Modification of SBA-15 mesoporous silica as an active heterogeneous catalyst for the hydroisomerization and hydrocracking of n-heptane

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ABSTRACT

In this study, a mesoporous SBA-15 silica catalyst was prepared and modified with encased 1% platinum (Pt) metal nanoparticles for the hydrocracking and hydroisomerization of n-heptane in a heterogeneous reaction. The textural and structural characteristics of the nanostructured silica, including both encased and non-encased nanoparticles, were measured using small-angle X-ray diffraction (XRD), nitrogen adsorption-desorption porosimetry, Brunauer–Emmett–Teller (BET) surface area analysis, Fourier-transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Catalytic testing was carried out in a plug-flow reactor under highly controlled operating conditions involving the reactant flow rate, pressure, and temperature. Gas chromatography was used to analyze the species as they left the reactor. The results demonstrated that 1% Pt/SBA-15 has a high n-heptane conversion activity (approximately 85%). Based on the results of this experimental work, there is no selectivity in the SBA-15 catalysts for isomerization products because they are inactive at the relatively low temperature that is essential for hydroisomerization. On the other hand, the SBA-15 catalysts have a considerable selectivity for products that have cracks, owing to their ability to withstand extremely high temperatures (300–400 °C) as well as the availability of Lewis acid sites within the catalyst structure.

1. Introduction

Isomerization is the process of transforming light straight-chain paraffins (i.e., C₆, C₅, and C₄) with low research octane numbers (RONs) towards components characterized by the appearance of branching chains with similar carbon numbers and higher octane ratings using the appropriate kind of catalyst. However, the hydrotreated naphtha (HTN) of petroleum cut between 90 and 190 °C is segregated into heavy naphtha, which could be delivered to the reforming unit. In contrast, the isomerization unit is supplied with light naphtha (C₅) at 80 °C. The fractionation of naphtha is performed for two reasons: first, that light hydrocarbons have a tendency toward hydrocracking in the reformer; and second, that in the reformer, C₆ hydrocarbons, have a proclivity for forming benzene. Because of benzene’s carcinogenic effect, gasoline specifications are required to have an extremely low benzene content [1, 2, 3, 4]. Furthermore, catalytic isomerization involves two major types: The Pt/zeolite catalyst and the traditional Pt over-chlorinated alumina with a high concentration of chlorine, which is classified as a catalyst with considerable activity.

At low-temperature catalytic reactions, linear paraffins convert to isoparaffins in the presence of hydrogen under a process called hydroisomerization. It provides a better alternative to the reforming process because it does not generate aromatic compounds. There are two kinds of active sites in hydroisomerization catalysts: metal sites facilitating both dehydrogenation and hydrogenation as well as acidic support sites for hydrocarbon structural reconfiguration. The hydroisomerization of C₆–C₈ hydrocarbons is accomplished over a large scale, but a catalyst for heptane isomerization has yet to be established [5, 6]. Catalysts with a solid acid (e.g., chloride alumina with platinum) run at a considerably low temperature (less than 150 °C). These are the most commonly
applied catalysts in the oil and gas industry as they provide great catalytic conversion at relatively low temperatures, which is favorable for yielding isomers due to the isomerization reaction’s exothermicity [7, 8]. Corrosion and waste management are the two major issues with this kind of catalyst. A sulfated zirconia-based catalyst is frequently cited as being active at low temperatures [9, 10, 11, 12, 13, 14]. Furthermore, the deactivation of this type of catalyst is caused by large quantities of carbonaceous formations due to higher alkane cracking, sulfate loss at deactivation of this type of catalyst is caused by large quantities of carbonaceous formations due to higher alkane cracking, sulfate loss at deactivation of this type of catalyst is caused by large quantities of carbonaceous formations due to higher alkane cracking, sulfate loss at deactivation of this type of catalyst is caused by large quantities of carbonaceous formations due to higher alkane cracking, sulfate loss at deactivation of this type of catalyst is caused by large quantities of carbonaceous formations due to higher alkane cracking, sulfate loss at deactivation of this type of catalyst is caused by large quantities of carbonaceous formations due to higher alkane cracking, sulfate loss at deactivation of this type of catalyst is caused by large quantities of carbonaceous formations due to higher alkane cracking, sulfate loss at deactivation of this type of catalyst is caused by large quantities of carbonaceous formations due to higher alkane cracking, sulfate loss at deactivation of this type of catalyst is caused by large quantities of carbonaceous formations due to higher alkane cracking, sulfate loss.

