

Skelton isomerization of n-heptane under the effects of Pt content, particle size and reduction technique

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Abstract

A synthetic approach is developed to produce highly disperse, low loading (0.1- wt%, 0.3-wt% and 0.6- wt%) Pt nanoparticles incorporated montmorillonite (MMT) with average diameter of less than 4.0 nm using economical reduction processes. This was achieved by using formalin followed by chemical reduction with hydrogen to produce Pt nanoparticles incorporated MMT support. The physicochemical characterizations of the Pt nanoparticles incorporated MMT were performed by elemental analysis, FTIR, XRD, N₂-adsorption and transmission electron microscopy. The results show that the Pt nanoparticles were uniformly distributed throughout the MMT support with Pt loading of less than 4.0 nm and the size of Pt is dependant on its loading. The catalytic activity for heptane isomerization reaction was evaluated over the prepared catalysts. At 0.1-wt% of Pt, the catalyst shows high activity for heptane isomerization, while at high Pt loading showed high tendency to cracking. The preparation procedure is simple and favorable for a variety of metal nanoparticles syntheses for catalysis applications.

Keywords: montmorillonite, n-heptane hydroisomerization, effect of Pt

1. Introduction

The stringent environmental restrictions call for reduce aromatics and olefins in gasoline, however reduction of aromatics has a negative impact on gasoline octane number. Researchers paid more attention to looking for alternatives to compensate this loss of octane [Busto et al., 2008].

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The isomerization process became one of the effective ways for manufacturing high performance gasoline with high octane number from straight-run naphtha fractions containing significant amounts of linear aliphatic hydrocarbon chains with a low octane number [Belandria et al., 2011].

The catalytic isomerization involves conversion of linear hydrocarbon to their corresponding branched isomers. This reaction is done over bifunctional catalysts that have metal species supported on a matrix having acid sites [Wang et al., 2008]. This process has been reported on a wide variety of bifunctional catalysts such as Pt/alumina [Corma and Martinez 2002] and Pt, Pd or Ni on zeolitic structure material such as MOR [Karthikeyan et al., 2008 and Aguirre 2006], ZSM-5, SAPO-11 [Lopez et al., 2008], Pt/HPW/ZrO₂ [Ivanov et al., 2004], Pt/MCM-22 [Martins et al., 2008] and Pt/HPW/MCM-41 [Belandria et al., 2010]. There are many attempts to improve the octane number of gasoline/naphtha fraction included: (i) using very acidic catalysts with defined pore structure such as zeolites and superacidic materials. The reaction can be carried out at lower temperatures favoring the formation of isomerization products. Literature indicates that the HZSM-5 catalyst with well-defined porous structure, large pore volumes, narrow pore sizes, high external surface areas, and high populations of external active centers, possesses good stability and high selectivity to aromatics. Due to the high aromatic yield, the carbon is deposited on the active sites (coke formation), owing to the high acidity of the pore surfaces [Rownaghi et al., 2011], and (ii) using composite zeolites consisting of the zeolite component and an inert meso- or macro-porous material, which should facilitate the diffusion properties and, hence, increase the yield of isomerized products [Kinger et al., 2002], however the acidity of such material till now is under studies due to the low hydrothermal of this material.

The isomerization reaction mechanism (ideal unimolecular mechanisms) of normal alkanes such as n-hexane and n-heptane on a bifunctional catalyst involves the dehydrogenation of the alkane to an alkene at a metal site [Belloum et al., 1991 and Sie 1997]. The alkene then transport from the metal site to an acidic site. A protonation of the resultant alkene then takes place on the acid site, converting the alkene to an alkylcarbenium ion intermediate. The resulting alkylcarbenium ion then goes through a structural rearrangement. This is followed by migration and hydrogenation on a metal site to

produce isomers of the initial alkane which have higher research octane number (RON), or a β -scission followed by hydrogenation on a metal site to form cracked products [Van de Runstratt 1997 and Denayera et al., 2000]. A bimolecular reactions of intermediate alkenes may be significant if the catalysts that have Brønsted acidity, cannot be countered by their hydrogenating–dehydrogenating activity, [Blomsma et al., 1995 and Blomsma et al., 1996]. The contribution of the dimerization–cracking reaction relative to the unimolecular reaction decreases with increasing chain length of the hydrocarbon.

Montmorillonite (MMT), common smectite clay is abundant and inexpensive clay mineral material that belong to 2:1 layer-type clay mineral and its basic structural unit is composed of two tetrahedrally coordinated sheets of silicon ions surrounding a sandwiched octahedrally coordinated sheet of aluminum ions [Wu et al., 2011]. Montmorillonite shows excellent sorption ability, swelling behavior, high surface area, ability to exchange or intercalate ions and molecules, catalytic properties, and surface acidity or basicity. Owing to these properties, it was used as heterogeneous catalyst in many chemical reactions as isomerization reaction.

The activity and stability of the montmorillonite catalyst in the isomerization reaction of light paraffins was increased by introducing platinum species to montmorillonite [Iglesia et al., 1993 and Ebitani et al., 1991]. The formation of new proton centers [Ebitani et al., 1991] due to the interaction of hydrogen with platinum explained the effect of platinum during the isomerization reaction. Scheme of n-hexane isomerization has been proposed In [Iglesia et al., 1993 and Duchet et al., 2002], in which platinum acts as a mediator of the transfer of hydride ions formed as a result of the heterolytic dissociation of hydrogen molecules on platinum.

The present study deals with Pt-Montmorillonite, bifunctional catalyst that has both metal and acid sites with different loading of platinum (0.1- 0.6 wt.%) and their catalytic activity towards n-heptane isomerization reaction. The catalytic activity and selectivity of the prepared catalysts were measured, and the effects of catalyst characteristics, including acidity, Pt dispersion and the ratio of available platinum to acid sites, on activity and selectivity were also examined.

