and then cooled afterwards. The molecular sieve was then obtained in a powder form. The molar composition of molecular sieve after calcination is Al_2O_3:0.93P_2O_5:0.414SiO [13].

c. Synthesis of Pt/SAPO-11

Pt/SAPO-11 was prepared using impregnation method. A SAPO-11 catalyst was dried at 110°C in a furnace in two hours. The impregnation needs hexchlorplatinic acid solution containing 0.368 g of H_2PtCl_6 with deionized water till the volume of solution equal to pore volume of SAPO-11. Then the catalysts was dried at 110°C overnight and the calcinated at 300°C in a furnace for 3 hours [14].

d. SAPO-11 Characterization

- X-ray Diffraction (XRD)

The purity of the prepared SAPO-11 was examined after comparison between 2Ɵ and d-spacing of the prepared samples with 2Ɵ and d-spacing which are synthesized by Zhang et al [17]. The prepared sample was tested using X-ray diffractometer Shimadzu SRD 6000, Japan, with Cu wave length radiation 1.54060 cm^{-1} in the 2 theta ranges from 5-60°, and fixed power source 40Kv, 30mA. XRD for prepared samples was performed at the Ministry of Science and Technology.

- X-ray Florescence (XRF)

The percentage of oxides was tested using X-Ray Fluorescence (SPECTRO XEROS, AMETEK, GERMANY) Germany. XRF sample was performed at University of Baghdad/College of science/ Department of Geology.

- AFM

The atomic force microscopy (AFM) method was used to find the average particle size of the prepared catalyst. It was tested at the Department of Chemistry/ College of Science/ University of Baghdad using Atomic Force Microscope Device (type Angstrom, Scanning Probe Microscope, Advanced Inc, AA 3000, USA).

- BET Surface Area and Pore Volume

Specific surface area was determined by The Brunauer-Emmett-Teller method using 0.01 as the value of maximum relative and pore volume was performed using a micrometrics ASAP 2020. The samples were disarmament of gas for 2 hr under vacuum at 250°C. Surface area and pore volume samples were performed at PRDC Laboratory, Ministry of oil /Iraq.

- Fourier –Transform Infrared Spectroscopy (FTIR)

This test was applied using (IR-Affinity,Shimazdo,Japan) with wave range between (400-4000)cm^{-1} at Ibn-Sina State Company / Ministry of Industry and Minerals.

e. Isomerization process

Reactor was charged with 44.4 cubic centimeters of fresh catalyst which insert between two layers of glass balls as inert materials. Then hydrogen was flow at 350°C for 3hours in the reactor to reduce the catalysts [15]. After that the air was expelled from the reactor using nitrogen gas, meanwhile, the reactor is heated to the desired temperature. After reaching the reaction temperature, the nitrogen valve was closed.

n-decane feed was heated first then enter to evaporator to be vaporized then it was mixed with hydrogen and entered from the top of the reactor, distributed uniformly and reacted on the catalyst inside the reactor. The product gases passed through the condenser and the condensate was collected. Pt/SAPO-11 catalysts were used for kinetic study of the isomerization reaction.

The conditions employed are temperatures of (200-275) ºC, liquid hourly space velocity of 0.5-2hr^{-1}, hydrogen to n-decane mole ratio of 2.1-8.2 and finally the pressure was kept atmospheric.

f. Test of Isomerization

Gas Chromotograph (GC)

The reaction product analysis was obtained at Ibn-Sina State Company/ Ministry of Industry and Minerals using a chromatographic analysis on packed model 438Aa-VSA.

g. Reaction Unit

The experiments were carried out in a continuous laboratory scale unit.

Fig. 1 show the process flow diagram.The unit consists of feed drum, gas flow meters, feed pump, evaporator, reactor, separator, collector and cooler with appropriate control system for heating.

