Advanced Study of Promoted Pt /SAPO-11 Catalyst for Hydroisomerization of the n-Decane Model and Lube Oil

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Abstract

SAPO-11 is synthesized from silicoaluminophosphate in the presence of di-n-propylamine as a template. The results show that the sample obtained has good crystallinity, 396m²/g BET surface area, and 0.35 cm³/g pore volume. The hydroisomerization activity of (0.25)Pt (1)Zr (0.5)/SAPO-11 catalyst was determined using n-decane and base oil. All hydroisomerization experiments of n-decane were achieved at a fixed bed plug flow reactor at a temperature range of 200-275°C and LHSV 0.5-2h⁻¹. The results show that the n-decane conversion increases with increasing temperature and decreasing LHSV, the maximum conversion of 66.7% was achieved at temperature 275°C and LHSV of 0.5 h⁻¹. Meanwhile, the same catalyst was used to improve base oil specification by increasing viscosity index and decreasing pour point. The isomerization reaction conditions, employed are temperature (200-300)°C, the liquid hourly space velocity of 0.5-2h⁻¹ and the pressure kept atmospheric. The present study shows that Pt Zr W/SAPO-11 minimizes the pour point of lubricating oil to -16°C at isomerization temperature of 300°C and LHSV of 0.5 h⁻¹ and viscosity index 134.8.

Keywords: SAPO-11; Isomerization; n-Decane; Bifunctional catalysts; lube oil; pour point; viscosity index.

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1- Introduction

Many processes have been proposed to improve the properties of base oil by upgrading the ordinary base oil which would be converted into other products [1]. Base oil hydroprocessing includes hydrocracking and catalytic dewaxing processes that have been used. The hydrocracking process is converted the low viscosity index of long-chain alkanes with a high viscosity index of lower chain alkanes. [2-4].

Isodewaxing is a new technology for improving the hydroisomerization process. In this process isomerization of long-chain alkanes gives higher amounts of base oil yield, higher viscosity index, and low pour point with respect to other processes like; solvent dewaxing, and catalytic dewaxing. Also, this process improves other properties of base oil such as viscosity index and pour point (highest VI component and lower pour point) and this is due to the isomerization of waxes [5].

Producing low pour point and high viscosity index base oil by isomerization of long-chain n-alkanes is important in petrochemical industries and petro refining, also to get the required identification of converting n-alkanes into their monobrached isomers [6]. Isomerization is a fundamental molecular transformation without altering the number of atoms present in the molecules. This reaction has both scientific and commercial importance in petroleum, lubricants, and various industries [7,8].

Catalysts with 12 MR (member ring) pores channels can give mono-branched, di-branched, and tri-branched hydrocarbons, so the isomerization process using these catalysts tend to give a significant amount of di- and tri-branched. On the other hand catalysts with 10 MR pores which tend to give mono-branched hydrocarbons will be more suitable choice for the isodewaxing process than catalysts with 12 MR [9,10].

For good performance, suitable catalysts are used for the conversion of hydrocarbons. Many catalysts were used for isomerization of long-chain n-alkanes, but SAPO-11 was one of the most active for 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 [11]. The microporous structure of SAPO-11 prevents producing multi-branched isomers. So, SAPO-11 showed excellent conversion of hydrocarbons into isomers [12]. However, it is observed that the active sites for isomerization are found near the pore mouths of the zeolite. Consequently, the realization of SAPO-11 with a suitable pore structure is important to produce the mono-branched isomers from long-chain n-paraffins [13].

The acidity and pore structure of support is the important factors influencing the hydroisomerization performance of the bifunctional catalyst [14]. For the catalyst activity and isomerization selectivity, the acid site density and the acid strength distribution are both important [15].
Strong acidity promotes hydrocracking, whereas medium-strength acidity is favorable to high isomerization selectivity [16, 17]. The present study aimed to synthesize the SAPO-11 catalyst with improved characteristics for isomerization of the long-chain n-alkanes.

Characterization of the prepared catalyst by detection of the x-ray configuration, FTIR analysis, particle size, surface area, pore volume, and adsorption isotherm. Deposition of platinum, zirconium, and tungsten on the SAPO-11 to produce Pt Zr W/ SAPO-11 catalysts and study the isomerization of a simulated model (n-decane) and base oil (after furfural extraction) to detect the generation of the relevant isomers in a fixed bed reactor unit.