2. Materials and methods

2.1. Materials

All chemicals, unless explicitly specified, were purchased from Sigma–Aldrich and used without any further purification: K 10-montmorillonite (MMT; Si/Al = 40) purchased from (Sigma-Aldrich) and was used as support for platinum nanoparticles, Hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$; ≥ 37.4 wt% Pt basis), tetrahydrofuran and n-heptane (use as model for hydrocarbon feed), ethanol (99.8%) and formaldehyde solution (36.5-38% aqueous).

2.2. Catalyst preparation

For the platinum impregnation with different loading: 5.0 g of the MMT was suspended in 75 ml of ethanol. A second solution containing 5.0, 15.0 and 30.0 mg of hexachloroplatinic acid in 1.35, 4.06 and 8.15 ml of water is prepared. The previous solutions of hexachloroplatinic acid that equal 0.1, 0.3 & 0.6 wt-% Pt were added dropwise to the MMT slurry and stirred at room temperature for 2 h before adding 0.55, 0.165 and 0.332 ml of aqueous formaldehyde (as reducing agent) and the prepared catalysts is donated as 0.1-Pt/MMT, 0.3-Pt/MMT and 0.6-Pt/MMT, respectively. The resulting slurry is then aged in a sealed round bottom flask overnight at 45°C and the solvent is evaporated at 75°C under stirring until the majority of the solvent has evaporated. While the semisolid material still at 35°C, the inside of the round bottom flask is scratched, grinded and left to cool to impregnate the unadsorbed platinum onto MMT support. The resulting material is recovered by rotary evaporator, soaked with tetrahydrofuran overnight and air dried in three stages at temperatures of 50, 70 and 90 °C, with each temperature being maintained for a minimum of 2 hours to release the remained solvent. A further reduction step using a flow of 20 ml min⁻¹ of 10% diluted hydrogen (90 N₂/10 H₂ CC/CC) at 150 °C was done to ensure complete reduction of Pt salt before catalytic process evaluation.

2.3. Characterization of the catalysts

The crystalline structure of the catalyst was determined by X-ray diffraction (XRD) recorded on X'Pert PRO Powder X-ray Diffraction with CuK α radiation ($\lambda = 0.1542$ nm), Ni-filter and general area detector. The diffractograms were recorded in the 2θ range of 0.5–70° with step size of 0.02 Å and a step time of 0.605. Nitrogen adsorption-desorption isotherms of

the prepared catalysts were measured on NOVA 3200 system (USA), after degassing at 300 °C overnight in flowing N₂. The BET surface area (S_{BET}) of the investigated samples was calculated from adsorption isotherm data using the BET method. Pore size distribution (PSD) curves were calculated from the desorption branch of the isotherms using the Barrett-Joyner-Halenda (BJH) method. Transmission electron microscopy (HRTEM-EDS) images were obtained using a JEOL 2011 electron microscope operating at 200 kV. The calcined materials were crushed and dispersed ultrasonically in water and then spread onto a perforated carbon-copper microgrid. The FT-IR spectra were recorded on a Nicolet Is-10 spectrometer. The spectra were acquired at room temperature by accumulating 64 scans at 4 cm⁻¹ resolution in the range of 400–4,000 cm⁻¹.

2.4. Catalytic activity tests

The hydroconversion of n-heptane on Pt/MMT catalysts was performed in a microactivity-reference unit (PID Eng & Tech, Spain). A fixed-bed tubular reactor (autoclave engineers, 505 mm length, 19 mm outer diameter, 13.1 mm inner diameter) containing 5.0 g of the prepared catalyst diluted with 5.0 g of inert silica. Before catalytic test, the catalyst was activated at 300 °C for 2 h under N₂ gas (50 ml min⁻¹) and the N₂ gas was replaced by H₂ gas for 2 h to further Pt salt reduction. After cooling the sample to 200 °C, the n-heptane was introduced into the unit using a HPLC positive alternative displacement pump (Gilson, model 307). The product gas mixtures were analyzed online with certificated TCD-FID Agilent 7890A GC system equipped with capillary column (HP-1) and packed column (DC-200) with chem-station program. The experimental conditions of n-heptane hydroconversion are; constant atmospheric pressure, 1 bar, constant liquid hourly space velocity (LHSV; W/W) of 1 h⁻¹, H₂/n-heptane ratio of 20 ml ml⁻¹ and reaction temperature regime of 200-450 °C.

3. Results and discussion

3.1 Textural characterization

The use of formalin reduction synthesis for Pt/MMT results in very homogeneous Pt crystals making separation of the Pt phase on MMT material. The optimized procedure for the impregnation of the metal precursor involved the use of ethanol-water mixtures. The use of formalin was found crucial during the solution impregnation step, the majority of platinum was deposited on the outer and inside surface of MMT catalysts (**Figure 1**). The HRTEM images (**Figure 1**) indicate that the Pt are well dispersed on both MMT surface and

pores, and the bright region is decreased with increasing Pt content. According to Neri et al. (2007), the high bright space intensity of some supported metals over porous materials resulted from high dispersion and diffusion of this metal inside pores. Thus, Figure 1(b-d) illustrates the correspondence between the Bright Field images of metal particles and dark field of the MMT. For the catalyst 0.1Pt/MMT; one observes that most of the metal particles are highly dispersed over the MMT support, and have particle diameters of about 6.7 nm (Figure 1a).