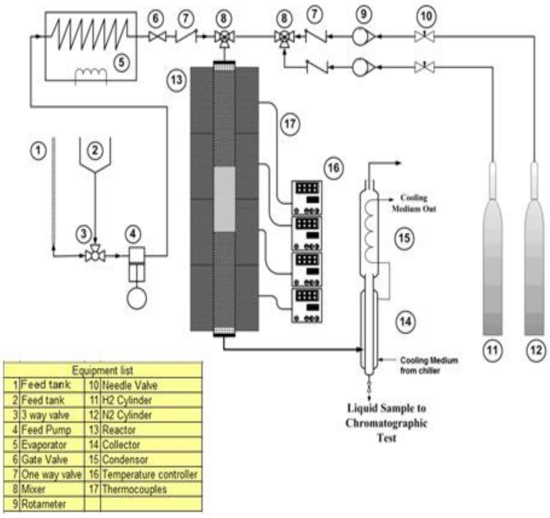

Fig. 1 The catalytic hydro-conversion unit process flow digrame

3- Results and Discussion

3.1. X-Ray Diffraction

The purity of SAPO-11 which prepared was tested after a comparison between 2ϴ and d-spacing of the prepared samples with 2ϴ and d-spacing which are synthesized by Zhang et al., [17].

Fig. 2 shows the x-ray diffraction patterns of SAPO-11 sample. The sample was hydrothermally crystallized at 190 °C.

Table 1. Comparison of lattice spacing and angle, between prepared SAPO-11 catalyst (190°C crystallization temperature, aging and double water contents) and standard SAPO-11 [16].

Synthesis SAPO-11 catalyst		Standard SAPO-11catalyst	
Angle(2Theta) deg.	D, spacing(Å)	Angle(2Theta) deg.	D, spacing(Å)
8.127	10.87	8.08	10.93
9.778	9.04	9.30	9.30
13.236	6.683	13.09	6.76
13.861	6.383	13.79	6.42
15.573	5.686	15.76	5.62
20.238	4.384	20.29	4.372
21.26	4.174	21.22	4.183
22.48	3.9513	22.24	3.994
23.00	3.951	22.89	3.881
23.39	3.800	23.31	3.813
24.80	3.58	24.48	3.364
25.12	3.514	24.99	3.560
26.67	3.339	26.46	3.366
28.782	3.099	28.90	3.087
29.641	3.011	29.56	3.020

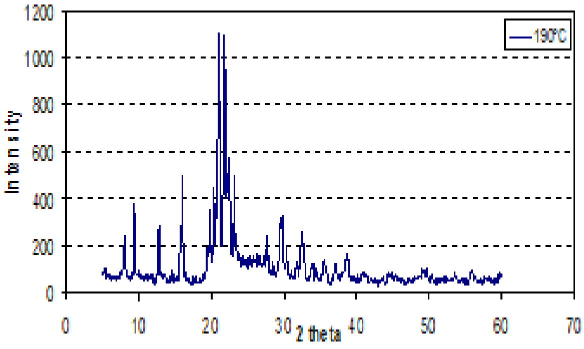

Fig. 2. X-ray diffraction of SAPO-11

3.2. X-ray Florescence

The molar composition of SAPO-11 after calcination is $1Al_2O_3:0.93P_2O_5:0.414SiO_2$

3.3. Particle Size of SAPO-11 Catalyst

The atomic force microscopy (AFM) method was used to find the average particle size, the average particle diameter reaches 57.39 nm for the synthesized catalysts.

3.4. Surface Area and Pore Volume

SAPO-11 displays larger surface area and pore volume 396.17 m^{2}g^{-1} and 0.3159 cm^{3}g^{-1} respectively at a temperature 190°C with aging for 24 hr. These values (surface area and pore volume) in this research are higher than previous work [17].

The decline in particle size of zeolite crystals from the micro-level to nano-level resulted in considerable rise in surface area, thus yielding more active sites.

3.5. Fourier Infrared Spectroscopy FTIR

A SAPO-11 catalyst was analyzed using FT-IR spectroscopy to study the structure and the chemical bonds between molecules.

FT-IR spectra measured the intensity of the lattice vibration in the range 4000 to 500 cm^{-1} by using a spectrometer for the adsorption of KBr studies.

FTIR was used to investigate the nature and quantum of hydroxyl groups produced by Si. The spectra of the catalyst sample in the OH$^-$ stretching are shown in Fig. **3** SAPO-11 sample has three bands at 3743, 3677 and 3625 cm^{-1}, the former two bands refer to Si-OH, P-OH groups respectively. The third one represents the spectra of the prepared Brønsted acid site and the bridge Si-OH-Al that describes the acid properties of the sample [18].