2- Experimental Work

2.1. Chemicals

n-Decane 99% (BDH, England) and 3SS (Base oil after the furfural extraction process from Al-Dura Refinery) are used as feedstock in this study.

Ortho phosphorous acid (85 wt% H₃PO₄) (Panreac, Spain); Aluminum isopropanoxide (BDH, England); di-n-propylamine, m.wt. 101.19 (BDH, England) as template.

Silica sol. 99.9% (Qingdaw Jiyyda, China); deionized water; Poly Vinyl Alcohol (PVA) 99% (Sigma) and γ-nano-alumina. 99.99% (HWNANO, China) as a binder; are used to synthesized SAPO-11.

2.2. Synthesis of SAPO-11

SAPO-11 was synthesized at 190°C crystallization temperature, 550°C calcination temperature with aging and double water contents according to Hussein and Aljandeel [18].

2.3. Synthesized of Pt/SAPO-11 and Pt Zr W/SAPO-11

For preparing 0.25wt.% of Pt on 50 g of SAPO-11 by impregnation method. The carrier catalyst SAPO-11 was dried at 110°C with air for two hours. The impregnation requires an appropriate solution of hexchlorplatinic acid containing 0.368 g of H₂PtCl₆ and deionized water till the volume of solution equal to the pore volume of 50 g under vacuum. The impregnated catalyst was then dried at 110°C, overnight and calcinated at 300°C for 3 hours in a furnace with dry air [19].

While preparing Pt Zr W/SAPO-11 the mole ratio of W/Zr used in this work was 2. The selected ratio was based on the work of Chang et al. [20] who suggested the ratio of W/Zr was from 1 to 5. For the preparation of 50g catalyst, the impregnation solution was prepared by dissolving 1.27 g ammonium meta tungsten and 1.065 g zirconium tetrachloride and deionized water till the volume of solution equal to the pore volume of 50 g (i.e. 16 ml). The co-impregnation process was carried out under a vacuum.

The impregnation solution was added as drop wise with mixing for homogenous distribution at a fixed temperature of 80°C.

The impregnated extrudates were then dried at 110°C, overnight and calcinated at 500°C for 2 hours in a furnace with air and then stored in a desicator.

The concentrations of W and Zr were measured by Atomic Absorption Spectrometer (PYE UNICAM SP9) and found to be 1 and 0.5 wt% respectively. The next step is to prepare 0.25wt.% of Pt on 50g of Zr W/SAPO-11 by the impregnation method.

The carrier catalyst Zr W/SAPO-11 was dried at 110°C with air for two hours then the same steps used for preparing Zr W/SAPO-11 catalyst were adopted apart from the fact that the temperature of the operation was decreased to 40°C instead of 80°C. The impregnation requires a proper solution of hexchlorplatinic acid containing 0.368 g of H₂PtCl₆ and 16 ml of deionized water for a 50 g catalyst. The impregnated extrudates were then dried at 110°C overnight and calcinated at 300°C for 3 hours in a furnace with dry air.

2.4. SAPO-11 characterization

a. X-ray Diffraction (XRD)

The prepared sample was tested using X-ray diffractometer Shimadzu SRD 6000, Japan, with Cu wavelength radiation 1.54060 cm⁻¹ in the 2 theta range from 5-60°, and fixed power source 40Kv, 30mA. XRD for prepared samples was performed at the Ministry of Science and Technology.

b. X-ray Fluorescence (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.

c. AFM

Average particle size 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).

d. BET Surface Area and Pore Volume

The 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 micrometric ASAP 2020.
The samples were disarmed 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.

e. Fourier–Transform Infrared Spectroscopy (FTIR)

This test was applied using (IR-Affinity, Shimazdo, Japan) with a wave range between (400–4000)cm⁻¹ at Ibn-Sina State Company / University of Baghdad.

2.5. Reactor

The reactor is a stainless-steel tube with 2cm inside diameter, 2mm wall thickness, and 62 cm length. It was packed with 44.4 cm³ of the catalyst between two layers of the inert glass ball.

