

Article

The Synthesis of a Pt/SAPO-11 Composite with Trace Pt Loading and Its Catalytic Application in *n*-Heptane Hydroisomerization

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Abstract: *n*-Alkane hydroisomerization over bifunctional catalysts is an effective approach for clean fuel production. However, achieving metal–acid synergy and enhancing the catalytic performance by the preparation of bifunctional catalysts with suitable proximity between the metal sites and Brønsted acid sites are still challenging. In this work, a series of Pt/SAPO-11 catalysts with different Pt loading applied in *n*-heptane hydroisomerization was synthesized. SAPO-11 was synthesized by the Instant Exactness Synthesis (IES) method, which, with unique morphology and pore structure, was chosen as support for the hydroisomerization catalysts; Pt/SAPO-11 was synthesized with the impregnation method, Pt nanoclusters with trace loading were fabricated over the SAPO-11 support, and the as-synthesized catalysts with different Pt loading were labeled as xPt/SAPO-11 ($x = 0.1, 0.3, 0.5, 0.8$ and 1.0). Various characterizations, including XRD, nitrogen adsorption–desorption, SEM, TEM, NH_3 -TPD and XPS, were carried out on catalysts to obtain deep insights into the microstructure and valence states of xPt/SAPO-11. The catalytic performance of xPt/SAPO-11, including catalytic selectivity and conversion, was investigated in the *n*-heptane hydroisomerization in detail. Pt loading affected the catalytic properties of xPt/SAPO-11 in the hydroisomerization of *n*-heptane. The selectivity of 0.5Pt/SAPO-11 toward isomers was about 65% with a conversion of 77% at 310 °C, which was obviously higher than other xPt/SAPO-11 catalysts.

Keywords: Pt cluster; SAPO-11; *n*-heptane hydroisomerization; catalytic mechanism



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1. Introduction

n-Alkane hydroisomerization is an important technology in petroleum refining areas. *n*-Alkanes can be converted into corresponding *iso*-alkanes through the hydroisomerization process, resulting in high-octane gasoline, low-pour-point diesel and high-viscosity-index lubricant oil [1–4]. It is important to develop an efficient catalyst for hydroisomerization.

Acidic sites play a catalytic role in *n*-alkane isomerization; this is generally caused by carriers with Brønsted acidic sites. Acidic carriers, including amorphous silicon aluminum [5], zeolite [6], phosphate silicon aluminum molecular sieves [7] and mesoporous silicon materials [8], are commonly used carriers. For acidic carriers, most research has focused on regulating acid content to obtain catalytic materials with metal functional and acid functional equilibrium. In general, if the acid function is strong in metal–acid bifunctional catalytic materials, the intermediate of *iso*-olefins will undergo continuous isomerization and cracking reactions before hydrogenation, resulting in a decrease in the yield of isomers;

if the acid function is weak, it is not conducive to the isomerization of *n*-olefin intermediates, resulting in lower conversion rates [9,10]. As for SAPO-*n* (*n* = 11, 31, 41) carriers, Brønsted acidic sites are formed by the replacement of Al and/or P atoms with Si atoms. Si atoms can access the molecular sieve framework to form Si–OH–Al units through the SM2 and/or SM3 substitution mechanism [11]. As it is relatively difficult for Si atoms to access the framework, the Si/Al ratio in the SAPO-*n* molecular framework is relatively small, resulting in moderate Brønsted acidity. Meanwhile, the proportion of Si atoms in SAPO-*n* molecular sieves with Si(0Si4Al), Si(1Si3Al) and Si(2Si2Al) is relatively higher than in other carriers, and these Si–OH–Al units are regarded as moderate acid sites. Therefore, SAPO-*n* molecular sieves are more suitable than other carriers to be hydroisomerization catalyst carriers [12].

The metal sites of catalysts have a significant impact on catalytic behavior, which is generally caused by active metal species loading onto acidic supports. Precious metals are widely used in industrial hydrogenation isomerization catalysts as metal components due to excellent hydrogenation activity and stability [13,14]. Small-sized and highly dispersed precious metal nanoparticles not only provide more surface metal sites but also promote contact and synergy between the metal sites and acidic sites of the carrier. *Iso*-olefin intermediates formed at acidic sites can easily diffuse to metal sites for hydrogenation, improving the selectivity of isomers. The hydrogenation activity of metal sites is closely related to the exposed crystal planes of metal particles. Some research proves that the catalytic performance of octahedral Pt (111) crystals is significantly superior to spherical and cubic Pt (100) crystal planes in hydroisomerization reactions and that catalytic performance decreases with an increase in the proportion of Pt (100) crystal planes. The Pt (111) crystal surface has more defect sites, which increases the ability of surface Pt atoms to bind hydrogen and, thus, enhances hydrogenation activity [15].