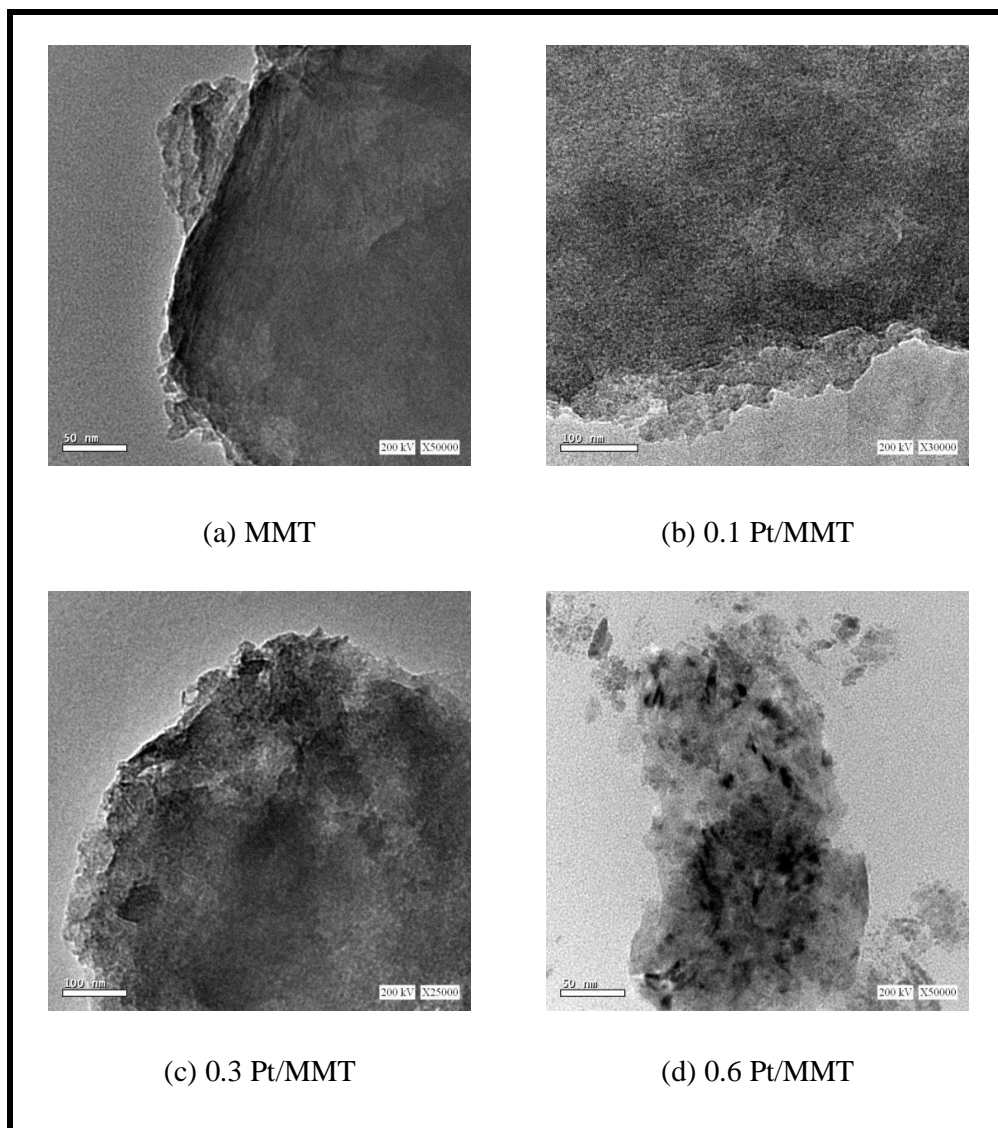


Figure 1: HRTEM of MMT and 0.1-0.6 Pt/MMT catalyst samples.

X-ray diffraction patterns of the MMT and 0.1-0.6 Pt/MMT are illustrated in **Figure 2 (a-d)**. Here, the peak positions at $2\theta = 8.87, 17.8, 19.9, 20.82, 26.6, 35.03, 45.53$ and 62.31° are the characteristics of montmorillonite type of 2:1 swelling clays. These patterns are ascribed to (1 1 0), (0 2 0), (0 0 4), (1 3 0), (2 0 0), (3 3 0) and (0 6 0) diffractions. The dried MMT exhibits a diffraction peak of the (0 0 1) plane at 2θ value of 8.87° , and its basal spacing is 0.996 nm. From Figure 2(a-d), one can also see that the MMT have clearly defined peaks and peak intensities are unaffected and no diffraction of Pt is detected, indicating that the structure of MMT almost remains intact and not be damaged after the impregnation of Pt particles in/into the interlayer surface [Sheng et al., 2009; Shahwan and Erten 2005 and Sun et al., 2012].

After the impregnation of Pt particles into MMT interlayer surface, no intensities of reflections of Pt (JCPDS PDF card No. 04-0802) were observed. This suggests that the quantity of Pt loading was finely dispersed. The basal reflection was displaced to lower angles spectrum, which meant that the interlayer distance was increased due to the incorporation of platinum particles into the MMT interlayer surface, which indicated that the basal space progressively increased [Ezquerro et al., 2015].