The band 1100 cm^{-1} attributed to the asymmetric stretch of O–P–O; 730 cm^{-1} arising from the symmetric stretch of O–P–O; 640 cm^{-1} due to the bend of double 6-ring; 575 cm^{-1}, 530 cm^{-1} and 480 cm^{-1} ascribed to the bend of PO_4, AlO_4, and SiO_4, respectively.

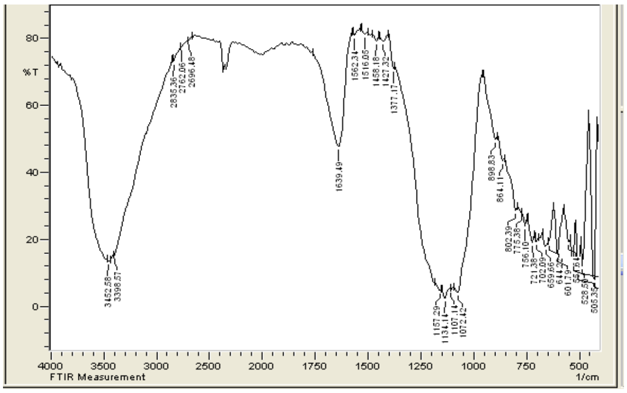

Fig. 3. FT-IR of synthesized SAPO-11

3.6. Pyridine FTIR

FT-IR spectroscopy is a technique which is used for intensifying of Brønsted and Lewis acid sites by adsorption of pyridine on the catalysts [19]. The FT-IR spectra of pyridine adsorbed on SAPO-11 , and Pt/SAPO-11 are shown in Fig. 4 and Fig. 5. The intensity of the bands at 1550 and 1450 cm^{-1} were believed to be proportional to Brønsted and Lewis acid sites concentrations, respectively.

It is clear from these figures that all the samples gave broad vibrational bands at 1455 cm^{-1} and 1545 cm^{-1}, from pyridine molecules adsorbed on Lewis (L) and Brönsted (B) acid sites, respectively [20]. The band at 1490 cm^{-1} corresponds to pyridine molecules adsorbed on both L and B acid sites [19]. The absorbance peaks for pyridine molecules adsorbed on the L or B acid sites changed after the introduction of platinum , for all samples, its contain medium acidic sites indicating that the acid sites were only slightly affected by the metal component.

Because of the low content of the metal component, the addition of Pt had small influence on the acidity of the catalysts. This is in agreement with Chen et al [19] and Zhang et al [20].

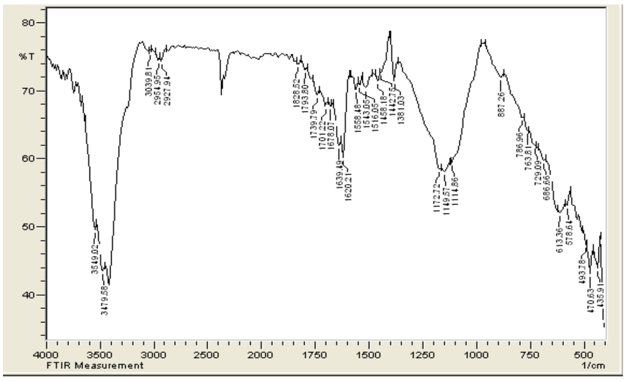

Fig. 4. FT-IR of synthesized SAPO-11with adsorption of pyridine

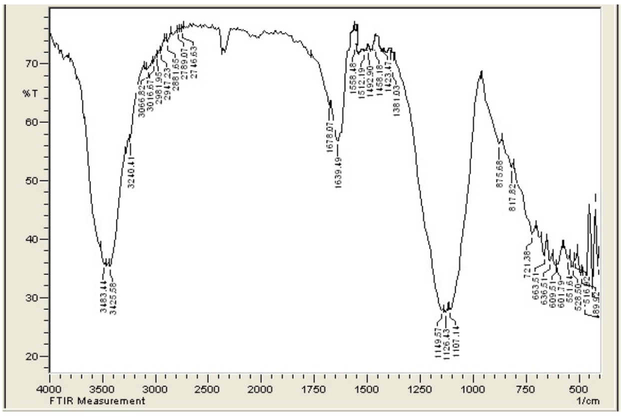

Fig. 5. FT-IR of synthesized Pt/SAPO-11 with adsorbed pyridine

3.7. Isomerization of n-decane

The activity of Pt/SAPO-11 was tested for isomerization of n-decane at different temperatures (200-275°) and LHSV (0.5-2 hr^{-1}).