The desire to produce clean types of gasoline with the highest octane number has motivated the development of modern kinds of solid catalysts with superior nC7 isomerization selectivity [17, 18, 19]. As a result, several efforts have been made to find the most suitable catalysts that can enhance the selectivity of branching paraffin in the hydroisomerization of paraffin chains with lengths higher than C8 [20,21]. A wide range of supports have been investigated, including silica [22], activated carbon [23], silica-alumina [24], SBA-15 [25], MCM-41 [26], zeolites [27, 28, 29], etc. This reaction is generally considered to be performed using catalysts with dual functions comprised of noble metal particles maintained on an acid-sited matrix [30]. Hydrogenation, dehydrogenation, cyclization, isomerization, and hydrocracking are the primary reactions promoted by bifunctional catalysts [31].

Recently, in formulating novel catalysts for heavier hydrocarbon conversion, researchers have focused on alkaline hydroconversion using catalysts with solid acids and large pore sizes, which include molecular sieves with a mesoporous structure [32]. Among these, the most highly recommended are mesoporous molecular sieves with high hydrothermal stability and acidic sites. Zhao et al. [33, 34] synthesized materials with Santa Barbara Amorphous (SBA) to enlarge the silicate family by adding a highly ordered mesoporous structure. Due to its excellent thermal stability and varying pore diameter, SBA-15 has gained much interest since its discovery in 1998 as (1) an adsorbent, (2) for hydrogen storage, (3) as a potential catalyst support, (4) as a medium for drug delivery, and (5) as a durable template for other nanomaterials [35]. SBA-15 has a large surface area of 600-1000 m² g⁻¹ and is constituted of cylindrical channels with tunable pore sizes ranging from 5 to 30 nm in hexagonal arrays. These channels are connected by micropores situated within the pore walls. SBA-15 also has larger pore walls (2-8 nm) and has shown improved thermal and hydrothermal stability [36].

The current research investigated the catalytic activity of Pt on SBA-15 for n-Heptane reactions in hydrocracking and hydroisomerization processes. The SBA-15 was encased with 1% Pt metal nanoparticles. The SBA-15 catalyst was impregnated, dried at room temperature overnight, exposed to heat at 120 °C for 24 h; afterward, the treated catalysts underwent a calcination process at a temperature of 550 °C for 4 h [37].

2.3. Metal loading into the SBA-15 catalyst

The incipient wetness impregnation (IWI) technique was employed to load metal into the SBA-15 samples using Pt (NH₃)₄ Cl₂.H₂O as a precursor to platinum. A suitable quantity of metal (1% loading) was dissolved in an HCl solution with a molarity of 0.1 to encapsulate the metal with the Pt catalyst with a total weight of 1% to generate the impregnation solutions. To achieve optimal metal dispersion and prevent salt agglomeration during solvent vaporization, the solution's total volume was the same as the support's utilized pore volume. To obtain a 1% Pt/SBA-15 catalyst, the catalysts were impregnated, dried at room temperature overnight, exposed to heat at 120 °C for 24 h; afterward, the treated catalysts underwent a calcination process at a temperature of 550 °C for 4 h [37].

2.4. Characterization

By employing Cu Kα radiation with λ = 1.5406Å on a MiniFlex diffractometer (Rigaku), small-angle XRD spectra were observed within atmospheric conditions. At 30 mA and 40 kV, an X-ray tube was used to collect data in the 0.5–8° range with a 20 step size of 0.01 and a 10 s step duration. The formulas n = 2dsin and o = 2d100/3 were also used to calculate the unit cell and c-spacing specifications. The tests of nitrogen adsorption/desorption were performed with a Micromeritics ASAP 2020 pore analyzer and N2 physisorption at −196 °C. Substances were subsequently degassed for 3 h at 350 °C under vacuum conditions in the sorption analyzers degas port (p < 10-5 mbar). The Brunauer–Emmett–Teller (BET) approach was applied to estimate the BET specific surface areas of the specimens in the relative pressure (P/P₀) range from 0.05 to 0.35. The Barrett–Joyner–Halenda (BJH) technique, which is based on thermodynamics, was employed to estimate the distributions of the pore size from the isotherm's desorption branch. At a relative pressure of 0.995, the adsorbed quantity of liquid nitrogen indicated the total volume of the pores by inspecting the adsorption branch of the N2 isotherm. In addition, the thickness of the pore walls (t_w) was obtained by using the parameter of the unit cell (a) and the pore size diameter (d_p). In addition, BET analysis (4V/A) was employed to measure the mean mesopore sizes for the individual samples depending on the nitrogen sorption data. The FT-IR of the compounds diluted in 8 wt.% KBr was measured in the range of 4000 to 400 cm⁻¹ at ambient temperature using transmission mode with 4 cm⁻¹ resolution zones, employing a Nicolet™ 380 FT-IR spectrometer. On the other hand, SEM with a JEOL (JSM-5600 LV) was used to investigate the macropore structure. A Titan TEM was used to investigate the distribution as well as the size of the metal clusters on the surface of the catalyst.