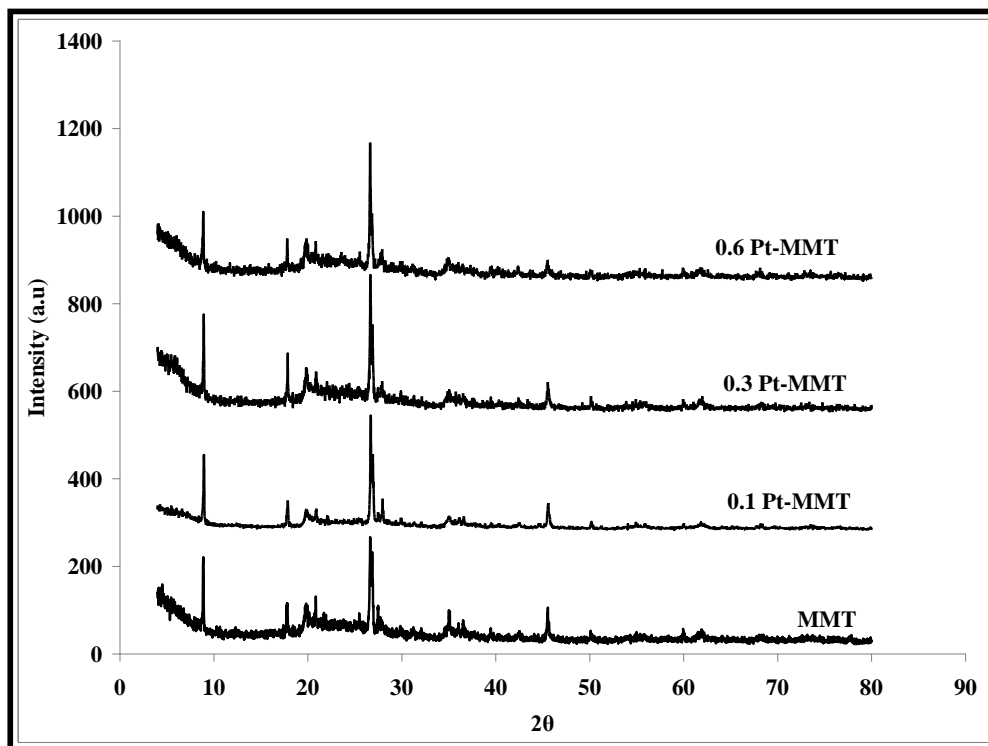


Figure 2: The XRD patterns of (a) MMT, (b) 0.1 Pt/MMT, (c) 0.3 Pt/MMT, (d) 0.6 Pt/MMT catalyst samples.

Figure 3 shows the FTIR spectra of MMT and 0.1- 0.6 Pt/MMT catalyst samples. The FTIR spectrum of MMT shows intense and large bands due to the clay structure: in the regions 3700–3300 and 1650 cm^{-1} , which are assigned to the surface hydroxyl groups from the acidic Al–OH group [Hassan et al., 2014] and Si–OH, and in the range 1300–400 cm^{-1} can be assigned to lattice vibrations [Betiha et al., 2015] (asymmetric stretching vibrations of SiO_2 tetrahedra). In addition, the low intense bands of MMT after Pt impregnation in the 1300–400 cm^{-1} regions are attributed to the coalescence of MMT layer after Pt impregnation. The MMT bands are slightly broader than the Pt/MMT and their wave numbers are red shifted by $\sim 35 \text{ cm}^{-1}$ due to hydrogen bond between Pt and silica hydroxyl groups, however this shift is increased by increase Pt ratios. These results suggest that the Pt is physically attached to MMT surface. Moreover, new bands appeared after Pt impregnation at 674 cm^{-1} and 539 cm^{-1} , these bands might be attributed to Pt nanoparticle bridged of Pt-silica hydroxyl groups. This Bridged metal- hydroxyl complexes are known for many metals including platinum.

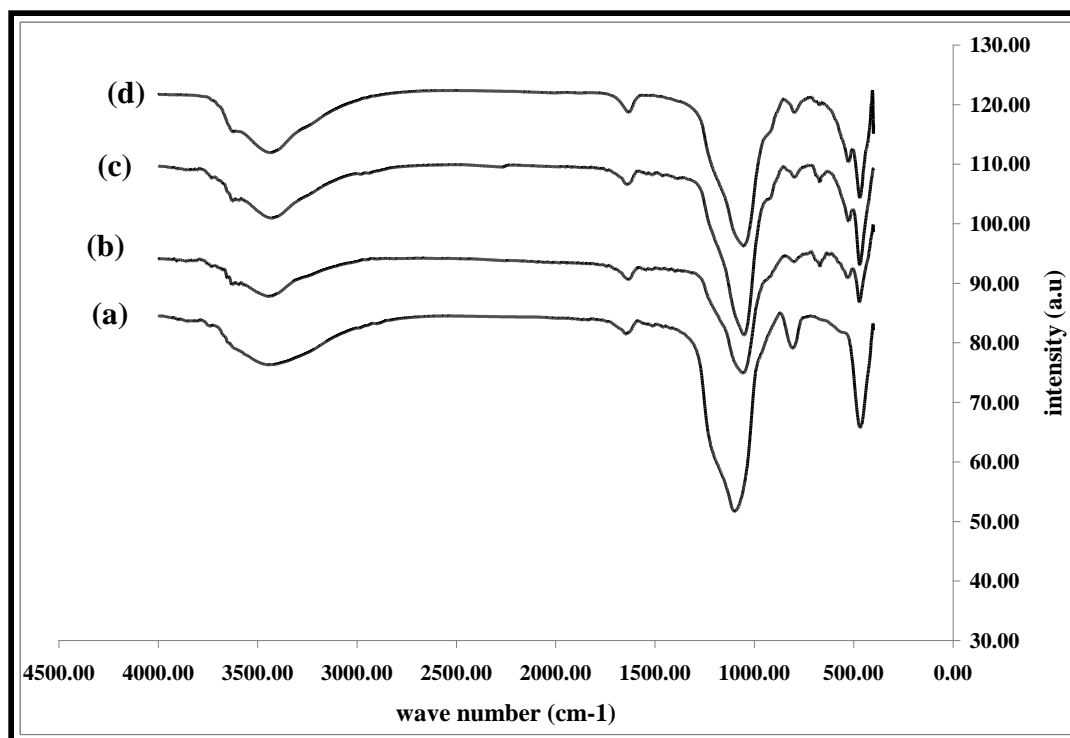
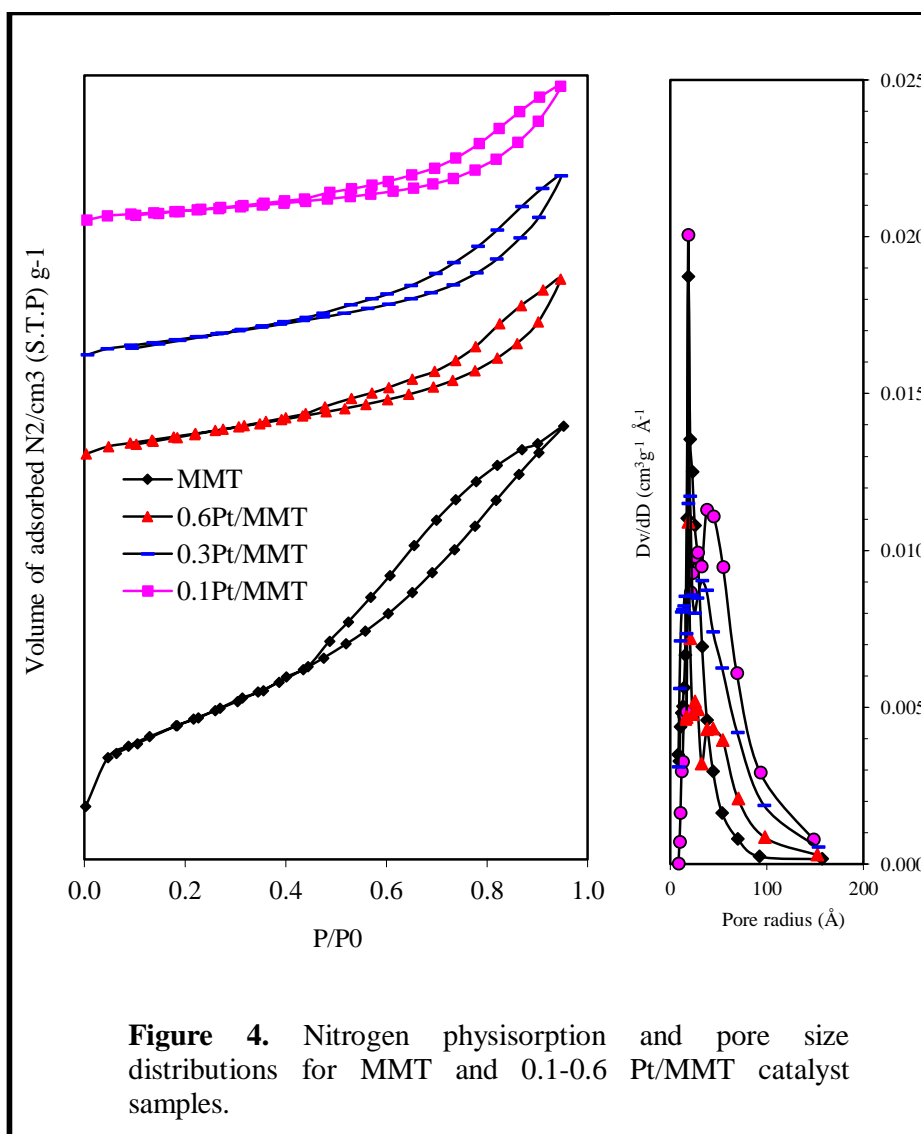