a. Effect of Temperature

Fig. 6 shows the effect of temperature on isomerization process, it is clearly shown from this figure that increasing the temperature leads to increases the conversion of n-decane at constant LHSV and this is due to the nature of isomerization reaction which is endothermic while the change of the chain from n-alkanes to iso-alkanes is exothermic and this is in agreement with Alhassani [21].

As an example, the conversion of n-decane using LHSV of 0.5 hr^{-1} on Pt/SAPO-11 increases from 40.32 % at 200°C to 56.77% at 275°C.

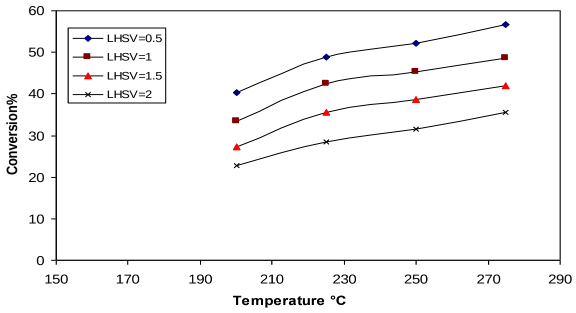

Fig. 6. Conversion of n-decane at different temperature and LHSV on pt/SAPO-11.

b. Effect of LHSV

Fig. 7 show the changes of n-decane conversion as a function of contact time which is expressed by LHSV.

As LHSV decreases the conversion increases. This means that increasing the residence time leads to increase the contact time of the feed with the catalyst inside the reactor. All results indicate that low LHSV is favored for an isomerization process as long as higher space velocities conversions are lower, unless the temperature is raised [9].

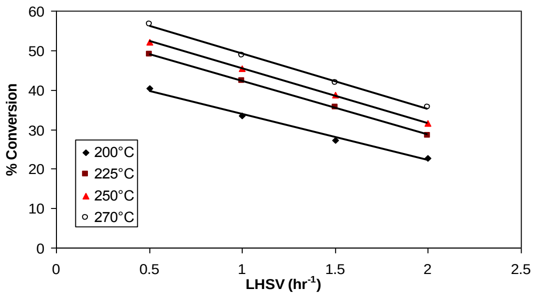

Fig. 7. Conversion of n-decane at different contact time on pt/SAPO-11

c. Kinetic Study

In catalytic systems and based on the weight of catalyst pellets, the rate equation can be expressed in the following form:

$$\frac{W}{F_{A0}} = \int_{0}^{X_A} \frac{dX_A}{-r_A} \qquad (1)$$

Differentiation equation 1 yields:

$$-r_A = \frac{dX_A}{d\left(\frac{W}{F_{A0}}\right)} \qquad (2)$$

According to the differential method, the rate of reaction can be estimated by finding the slopes of the line tangent to the curve which represents the relationship between n-decane conversion and $\left(\frac{W}{F_{Ao}}\right)$ at any given point. Figure 8 show the plots of %conversion vs. the $\left(\frac{W}{F_{Ao}}\right)$.

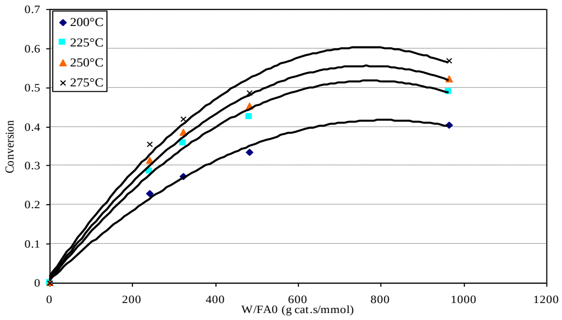

Fig. 8. Experimental value of conversion of n-Decane vs W/FAo on Pt/SAPO-11 at different temperature

d. The Reaction Order With Respect To N-Decane

The reaction is a first order reaction due to the linear relationship between $-r_A$and C_A as shown in Fig. 9.