The reactor is heated and controlled automatically by four steel-Jacket heaters (Sotelem, Rueil, France, 250 watt). For measuring the temperature of the catalyst and heaters, chromal alumel thermocouples (type K) fixed inside the reactor at three different locations were used to measure the temperature in the reactor.

2.6. Isomerization Process

44.4 cm³ of fresh catalyst was charged to the reactor between two layers of inert materials (glass balls). The catalyst was then reduced with hydrogen at 350°C for 3 hours in the reactor [20].

After that, the charged reactor was flushed with nitrogen to purge the air from the system. Meanwhile, the reactor is heated to the desired temperature. After reaching the reaction temperature, the nitrogen valve was closed.

A pre-specified flow rate of n-decane was set on, vaporization of the feed occurs in the evaporator, and the vapor of n-decane mixed with the hydrogen in the mixing section at specified flow rates.

The mixture entered the reactor from the top, distributed uniformly, and reacted on the catalyst charged inside the reactor. The product gases passed through the condenser and the final condensates were collected only after steady state operation was established and initial products were discarded.

Pt Zr W/SAPO-11 catalysts were used for kinetic study, the isomerization reaction conditions employed are temperatures of (200-275)°C, the liquid hourly space velocity of 0.5-2h⁻¹, hydrogen to n-decane mole ratio of 2.1-8.2 and finally, the pressure was kept atmospheric.

While the isomerization reaction conditions for base oil were employed at temperature (200-300)°C, the liquid hourly space velocity of 0.5-2h⁻¹ and the pressure kept atmospheric. Fig. 1 shows the process flow diagram.

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

a. Gas Chromotograph (GC))

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

b. Kinematic viscosity test

According to ASTM D, 446 [21] method kinematic viscosity of base oil was measured by using Canon-Fenske (Routine viscometer) of size number 300 for transparent liquid.

c. Pour Point Test

According to ASTM D97, the standard method of testing the Pour Point, the pour point of base oils samples was measured.

3- Result and Discussion

3.1. SAPO-11 Characterization

a. X-Ray Diffraction

Fig. 2 shows the x-ray diffraction patterns of SAPO-11 sample. The sample was hydrothermally crystallized at 190 °C.
The purity of the prepared SAPO-11 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., [22]. The comparisons indicate that the preparation method results are compatible with the crystal structure of SAPO-11 zeolite with an average crystallinity of 114.2%. This concludes that the preparation method gives good synthesized originality of SAPO-11.

b. X-ray Florescence

The molar composition of SAPO-11 molecular sieve after calcination is 1Al₂O₃:0.93P₂O₅:0.414SiO₂

c. Particle size of SAPO-11 catalyst

The atomic force microscopy (AFM) method was used to find the average particle size of SAPO-11 samples. The effects of aging and doubling the water content on the size of SAPO-11 were studied. The results show that the average particle diameter was fallen from 132.65nm (Without aging with double water content) to 57.39nm (24 h aging time with double water content), this means that using the aging process (double water contents for both sample) decrease the particle diameter 75.26 nm, while the average particle diameter was fallen from 149.35 nm (Conventional method) to 132.65 nm (Without aging with double water content), this means that increasing the water contents double (without aging for both samples) decrease the particle diameter 16.7 nm. It can conclude that the aging process has more effect on average particle size diameter than water contents, this is due to the increasing of nucleation rate and crystals growth during the aging process [23].

d. Surface Area and Pore Volume

SAPO-11 displays a larger surface area and pore volume (396.17 m²g⁻¹ and 0.3159 cm³g⁻¹ respectively) with double water at a temperature of 190°C with aging for 24 hr. These values (surface area and pore volume) in this research are higher than previous work which indicated that the surface area was 242.2 m²g⁻¹ and pore volume 0.196 cm³g⁻¹ [22].

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

e. Fourier Infrared Spectroscopy FTIR

FT-IR spectroscopy analysis of SAPO-11 was executed to study the structure of the chemical bonds between molecules.