Figure 3: FTIR spectra of (a) MMT, (b) 0.1 Pt/MMT, (c) 0.3 Pt/MMT, (d) 0.6 Pt/MMT catalyst samples.

The N_2 adsorption-desorption isotherms of the MMT and 0.1- 0.6 Pt/MMT are presented in **Figure 4**. All of the samples show a distinct hysteresis during an adsorption-

desorption cycle. The isotherm data can be classified as type I and IV shape along with H4-type hysteresis loop in the IUPAC classification [Carrado et al., 2002]. Such a type of isotherm underlines the presence of the open slit-shaped capillaries with very wide bodies and narrow short necks. In fact, as shown in Figure 4, the Pt/MMT displays the most prominent hysteresis due to the presence of mesopores in the house-of-cards structure of restacked crystallites. Furthermore, the presence of the Pt over MMT would reduce the surface area from 220 m² to 172 m²g⁻¹ (0.1 Pt/MMT), 141 m²g⁻¹ (0.3 Pt/MMT) and 120 m²g⁻¹ (0.6 Pt/MMT) and the diameter of the mesopores become narrower, indicating the Pt located inside pore or in the clay galleries space.



3.2. Catalytic isomerization of n-heptane (n-C₇)

3.2.1 Effect of reaction temperature on n-C₇ isomerization reaction

Temperature has a big influence on the conversion of normal alkanes. An increase in the conversion with the increase in the temperature was reported in the literature and the authors related this behavior to the activation of acid sites responsible for this reaction [Olaya et al., 2009]. As shown in **Figures 5-7**, the conversion nearly increases linearly with increasing the temperature from 200-450 °C. The conversion reaches 25, 35.3 and 43 wt. % over 0.1 - 0.6 Pt/MMT catalysts respectively.

Additionally, the hydroisomerization yield of the normal alkane feed (n-C₇) increases with temperature. Peaks at a certain point, i.e. maximum yield was observed at 350 °C and then starts dropping until it vanishes completely as cracking becomes the predominant reaction. In addition, the selectivity towards hydroisomerization decreases with increasing temperature above 300 °C [Jiménez et al., 2003 and Guisnet 1991]. It is clear from **Figures 5-7** that the isomerization increases with increasing the reaction temperature and reach its maximum values at 350°C, (13.2, 11.3, and 11 wt.%, for 0.1 - 0.6 Pt/MMT catalysts, respectively) and then leveled down.

Generally, it can be noticed that at low temperature (200°C), cracking was the lowest, and thus the selectivity towards isomerization was increased up to 300 °C, then goes to be decreased. Nevertheless, at higher temperatures (450°C) cracking became significantly reaches to 19, 30.3 and 39 wt.% for 0.1 - 0.6 Pt/MMT catalysts, respectively and the isomerization selectivity was deeply decreased.