Lucas [16] synthesized a series of Pd/Beta and Pt/Beta catalysts, and the experiments' results in hydroisomerization of *n*-octane over the catalysts showed that the octane isomer yield increased with the hydrogenating/acid balance and the branched isomers increased with the increase in Pt loading, whereas the octane isomer yield would not change for metal loading above 1.0 wt%. Batalha [17] studied *n*-hexadecane hydroisomerization over Pt/HBEA catalysts and found that the rate and selectivity of *n*-C₁₆ hydroisomerization was determined by only two parameters: the balance between the metal and acid functions and their degree of intimacy, which could be quantified separately by the C_{Pt}/C_{H+} ratio between the concentrations of accessible Pt and protonic sites, and *n*_{as}, the number of acid steps undergone by olefinic intermediates during their diffusion between two Pt sites which can be drawn from the initial product distribution. Sun [18] synthesized ordered mesoporous nanosheet SAPO-11 molecular sieves using uncalcined SBA-15 molecular sieves as a Si source. The synthesized sieves exhibited high isomerization activity and selectivity. When the conversion rate of *n*-dodecane reached 87.96%, the yield of *i*-dodecane was 68.08% and the yield of multibranched *i*-dodecane was 31.65%.

Aiming to synthesize catalysts with low metal loading and high catalytic properties, this work synthesized SAPO-11 by the Instant Exactness Synthesis (IES) method which, with unique morphology and pore structure, was chosen as support for the hydroisomerization catalysts. Pt nanoclusters with trace loading were fabricated over SAPO-11 via the impregnation method, and the catalysts with different Pt loading were labeled as xPt/SAPO-11 (*x* = 0.1, 0.3, 0.5, 0.8 and 1.0). Various characterizations were performed on the catalysts to obtain a deep insight into the microstructure and valence states of xPt/SAPO-11. The catalytic performance of xPt/SAPO-11 was investigated in *n*-heptane hydroisomerization, and a related catalytic mechanism was further inferred.

2. Results and Discussion

2.1. Phase Structure

The X-ray diffraction spectra of SAPO-11 and xPt/SAPO-11 are shown in Figure 1. It was clearly observed that sharp peaks appeared at the 2θ values of 17.9, 9.6, 12.6, 13.3, 15.9,

19.3, 19.8, 21.4, 21.6, 22.5, 23.1, 25.6, 29.6 and 38.4, which were attributed to typical SAPO-11 topology structure (JCPDS 00-047-0614, Figure S1). This finding indicated the existence of a SAPO-11 crystal phase in the prepared catalysts. No additional peaks attributable to the impurity phase were detected. The diffraction peaks of SAPO-11 were sharp and narrow, indicating that the zeolite had a good crystalline structure. The intensity of the diffraction peaks became weak after metal components were introduced onto SAPO-11; this might be due to the decrease in crystallinity through rehydration [19]. Pt diffraction signals were not detected, which might be due to the low amount and high dispersion of Pt over the support [18].