FTIR was used to investigate the nature and quantum of hydroxyl groups produced by Si. The FT-IR spectra of Pt Zr W/SAPO-11 is 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 [26]. 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 PO₄, AlO₄, and SiO₄, respectively [26].

f. Pyridine FTIR

FT-IR spectroscopy is a technique that is used for the sharpness of Brønsted and Lewis acid sites by adsorption of pyridine on the catalysts [24]. The FT-IR spectra of pyridine adsorbed on Pt Zr W/SAPO-11 is shown in Fig. 4.

The intensity of the bands at 1550 and 1450 cm⁻¹ was thought to be proportional to Brønsted and Lewis acid site concentrations, respectively.

It is interesting to understand that the number of acid sites is not only affected by the amount of Si incorporated into the framework, but also by the large external surface of the superfine particles which allow the acid sites to be bonded with pyridine molecules.
It is clear from this figure that the sample 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 [21]. The band at 1490 cm\(^{-1}\) corresponds to pyridine molecules adsorbed on both L and B acid sites [21].

The absorbance peaks for pyridine molecules adsorbed on the L or B acid sites changed after the introduction of platinum and zirconium-tungsten because zirconium has a combined effect on the degree of hydration and increases the active acid sites (Bronsted and Lewis) [25].

**Fig. 4.** FT-IR of synthesized Pt Zr W/SAPO-11 after pyridine adsorption

### 3.2. Isomerization of n-decane Model

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

**a. Effect of Temperature**

In order to maximize the production of isomerization products and, simultaneously, minimize cracking, the isomerization of n-decane should be at a temperature below 300\(^\circ\)C [26].

**Fig. 5.** Conversion of n-decane at different temperature and LHSV on Pt Zr W/SAPO-11

**b. Effect of LHSV**

Fig. 6 depicts 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 plenty of contact time in the feedstock 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. 6.** Conversion of n-decane at different contact time on Pt Zr W/SAPO-11

**c. Effect of Zr-W Promoters on the Catalyst Activity**

The effect of the mixture of zirconium and tungsten promoters on the activity of the prepared SAPO-11 catalyst was studied at different LHSV and temperature ranges 200 – 275\(^\circ\)C.

**Fig. 7.** Conversion in n-decane conversion, using two types of promoters on SAPO-11, the first one Pt/SAPO-11 and the second using Pt/ZrW/SAPO-11. It can be seen that the presence of platinum together with an acid component raises the mechanism for paraffin isomerization [18].
This figure shows that Pt Zr W/SAPO-11 gives higher conversion rate which means that the addition of these promoters (0.51% Zr and 1.1% W, which are measured by XRF), can enhance the catalyst activity. The increase in the transformation on Pt Zr W/SAPO-11 may be due to enhancement of the acid sites due to the presence of promoters [27].

Tungstate species also appeared to be more resistant to the loss of active sites during the catalytic cycle, therefore they are more stable and give strong catalysts [28], while the presence of platinum increases the hydration-dehydration reaction. On the other hand, zirconium is a combined effect of the degree of hydration and increases the active acid sites (Bronsted and Lewis) [27].

Lee et al. [30] found the maximum conversion using Pt W/SAPO-11 was 42% in comparison with our research; it can be seen that the conversion was higher.

The reaction rate constants (k) were calculated at different reaction temperatures according to the linear relation between $-\frac{\ln k}{T}$ and $C_A$, while Table 1 shows the values of rate constants that were obtained at different reaction temperatures.

Table 1. Values of rate constant at different reaction temperatures

| Reaction Temperature (°C) | K (liters/hr.kg catalyst) |
|---------------------------|---------------------------|
| Pt/Zr/W/SAPO-11           |                           |
| 200                       | 23.858                    |
| 225                       | 47.967                    |
| 250                       | 91.163                    |
| 275                       | 147.36                    |

e. The Apparent Activation Energy Measurements

The activation energy of isomerization reaction was calculated using Arrhenius equation, which satisfies the relationship between rate constant and the reaction temperature.

$$k = A e^{-\frac{E_a}{RT}}$$  \hspace{1cm} (1)

The plot of (ln k) vs. (1/T) was used for the calculation of the activation energy for the isomerization reaction and it was equal to 52.727 kJ/mol.

f. Isodewaxing Process for Iraqi Base Oil

Isodewaxing is a process for making a base oil of a low pour point, high viscosity index, and improved oxidation stability. It is important to find the benefits of this invention in dewing process to study the effect of temperature before the cracking becomes excessive.

f.1. Effect Of Operating Conditions On Pour Point

Temperature and LHSV have an obvious influence on the pour point of base oil (side stream comes from furfural extraction).