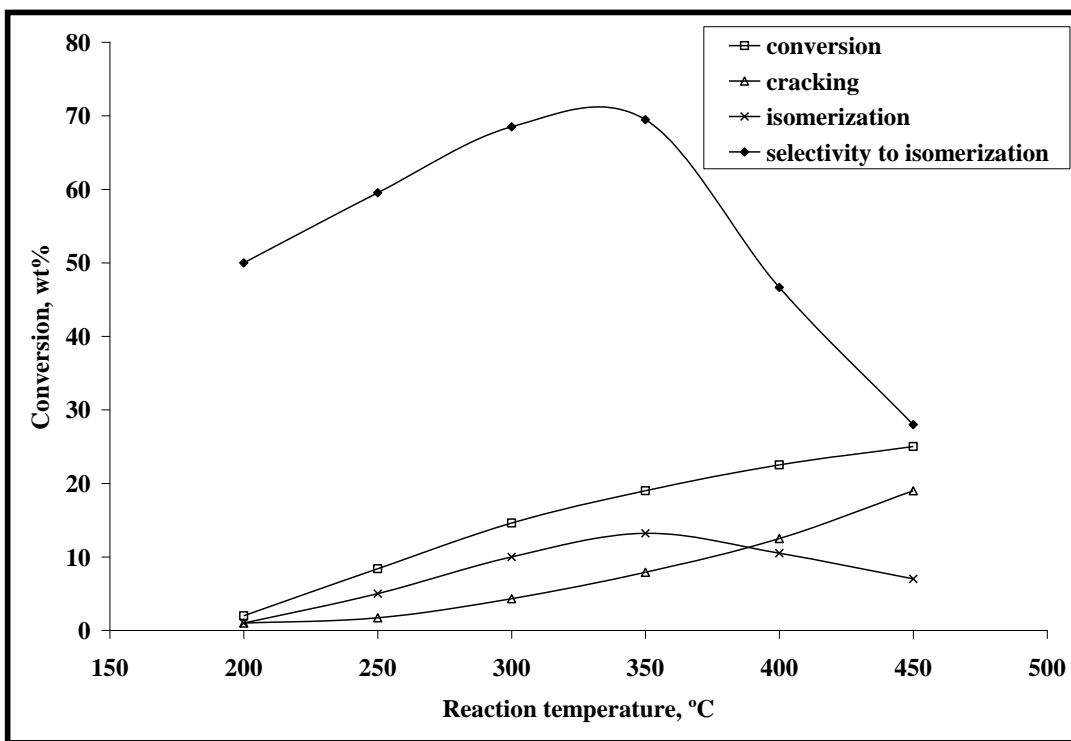


Figure 5: The effect of reaction temperature on conversion, cracking, isomerization and selectivity to isomerization of n- heptane over 0.1 Pt/MMT catalyst.

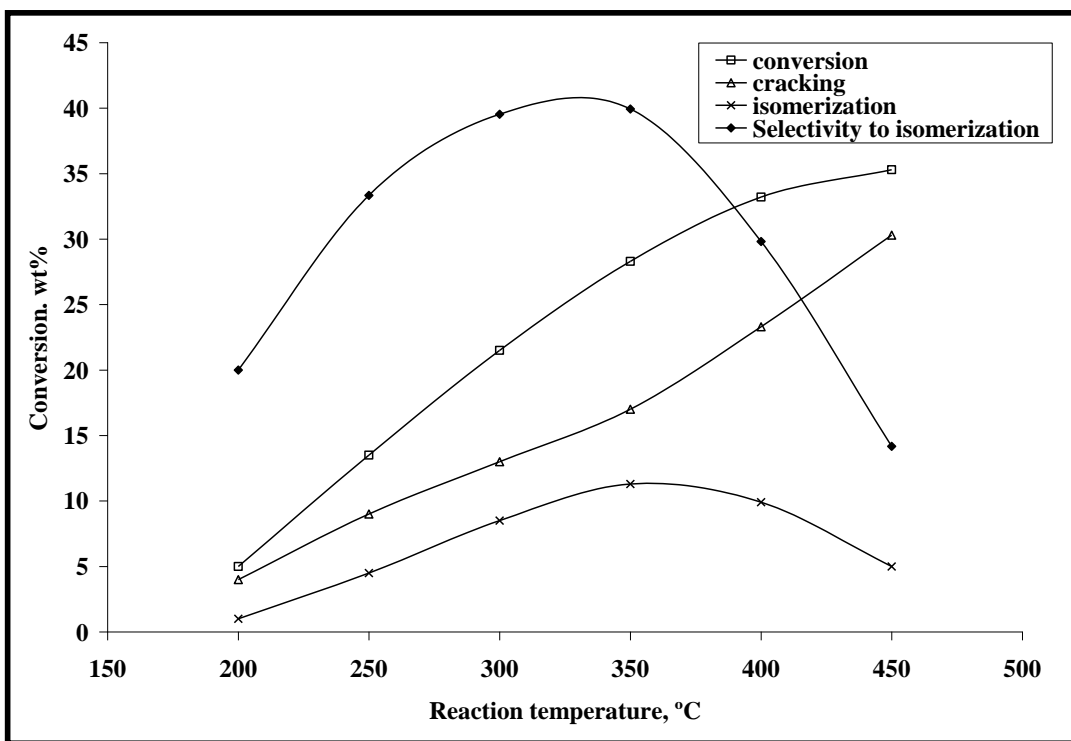


Figure 6: The effect of reaction temperature on conversion, cracking, isomerization and selectivity to isomerization of n- heptane over 0.3 Pt/MMT catalyst.