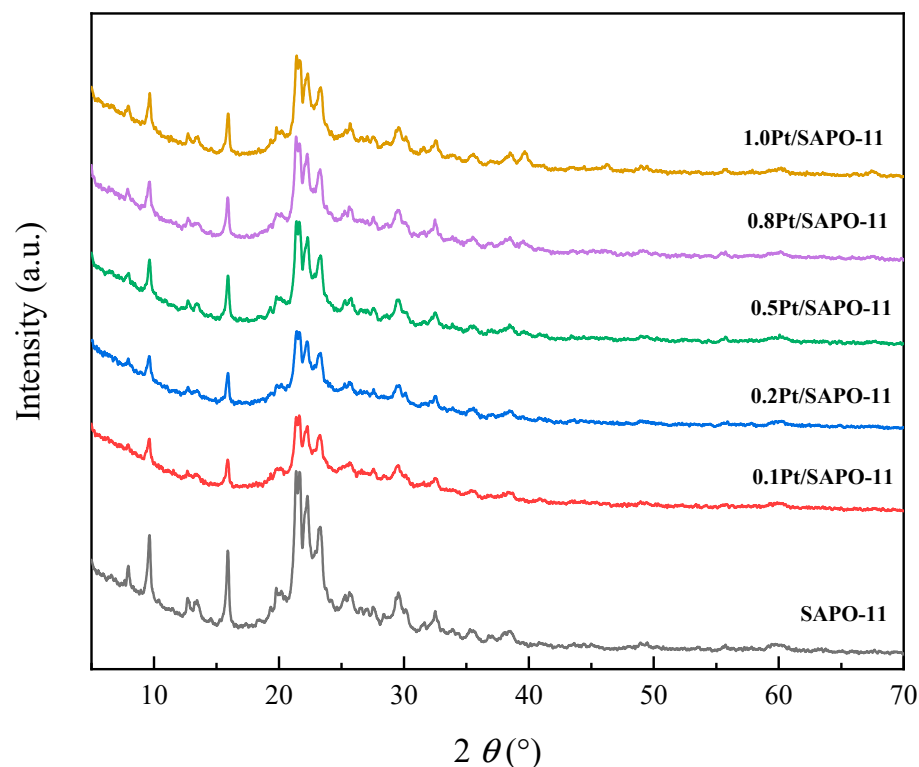


Figure 1. XRDs of SAPO-11, 0.1Pt/SAPO-11, 0.2Pt/SAPO-11, 0.5Pt/SAPO-11, 0.8Pt/SAPO-11 and 1.0Pt/SAPO-11.

2.2. Morphology

SEM images of SAPO-11 and xPt/SAPO-11 are presented in Figure 2. Typical spherical crystals assembled in layers with particle sizes from 2 to 3 μm can be observed. Pt/SAPO-11 is evenly distributed, with slight agglomeration, which might be caused by metal loading [20]. With the increase in Pt loading, the phenomenon of agglomeration was enhanced. EDS mapping images of xPt/SAPO-11 (Figures S2–S7) showed that Pt uniformly dispersed in SAPO-11 zeolite, and the number of Pt sites was obviously less than other elements because of low loading. TEM image measurements were carried out to investigate the submicroscopic structure of 0.5Pt/SAPO-11 and the distribution of Pt over SAPO-11 as shown in Figure 3. Spherical 0.5Pt/SAPO-11 (Figure 3a), the lattice fringe of SAPO-11 ($d = 0.477$) attributed to the 311 crystal plane, could be observed (Figure 3b), and Pt clusters (≈ 5 nm) composed of Pt atoms that were well-dispersed on the SAPO-11 support (Figure 3c–e) could be clearly observed. The formation of Pt clusters could be attributed to the adsorption of $[\text{PtCl}_6]^{2-}$ ions on SAPO-11 and the interaction with the supports [21].