2.5. Catalytic test

First, every catalyst was crushed and sieved in amounts from 0.1 g to the appropriate size of 250-425 m to prepare for the experiments. Next, the produced sample was placed into a fixed bed microreactor made of Pyrex™ with a cylindrical shape, 400 mm in length, with a 4-mm ID. Furthermore, glass wool was used to keep the sample in place in the reactor. The calcination process was performed on the catalysts in the presence of air before being reduced in H2 in situ at 450 °C for 4 h employing 50 ml/min⁻¹ H2. During activation, a maximum temperature
of 450 °C and a heating rate of 1 °C min⁻¹ was applied to prevent the metal from aggregating and sintering on the catalyst, ensuring maximal performance of the catalyst. The H₂ gas was fed across a saturator containing 99.33 wt.% of n-Heptane (Sigma-Aldrich). The volumetric flow rate of H₂ ranged from 20 to 45 ml/min⁻¹, while the n-C₇ volumetric flow rate ranged from 0.287 to 0.686 ml/min⁻¹. However, n-C₇ was supplied with a molar component of 1.436 mol percent, as experimentally determined. This determination was based on values of the n-C₇ extrapolated molar response factor by analyzing the entire area of the feed utilizing the gas chromatograph flame ionization detector (GC-FID) over blank tests with flow rates ranging from 20 to 72 ml/min⁻¹. It was observed to be very similar to the values of the molar composition, which were estimated theoretically from the standard vapor pressure of n-C₇ at 0 °C, demonstrating that the saturator was running at or near the theoretical optimum through a wide range of H₂ flow rates. The catalysts were evaluated at temperatures ranging from 250 to 400 °C, at atmospheric pressure. All gaseous products were analyzed with a Plot Al₂O₃ saturator via FTIR spectroscopy and a Varian 3400 GC-FID.

3. Results and discussion

3.1. Characterization

The XRD patterns of the SBA-15 specimens with and without modification are shown in Figure 1, and both exhibit a significant diffraction peak at around 20 of 0.9°. Furthermore, the XRD patterns revealed two more peaks which could be categorized as [1 1 0] as well as [2 0 0] hexagonal P6 mm symmetry reflections [38]. The results revealed that SBA-15's periodic ordered structure was maintained despite modification. However, as compared to SBA-15, the spacing values (ɑₒ) of the SBA-15 specimens grafted with 1% Pt metal nanoparticles decreased considerably (see Table 1), indicating that the deposition of the loaded metals had an impact on the pore size and wall thickness.

S_BET refers to the surface area calculated utilizing the BET technique between 0.05 and 0.25 relative pressures (P/P₀). The t-plot technique provided the required measurements of micropore volume (VₘP) and total pore volume (Vₚ). At a relative pressure of 0.97, the amount adsorbed was used to determine the total pore volume. DP is the pore diameter estimated employing the Barrett-Joyner-Halenda (BJH) approach from the isotherm that deals with the adsorption branch. The parameter ɑₒ = 2d₁₀₀/₃ represents the unit cell measured by XRD. The formula ɑₚ = ɑₒ – DP is used to measure the thickness of a wall [39].

The isotherms involve nitrogen adsorption materials being combined with SBA-15 as well as with the grafted 1% Pt/SBA-15, which resembled an isotherm of type IV, and a type H1 hysteresis loop, as explained in Figure 2. In addition, the abrupt adsorption and desorption branches indicate a narrower particle size distribution. Figure 2 also demonstrates that when the loaded metals were grafted onto the SBA-15, the amount of nitrogen adsorbed tended to decrease. Table 1 provides the parameters of the structure obtained from measurements of nitrogen adsorption. As this table shows, the samples’ specific surface area, pore size, and pore volume ranked in the following order: SBA-15 is greater than 1% Pt/SBA-15; however, the measurements of the wall thickness fell in reversed order. The loaded samples had a reduced surface area compared with the SBA-15 due to the contribution of metal groups that are supported within the pores. This could be an indication of one of two potential factors: partially blocked pores or metal particles being deposited on the interior silicon walls and/or pore apertures.