As shown in Fig. 9 and Fig. 10 by increasing the space velocity (less contact time), the pour point increases at a constant temperature which means that an increase in the residence time, leads to plenty of contact time of the feedstock with the catalyst inside the reactor [10].

It can be concluded that when the temperature increases the pour point decreases however at moderate temperatures there is a chance for a hydroisomerization reaction to occur, resulting in an isoparaffin formation which has a low pour point (-16 °C at isomerization temperature of 300°C and LHSV 0.5 h$^{-1}$). This conclusion was supported by Thomas et al., [30].
The effect of the mixture of zirconium and tungsten promoters on pour point at different LHSV and temperature range 200–300°C were studied. A comparison for hydroisomerization of lubricating oil using two types of promoters on SAPO-11, the first one Pt/SAPO-11 and the second using Pt Zr W/SAPO-11 shows that Pt Zr W/SAPO-11 gives a lower point (Reducing pour point from -13°C by using Pt/SAPO-11 to -16°C when using Pt Zr W/SAPO-11) which means that the addition of these promoters (0.51% Zr and 1.1% W, which measured by XRF) can enhance the catalyst activity[31].

f.2. Effect of Zr-W Promoters on Pour Point

Viscosity index is one of the most common properties of lube oil fractions. This property reflects the ability of the lube oil viscosity to vary with temperature. Fig. 11 and Fig. 12 investigates the variation of VI with operating conditions (Catalyst bed temperature and LHSV) and the effect of Zr/W promoters. It is obvious that the viscosity index increases with the catalyst bed temperature increasing and LHSV decreasing, for a given catalyst.

The effect of the feed quality (aromatic and saturated content) also affects VI, and it has a strong relationship with the aromatics and saturates. The temperature increasing will encourage the saturation of aromatic species or even decomposition resulting in the conversion of aromatics to paraffinic or the conversion of alkanes to isoalkanes. This influence was in agreement with Thomas et al [28] which indicates that the increase of a reaction temperature leads to an increase in the rate of isomerization while the LHSV decreasing leads to an increase in the time of contact and gives the same results. Gortesema et al [29] and Miller [3] obtained that the catalyst impregnated by platinum gives the best result for both viscosity index and pour point. It can be observed that using zirconium and tungsten promoters has the highest effect on VI and pouring point when compared with platinum alone.
4- Conclusion

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 was 56.77% which was achieved at 275°C and 0.5 hr⁻¹ LHSV, while the reaction order was first order.

While isodewaxing of 3SS base oil was achieved and the flow properties of the base oil were improved. The best isodewaxing conditions were a temperature of 300°C and LHSV 0.5 h⁻¹. The pour point of base oil was reduced to -16°C, while the viscosity index was improved to 134.8 by using Pt Zr W/SAPO-11.

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Symbols

| Symbol | Definition | Unit |
|--------|------------|------|
| A      | Pre-exponential factor | For 1st order reaction: min⁻¹ |
| CA     | The concentration of decane at any time | mol/liter |
| Ea     | Activation energy | KJ/mol liters/h kg catalyst |
| k      | Reaction rate constant | |