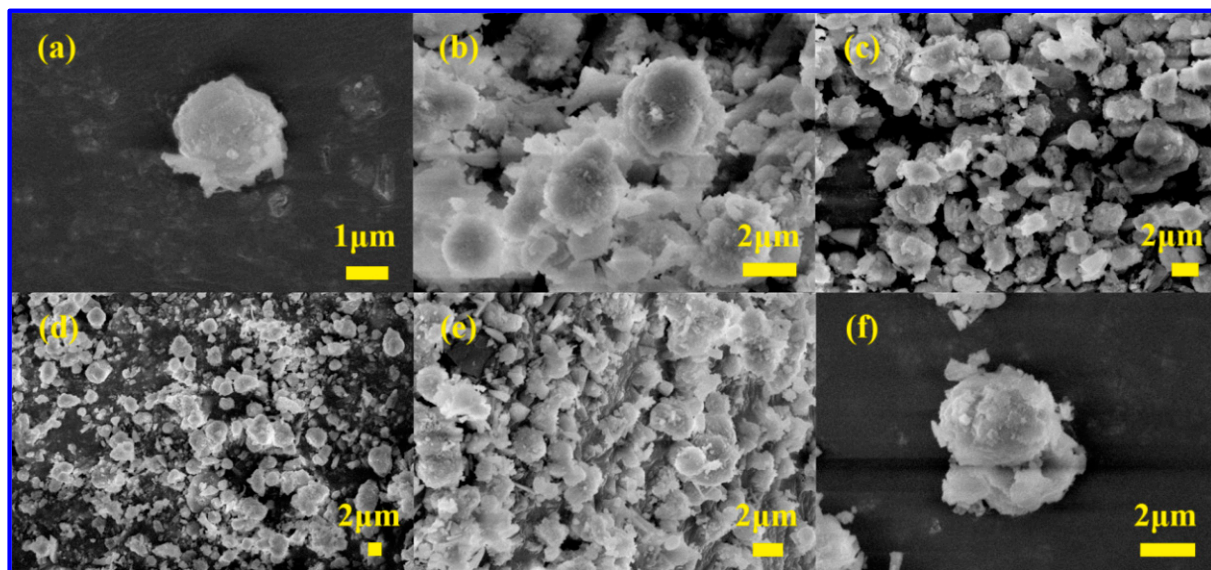


Figure 2. SEMs of (a) SAPO-11, (b) 0.1Pt/SAPO-11, (c) 0.2Pt/SAPO-11, (d) 0.5Pt/SAPO-11, (e) 0.8Pt/SAPO-11 and (f) 1.0Pt/SAPO-11.

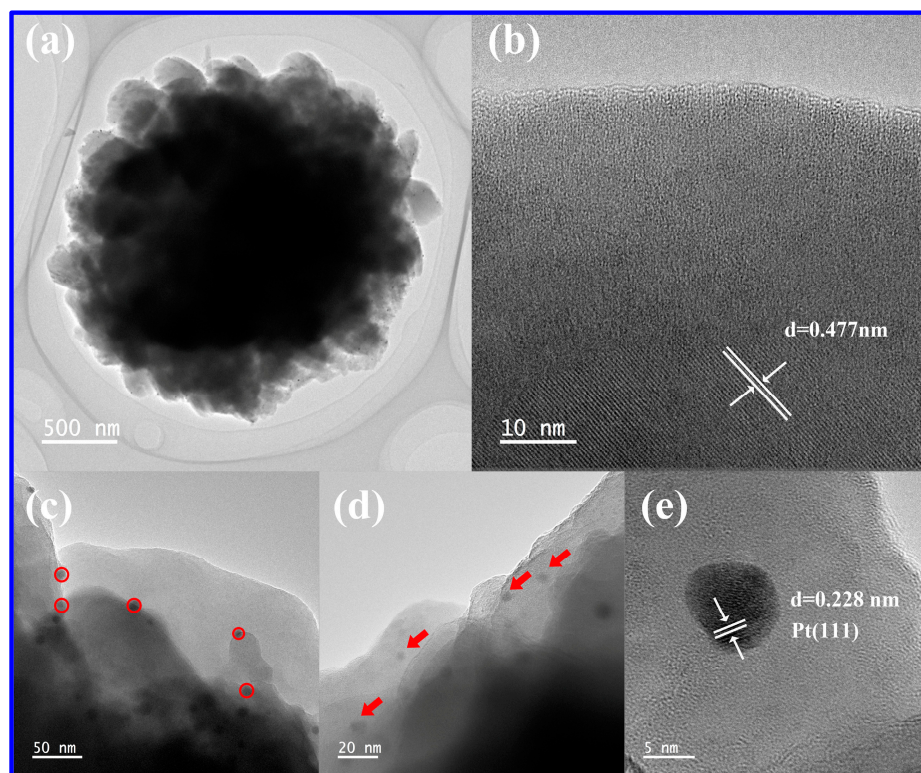


Figure 3. (a–e) TEM of 0.5Pt/SAPO-11.

2.3. Textural Properties

The N_2 adsorption–desorption isotherms and textural properties of SAPO-11 and xPt/SAPO-11 are shown in Figure 4 and Table 1. The pore distributions of SAPO-11 and xPt/SAPO-11 are displayed in Figure S8. For SAPO-11, an adsorption peak of N_2 appeared at $0.05\sim 0.1 P/P_0$, meaning SAPO-11 had a microporous structure; a hysteresis loop emerged at $0.4\sim 1.0 P/P_0$, indicating that SAPO-11 had a mesoporous structure, or this might have been caused by the accumulation of crystalline grains [22]. Compared with

SAPO-11, the surface areas and pore volumes of xPt/SAPO-11 decreased slightly after the deposition of Pt, suggesting weaker blockage of channels in SAPO-11 zeolite. With the increase in Pt loading, the surface areas and pore volumes gradually decreased because of blocked channels.