Figure 3 demonstrates the FT-IR infrared spectroscopy of SBA-15 and several catalysts. The bands which are generated by the stretching vibration of Si–O–Si, can be seen through the spectra of all materials with bands of 1077, 805, and 454 cm⁻¹. The stretching vibrations of Si–O–Si or Si–OH can be assigned to the absorption band at approximately 960 cm⁻¹. The existence of a powerful H-bonding with surface hydroxyl group (OH) interactions between them resulted in a broad band around 3400 cm⁻¹. Eventually, the OH bonds deformation modes of adsorbed H₂O can be attributed to the band at roughly 1631 cm⁻¹ [40,41]. Due to its low metal content, the loaded metal possessed a spectrum that is quite similar to SBA-15. The 1% Pt/SBA bands in metals are much more intense than the SBA-15 bands which is similar to SBA-15.

Table 1. Physicochemical properties of nanoporous material SBA-15 and supported catalysts.

| Sample       | S_BET (m²/g) | Vₚ (cm³/g) | VₘP (cm³/g) | DP (nm) | ɑₒ (nm) | ɑₚ (nm) |
|--------------|--------------|------------|-------------|---------|---------|---------|
| SBA-15       | 885          | 1.09       | 0.07        | 8.5     | 11      | 2.5     |
| 1%Pt-SBA-15  | 773          | 1.2        | 0.08        | 6       | 10      | 4       |

Figure 1. X-ray diffraction patterns of (SBA-15) and supported catalysts.

Figure 2. Nitrogen adsorption-desorption isotherms for SBA-15 and 1%Pt-SBA-15 samples.

Figure 3. FT-IR spectra of SBA-15 and 1% Pt-SBA-15.
powerful than those in SBA-15. This can be attributed to the existence of larger particles on the pores’ exterior surface, as 1% Pt/SBA-15 displays identical bands of absorption over the steadily growing intensity [42]. On the other hand, SBA-15 exhibited acidic characteristics even without the addition of Al. The involvement of Lewis acid sites along the SBA-15 can be seen in this graph, and these sites enhance dehydrogenation and hydrocracking by generating groups of silanol throughout the catalyst’s calcination process [43].

3.2. SEM and TEM of catalysts

SEM was used to characterize the synthesized catalyst specimens before analysis. SEM graphs of 1% Pt/SBA-15 and SBA-15 at magnifications of 5,000 are shown in Figures 4 and 5. The samples of 1% Pt/SBA-15 and SBA-15 have nearly identical surface morphology; nevertheless, the 1% Pt/SBA-15 sample has substantially larger catalyst particles than the SBA-15 sample.

Figure 6 displays TEM images for SBA-15 and for the 1% Pt/SBA-15 catalyst sample after testing. The pores with a hexagonal structure and an organized pore arrangement are easily distinguishable in the TEM image, making it useful for demonstrating the catalyst’s structure. Grafting was accomplished using incipient wetness impregnation, resulting in a 1% Pt/SBA-15 doping. As a result, the mesoporous structural arrays and long-range order were significantly disrupted. Figure 6 also demonstrates the structure of 1% Pt/SBA-15 for a portion of the catalyst, which is comprised of long cylindrical pores that run in the same direction, parallel to one another. Metal structural distribution on catalysts can be investigated using TEM. The dispersion of the metal atom groups and metal cluster sizes on the 1% Pt/SBA-15 catalysts can be seen in Figure 6, which are also shown in Table 1. The metal clusters are better distributed in the TEM image, which is in agreement with the literature [44], resulting in a larger surface area on which the reactions can occur.