No significant changes in the reaction order were detected when the temperature increases from 200-275ºC.

The reaction rate constants (k) were calculated at different reaction temperatures according to the linear relation between $-r_A$ and C_A.

Table 2 shows the values of rate constants that were obtained at different reaction temperatures.

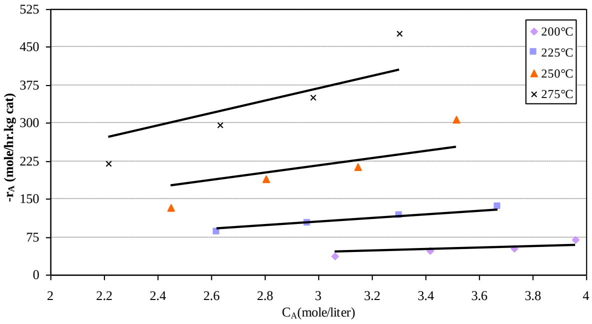

Fig. 9. Relation between - r_A and CA for Pt/SAPO-11

Table 2. Values of rate constant at different reaction temperatures

Reaction Temperature (°C)	k (liters /hr.kg catalyst) Pt/SAPO-11
200	14.78
225	35.233
250	72.04
275	122.80

e. The Apparent Activation Energy Measurements

The activation energy of isomerization reaction was calculated using Arrhenius equation, which relates the rate constant with the reaction temperature.

$$k = Ae^{\frac{-Ea}{RT}} \tag{3}$$

The plot of (ln k) vs. (1/T) shown in Fig. 10were used for the calculation of the activation energy for the isomerization reaction and it was equal to 61.1137 kJ/mol.

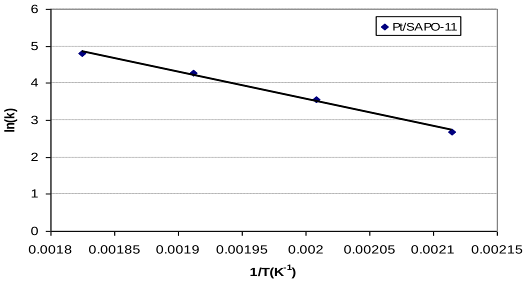

Fig. 10. Arrhenius plots for isomerization process of n-decane on pt/SAPO-11

4- Conclusion

SAPO-11 catalyst was prepared experimentally and subjected to many tests (XDR,XRF,AFM,BET and Pyridine adsorption) that showed its relevance for using in isomerization reaction. n-Decane was used in isomerization reaction, n-decane conversion increases as the temperature is increasing from 200 to 275°C and decreases as the LHSV is increasing from 0.5 to 2 hr^{-1}.

The highest n-decane conversion over Pt/SAPO-11 56.77% was achieved at 275°C and 0.5 hr^{-1}LHSV, while the reaction order was first order. Also, the catalysts gave a high activity in isomerization process, and no cracked product produced in this range of operating conditions.

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دراسة حركية تفاعل الازمرة الهايدروجينية للديكان الاعيتادي باستخدام العامل المساعد Pt/SAPO-11

الخلاصة

تمت دراسة عملية الازمرة الهايدروجينية للديكان الاعتيادي على محفزSAPO-11 حيث تم تحضير 0.25% Pt/SAPO-11 محليًا واستخدامه في العمل الحالي. يتم إجراء عملية الازمرة في منظومة ريادية تحتوي على مفاعل ذو الحشوات الثابتة. ان تجارب ازمرة الديكان تمت بدرجات حرارة تراوحت من 200 إلى 275 °م ، و سرع فراغية تراوحت من من 2-0,5 سا$^{-1}$، والهيدروجين إلى نسبة الديكان الاعتيادي من 2.1 إلى 8.2.ان اعلى نسبة تحول هي 56,77% في درجة حرارة 275°م وسرعة فراغية 0,5 سا$^{-1}$. كذلك تمت دراسة حركية ازمرة الديكان وبينت النتائج ان تحول الديكان الاعتيادي يزداد مع زيادة درجة الحرارة وتقليل السرعة الفراغية. ان التفاعل هو من الدرجة الاولى. كذلك ان التحليل الحركي يبين ان الطاقة المنشطة تساوي 61,1137كجول/مول.