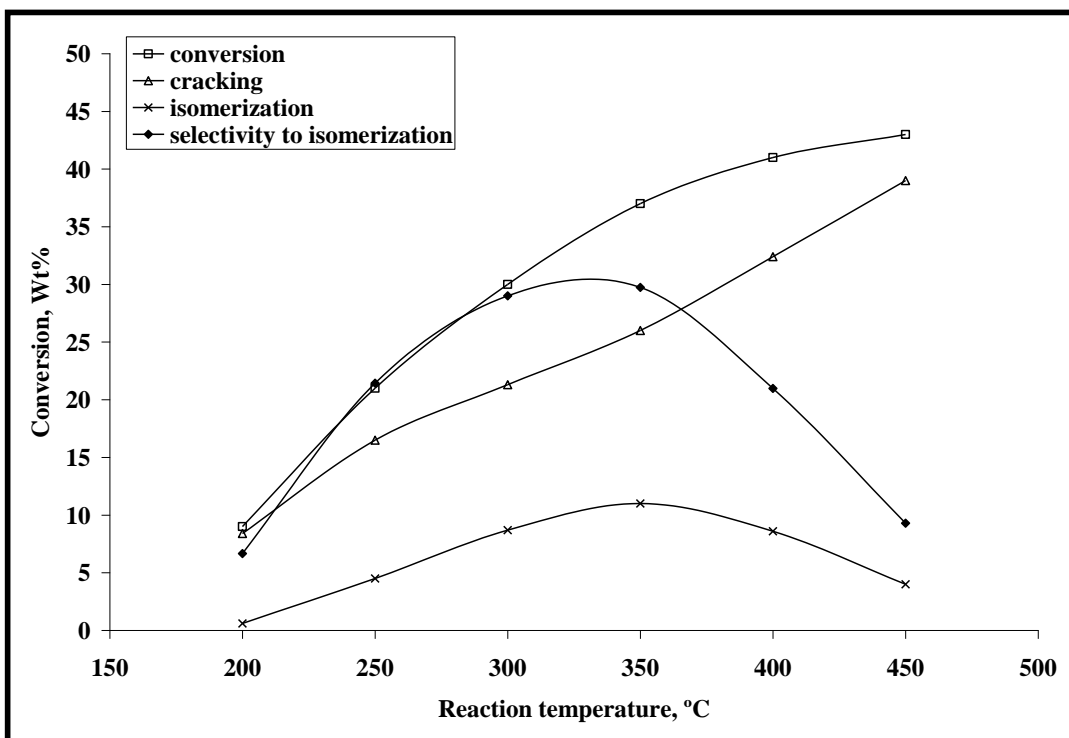


Figure 7: The effect of reaction temperature on conversion, cracking, isomerization and selectivity to isomerization of n- heptane over 0.6 Pt/MMT catalyst.

3.2.2 Effect of Acid-metal Balance (effect of platinum loading)

The acid-metal balance of the catalyst has a strong impact on the extent of hydroisomerization versus cracking i.e. the tendency to isomers versus cracked products. This balance is expressed by the ratio of metallic sites to acidic sites in a given bifunctional catalyst or by the percentage platinum loading on the catalyst [Soualah et al., 2008]. **Figure 8** indicates that (under 350 °C reaction temperature, 1 bar atmospheric pressure, LHSV 1 h⁻¹ and H₂/n-heptane ratio of 50 ml ml⁻¹) as Pt loading increased, the activity towards isomerization decreased significantly and 0.1 Pt/MMT catalyst appeared to have the highest isomerization (13.2 wt.%) while increasing of the Pt content from 0.3 to 0.6 wt % Pt, the isomerization was decreased (11.3 and 11 wt.%, respectively) and increase the cracking of n-heptane, (7.9, 17.4 and 26.5 wt.% for 0.1, 0.3 and 0.6 wt.% Pt in catalysts, respectively) and this is due to the increasing of metallic sites to acidic sites ratio.

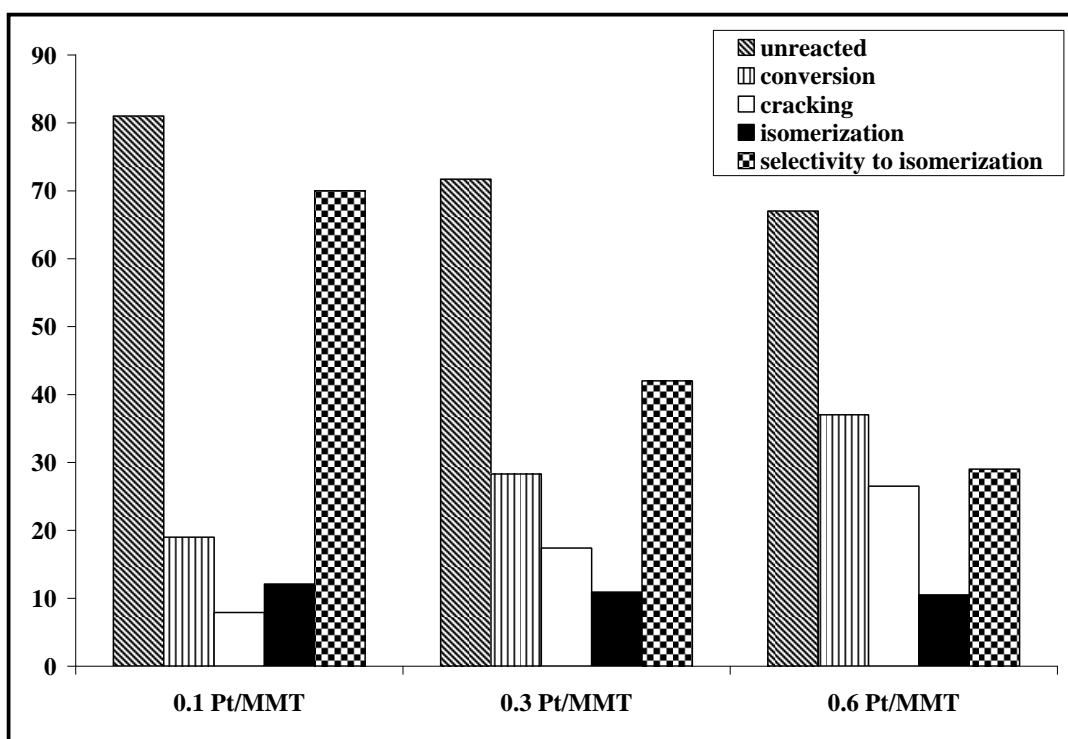


Figure 8: The effect of platinum loading on conversion, cracking, isomerization and selectivity to isomerization of n-heptane over (a) 0.1 Pt/MMT, (b) 0.3 Pt/MMT and 0.6 Pt/MMT at 350°C