References

[1] Tian S. and Chan J., "Hydroisomerization of n-dodecane on a new kind of bifunctional catalyst: Nickel phosphate supported on SAPO-11 molecular sieve", Fuel Processing Technology, 122, 2014, 120-128.
[2] Wang Z., Tian Z., Teng F., Wen G., Xu Y., Xu Z., Lin L., "Hydroisomerization of long-chain alkane over Pt/SAPO-11 catalysts synthesized from nonaqueous media", Catal Lett, 103, 2005, 109-116.
[3] Miller S.J., "Studies on wax isomerization for lubes and fuels", Studies in Surface Science and Catalysis, 84, 1994, 2319-2326.
[4] Song H., Liu Z., Xing W., Ma Z., Yan Z., Zhao L., Zhang Z., Gao X., "Preparation of hierarchical SAPO-11 molecular sieve and its application for n-dodecane isomerization", Appl Petrochem Res, 2014, 4:401-407.
[5] Krishna K.R., Rainis, A., Marcantonio, P.J., Mayer P.J., Chevron L., Biscardi J.A., "Next generation isodewaxing and hydrotreating technology for production of high quality base oils", 2002 NPRA Lubricants and waxes meeting, November 14-15, 2002. Omni Hotel Houston, Texas.
[6] H.Deldari, "Suitable catalysts for hydroisomerization of long-chain normal paraffins", Applied Catalysis A, 239, 2005, 1-10.
[7] Robert J. Taylor, Randall H. Petty," Selective hydroisomerization of long chain normal paraffins", Applied Catalysis A, 119, 1994, 121-138.
[8] Nieminen V., Kumar N., Heikkila T., Laine E., Villegas J., Salmi T., and Murzin D.Y.," Isomerization of 1-butene over SAPO-11 catalysts synthesized by varying synthesis time and silica sources", Applied catalysis A, 259, 2004, 227-234.
[9] Abdul Halim A. K.M., Rahman A.M., and Al-Hassani M.," Kinetic Study of Catalytic Hexane Isomerization", IJCPE Vol.10, No.1, 2009:17-22.
[10] Lok B.M., Messina C.A., Patton R.L., Gajek R.T., Cannan T.R. and Flanigen E.M., "Crystalline silicoaluminophosphates" US Patent, 4440871, 1984.
[11] Shengzhen Zhang, Sheng-Li Chen Peng Dong, Zhivong Ji, Junying Zhao, and Keqi Xu," synthesis, characterization and hydroisomerization catalytic performance of nanosize SAPO-11 molecular sieves", Catalysis letters, 118, 2007, p. 109-117.
[12] Sastre G., Chica A., and Corma A, "On the mechanism of Alkane isomerization (Iso dewaxing) with Unidirectional 10- member ring zeolites, A Molecular Dynamics and Catalytic study", Journal of catalysis 195, 2000, 227-236.
[13] Zhipeng Ma, Zhen Liu, Hao Song, Peng Bai, Wei Xing, Zifeng Yan, Lianhao Zhao, Zhongdong Zhang and Xiongguo Gao, “Synthesis of hierarchical SAPO-11 for hydroisomerization reaction in refinery processes, Appl Petrochem Res vol 4 (2014), 351-358.
[14] Cui X., Liu Y., and Liu X., "Controlling acidic sites to improve hydroisomerization performance of Pt/SAPO-11 catalysts", Catal lett, 145 (2015), 1464-1473.
[15] Sinha A. K., Sivasanker S., and Ratnasamy P., "Hydroisomerization of n-Alkanes over Pt/SAPO-11 and Pt-SAPO-31 Synthesized from Aqueous and Nonaqueous Media", Ind. Eng. Chem. Res. 37, 1998, 2208-2214.
[16] Al-Hassani M., "Effect ZRO₂ - WO₃ additives on catalytic performance of Pt/HY zeolite compared with Pt/Al₂O₃ for Iraqi naphtha transformation", Journal of Engineering, vol. 15, number 4, 2009, 4378-4394.
[17] Zhening Wang, Zhijian Tian, Fei Teng, Guodong Wen, Yumeng Xu, Zhusheng Xu and Liwu Lin, "Hydroisomerization of long-chain alkane over Pt/SAPO-11 catalysts synthesized from nonaqueous media", Catalysis Letters, vol.103 (2005), 109-116.
[18] Hussein Q. H. and Aljandeel H.A., "Studying Influence of Aging and Crystallization Temperature on Characteristics of SAPO-11 Catalyst Using Hydrothermal Method", 1st International Conference on Recent Trends of Engineering Sciences and Sustainability, 2017.
[19] Masologites, George, "Method of treating a used Pt group alumina catalyst with a metal promoter", US patent, 4070306, 1978.
[20] Chang C.D., Princeton N.J., Jose G., Sontiesteban, David L., Stern, "Isomerization process", US patent, 6080904, 2000.
[21] American, N. S., 1979. Standard Specifications and Operating Instructions for Glass Capillary Kinematic Viscometers. D446-74, Deutsche Norm DIN 366 und 51372.