3.3. Conversion of n-heptane

For the 1% Pt/SBA-15 catalyst, the overall conversion was determined in wt.% using the following equation (1), with an unchangeable rate of flow of 20–45 ml/min through each temperature.

\[
\text{Conversion}(n-C_7 \text{ wt.\%}) = \left(\frac{\text{C}_7 \text{ in(g)}}{\text{C}_7 \text{ out(g)}} - \frac{\text{C}_7 \text{ in(g)}}{\text{C}_7 \text{ out(g)}}\right) \times 100\% \quad (1)
\]

Figure 7 illustrates the estimated chemical conversion of the 1% Pt over the SBA-15 catalyst with a stable n-C7 flow rate of 0.287 ml/min at various temperatures. The activity of the SBA-15 catalysts was based on the availability of Lewis acid sites inside the configuration. With a conversion of about 85% at 400 °C, 1% Pt/SBA-15 had the greatest conversion. Because of the metal cluster size, it is possible that the activity of 1% Pt/SBA-15 was higher.

3.4. Selectivity to isomerization

The product yields (g) were used to evaluate the 1% Pt/SBA-15 catalyst’s. Selectivity to isomerization products (i-C7) at various testing temperatures was determined in wt.% using the following equation (2):

\[
\text{Selectivity to Isomerisation(wt\%)} = \frac{\sum \text{i-C}_7 (g)}{\sum \text{Total Products(g)}} \times 100\% \quad (2)
\]

Figure 8 shows the isomerization selectivity of the catalyst 1% Pt over SBA-15 at various working temperatures. Throughout the reaction process for isomerization over catalysts with dual functions, zeolite Brønsted acid sites contributed to the process of transforming alkenes in the intermediate state into structural isomers throughout the isomerization process.
process on bifunctional catalysts. Both hydrocracking and dehydrogenation are possible without the presence of these acidic sites, just as they occur on SBA-15 [44]. Because the 1% Pt/SBA-15 catalyst pores are considerably larger, they have little selectivity for products of isomerization and are therefore not product selective. The molecular diameter of cyclohexane is 0.6 nm, which is ten times smaller than the pore diameter of 1% Pt/SBA-15 (6 nm). However, the particles in the substrate reacted and then exited the catalyst pores before any kind of selectivity could occur [45].

3.5. Selectivity to cracking

Crack product selectivity \((C_1-C_6)\) for the catalyst containing 1% Pt and SBA-15 was determined using equation (3) below for all of the studied temperatures and a flow rate of 0.287 mℓ/min-1 for \(n\)-C7.

\[
\text{Selectivity to Cracking (wt%)} = \left( \frac{\sum \text{Cracked Products}[g]}{\sum \text{Total Products}[g]} \right) \times 100\%
\] (3)

Figure 9 shows the outcomes of the selectivity of the 1% Pt/SBA-15 catalyst to cracking at various temperatures. As shown in this graph, the cracking selectivity on 1% Pt/SBA-15 was enhanced by up to 90 wt.% at 400 °C. Furthermore, the SBA-15 catalyst revealed that cracked products have a higher selectivity as a result of the structure of their pores, in addition to the fact that the catalyst has Lewis acid sites.

Even though the SBA-15 catalysts showed high activity, they are nonselective structurally to targeted products for the hydroisomerization of \(n\)-C7 and are also missing the Bronsted acid sites that promote isomerization. According to the literature [46], hydroisomerization reactions take place in thermodynamic equilibrium with hydrocracking processes and commonly occur at low temperatures, between 210 and 270 °C.

There is no selectivity in the SBA-15 catalysts for isomerization products because they are inactive at the relatively low temperature that is essential for hydroisomerization. Instead, the SBA-15 catalysts have a considerable selectivity for products that have cracked, owing to their tolerance of extremely high temperatures (300-400 °C) as well as the availability of Lewis acid sites within the catalyst structure [47].

4. Conclusions

The pore size of SBA-15 was observed to be 8.5 nm. This expanded the number of metal reaction sites available and improved metal distribution, which improved the catalyst’s activity. SBA-15 was shown to exhibit no structural selectivity for products of isomerization owing to its large pores compared to the products of isomerization and to the unavailability of Bronsted acid sites. However, high selectivity to cracked products was revealed by applying 1% Pt/SBA-15 catalyst samples because the catalysts had Lewis acid sites. The 1% Pt/SBA-15 catalyst is considered to have high activity. The addition of Pt improved the metal cluster distribution, allowing for a larger available surface area for reactions. However, more study is required because the isomerization process has limited selectivity.

Declarations

Author contribution statement

Nisreen S. Ali, Ziad T. Alismaeel, Hasan Sh. Majdi, Hussein G. Salih: Performed the experiments; Contributed reagents, materials, analysis tools or data.

Mahir A. Abdulrahman, Noori M. Cata Saady: Conceived and designed the experiments; Performed the experiments.

Talib M. Albayati: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.