3.2.3. Catalyst activity–structure correlation

The catalytic performance tests combined with the physico-chemical characterization shows that the presence of Pt ratio is very important factor in deciding textual characteristics and finally the catalytic activity of MMT supported catalysts. The MMT which has 2θ at 8.87° peaks is slightly shifted to low angles with increasing Pt contents. This causes increase in the unit cell parameter. Such observation indicates successful incorporation of Pt into MMT structure. This incorporation of Pt over MMT framework is responsible for low pore size of Pt/MMT than pure MMT material and the pore size continuously decreases with increasing the Pt content. The incorporation of Pt in the framework of silica was also confirmed by FT-IR analysis which shows that the intensity of 977 cm^{-1} band corresponding to Si–O–Pt band continuously increases with the Pt content. FT-IR analysis also predicts about the functional hydroxyl group on the surface of silica and Pt. The Pt/MMT support have low functional –OH groups than pure MMT, which decreases with Pt content. These functional –OH group are responsible for anchoring higher metal content on the surface. The dispersion of Pt phase on MMT was clearly revealed by the FTIR

spectra of the catalysts. All the supported catalysts exhibited a major peak at 1115 cm^{-1} which is characteristic peak of bulk SiO_2 . The low intensity of this peak in the MMT indicates the high dispersion of Pt species due to the homogeneous distribution of Pt. This type of bulk metal formation on silica based support has also been previously reported [Huang et al., 2008]. The Si–O–Pt bond strength in silica based support is known to be relatively weaker than Al–O–Pt resulting in low metal support interaction, which decreases the tendency to form Pt–O–Pt bonds in MMT supported catalysts and leads to formation of dispersed Pt species. The intensity of formation of Pt in MMT at higher loading increases due to low surface area of MMT material in comparison to high surface at low loading.

The high catalytic conversion of 0.6 Pt/MMT relative to 0.1Pt/MMT can also be explained due to the high difference in the chemical nature of these catalysts. The imbalance between the strong Brønsted in MMT and Pt sites might have resulted in the low catalytic activity of the catalysts system. Proper distribution of acid sites in supported catalysts is known to improve the conversion.

Acidic supports facilitate an alternate hydrogenation route through saturation of olefinic molecules resulted from Pt sites. The acid sites in 0.1 Pt/MMT more provide protons in the close vicinity of the metal particles due to high surface that enable more hydrogenation site, leading to an accelerated hydrogenate olefin and decrease bond cleavage. This effect is less prominent in 0.3&0.6 Pt/MMT catalyst wherein the hydrogenation pathway may equally favored, due to the low concentration of available acid sites and this material has low surface area.

Conclusion

The isomerization of alkanes, using conventional catalyst have some disadvantage (high temperature and high H_2 -pressure). The novel prepared Pt/MMT catalyst overcome these advantages, and have a selectivity to isomerization of n-heptane at lower temperatures. Its skeletal rearrangement of carbenium ions was the important rule for catalyst isomerization selectivity. The reduction of Pt salt with formalin affects the platinum dispersion acid provides additional sites, which benefit the heptane isomerization activity. The improvement in platinum dispersion, which is mainly attributed to the isolation is the primary factor that benefits catalyst performance. The findings obtained herein highlight the

development of a new reduction method for Pt-catalysts for boosting high octane-rating gasoline via the branched isomerization of n-heptane with low octane rating.

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الملخص العربي

تأثير المحتوى البلاتيني وحجم جزيئاته وتقنيته اختزاله على أزمرة الهيبتان الخطى

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يناقش البحث منهج جديد لترسيب البلاتين علي سطح مسامي في صورته غاية في الانتشار عند نسب تتراوح بين 0.1 الي 0.6 من فلز البلاتين وتوصيف الحفازات المحضرة ودراسة تأثير هذه النسب المختلفة من البلاتين المحملة علي صلصال المنتمولينييت علي تفاعل الازمره الحفزي الذي يعد من اهم العمليات البترولية. تم تحضير هذه الحفازات بنسب مختلفة من البلاتين (0.1-0.6 %) باستخدام تقنية التثرب بمادة الهكسا كلورو بلاتينات كمصدر البلاتين واتبعت هذه الخطوة بعملية الأختزال الكيميائي لجزيئات البلاتين باستخدام الفورمالين ثم بعد ذلك باستخدام الهيدروجين علي التوالي قبل إجراء العملية الحفزية.

تم إثبات الخصائص الفيزيوكيميائية للحفازات المحضرة باستخدام تقنيات الأشعة السينية ومساحة السطح عن طريق إمتزاز غاز النيتروجين والتحليل الحراري والمجهر الالكتروني النافذ ومطياف الأشعة السينية الضوئية. وقد تم اختبار كل الحفازات المحضرة في عملية الأزمرة للهيبتان الخطى وقد كشفت النتائج بأن ظروف النشاط التحفيزي الأمثل وكذلك الانتقائية لإنتاج سلاسل الهيبتان المتفرعة تمت باستخدام الحفاز المكون 0.1% من البلاتين وأن زيادة نسبة تحميل البلاتين تزيد عملية التكسير الحفزي للهيبتان على حساب عملية الأزمرة.