[22] Zhang S., Chen S., Dong P., Ji Z., Zhao J., and Xu K., "synthesis, characterization and hydroisomerization catalytic performance of nanosize SAPO-11 molecular sieves", Catalysis letters, vol. 118, p. 109-117, 2007.

[23] Zhang F., Liu Y., Shu X., Wang W. and Qin F., "SAPO-11 molecular sieve, its synthetic method and a catalyst containing the molecular sieve", US patent, 6596156, 2003.

[24] Marjan R., Rouein H., and Sima A., " Recent advances in silicoaluminophosphate nanocatalysts synthesis techniques and their effects on particle size distribution", Rev. Adv. Mater. Sci. 29, 83-99, 2011.

[25] Liu Y., Quan Y., Li C., Juan L., Geok J., Eng Chew, Fethi K., "Effect of ZnO additives and acid treatment on catalytic performance of Pt/W/Zr for heptane isomerization," J. of cat. 244, 2006, 17-23.

[26] Aljandeel H. A., Hussein H. Q., "Kinetic Study of Hydroisomerization of n-Decane using Pt/SAPO-11 catalysts", Iraqi Journal of Chemical and Petroleum Engineering 2018, 19(3), 11-17. https://doi.org/10.31699/IJCPE.2018.3.2

[27] Risch M., Wolf E., "Effect of the preparation of a mesoporous sulfated zirconia catalyst in n-butane isomerization activity", Applied Catalysis A: General 206 (2001) 283–293.

[28] Thommes M., "Physical Adsorption Characterization of Nanoporous Materials", Chemie Ingenieur Technik, 82, No. 7, 2010.

[29] Gortsema, F.P., Pellet, R.J., Springer, A.R., Rabo, J.A., Armonk, Long, G.N., "Hydrocracking catalyst and processes employing non zeolitic molecular sieves", U.S. Patent No. 4818739, 1989.

[30] Lee E., Yun S., Park Y. K., Jeong S. Y., Han J., Jeon J. K., "Selective hydroisomerization of n-dodecane over platinum supported on SAPO-11", Journal of Industrial and Engineering Chemistry, 20, 2014, 775-780.

[31] Oliveira, L., Nunes, R., Ribeiro, Y., Coutinho, D., Azvedo, D., Dias, J., & Lucas, E., "Wax Behavior in Crude Oils by Pour Point Analyses", Journal of the Brazilian Chemical Society, 2018, 29(10), 2158-2168. doi:10.21577/0103-5053.20180092
دراسة متقدمة للعامل المساعد المحفز Pt/SAPO-11 الى لعمليات الازمرة الهيدروجينية للديكان الطبيعي و زيت التشحيم

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الخلاصة

تم تصنيع العامل المساعد SAPO-11 من السليكا , والالومينا والفسفيت بوجود البروبايل اماين كقلب . لقد أظهرت النتائج ان النموذج الذي تم تصنيعه لديه درجة تبلور جيدة, مساحة سطحية 396 م2/غم , حجم المسامات 35 سم3/غم . ان فعالية الازمرة للعامل المساعد 11 تم ايجادها بوجود الديكان وزيت الاتصال في مفاعل ذو الحشوة الثابتة في درجات حرارة 200°-275°م ومعدل جريان 0.5-2 سا-1. لقد اظهرت النتائج ان نسبة التحول تزيد بزيادة درجة الحرارة ونقصان معدل الجريان. ان أعلى نسبة تحول هي 66.7% وجدت عند درجة حرارة 275°م و معدل جريان 0.5 سا-1. في حين تم استعمال نفس العامل المساعد لتحسين مواصفات زيت الاتصال بزيادة معامل اللزوجة ونقل نقطة الانكساب , حيث تمت العملية في درجات حرارة 200-300°م ومعدل جريان 0.5-2 سا-1. وقد خفضت نقطة الانكساب الى -16°م في درجة حرارة 300°م ومعدل جريان 0.5 سا-1. ومؤشر لزوجة 134.8.

الكلمات الدالة: سابو-11 , ازمرة , ديكان , محفزات ثنائية, زيت التشحيم, نقطة الانكساب, مؤشر اللزوجة.