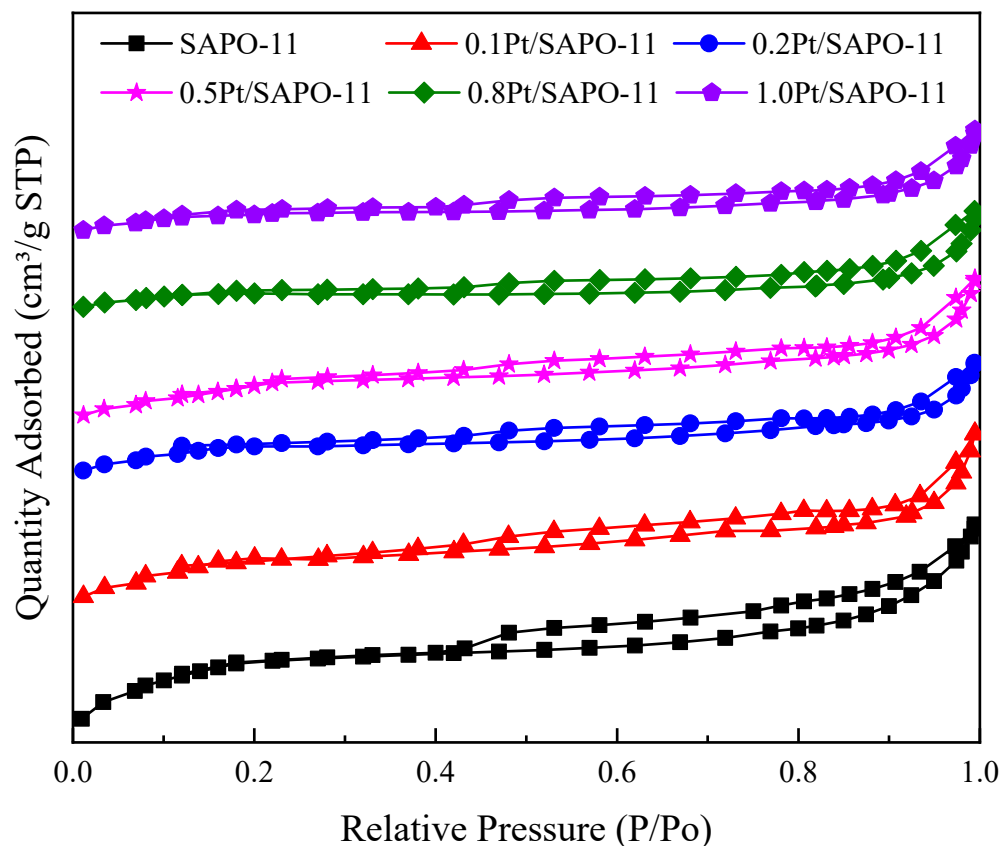


Figure 4. N_2 adsorption–desorption isotherms of SAPO-11, 0.1Pt/SAPO-11, 0.2Pt/SAPO-11, 0.5Pt/SAPO-11, 0.8Pt/SAPO-11 and 1.0Pt/SAPO-11.

Table 1. Parameters of SAPO-11 and xPt/SAPO-11 determined by BET.

Parameters	SAPO-11	0.1Pt/SAPO-11	0.2Pt/SAPO-11	0.5Pt/SAPO-11	0.8Pt/SAPO-11	1.0Pt/SAPO-11
$S/(\text{m}^2 \text{g}^{-1})$	121	119	118	117	115	115
$V_{\text{pore}}/(\text{cm}^3 \text{g}^{-1})$	0.101	0.098	0.087	0.085	0.083	0.078
$d_{\text{pore}}/(\text{\AA})$	22.6	21.9	21.3	22.5	18.7	18.9

2.4. Acid Properties

FT-IR spectra of SAPO-11 and xPt/SAPO-11 are displayed in Figure 5. The peak at 3605 cm^{-1} was due to the stretching vibrations of Si–OH–Al species, which corresponded to Brønsted acid centers, and the intensity depended on Si sources [23]. The bands, located at about 3455 cm^{-1} and 710 cm^{-1} , separately represented stretching vibrations of Al–OH and Al–O. The asymmetric vibration peak and bending vibration peak of Si–O–Si corresponded to the bands around 1130 cm^{-1} and 470 cm^{-1} , respectively. The bands at 520 cm^{-1} and 1650 cm^{-1} could be attributed to the bending vibration of O–P–O and the surface bending vibration of the molecular sieve, respectively. In addition, compared with SAPO-11, some bands of xPt/SAPO-11 such as stretching vibrations of Si–OH and Al–OH displayed a slight blue shift (Figure S9), and the intensity of some peaks (stretching vibrations of Si–O–Si) became weak while some peaks (such as stretching vibrations of zeolite–OH) became strong; this might be caused by the incorporation of Pt metal in the zeolite framework [24].

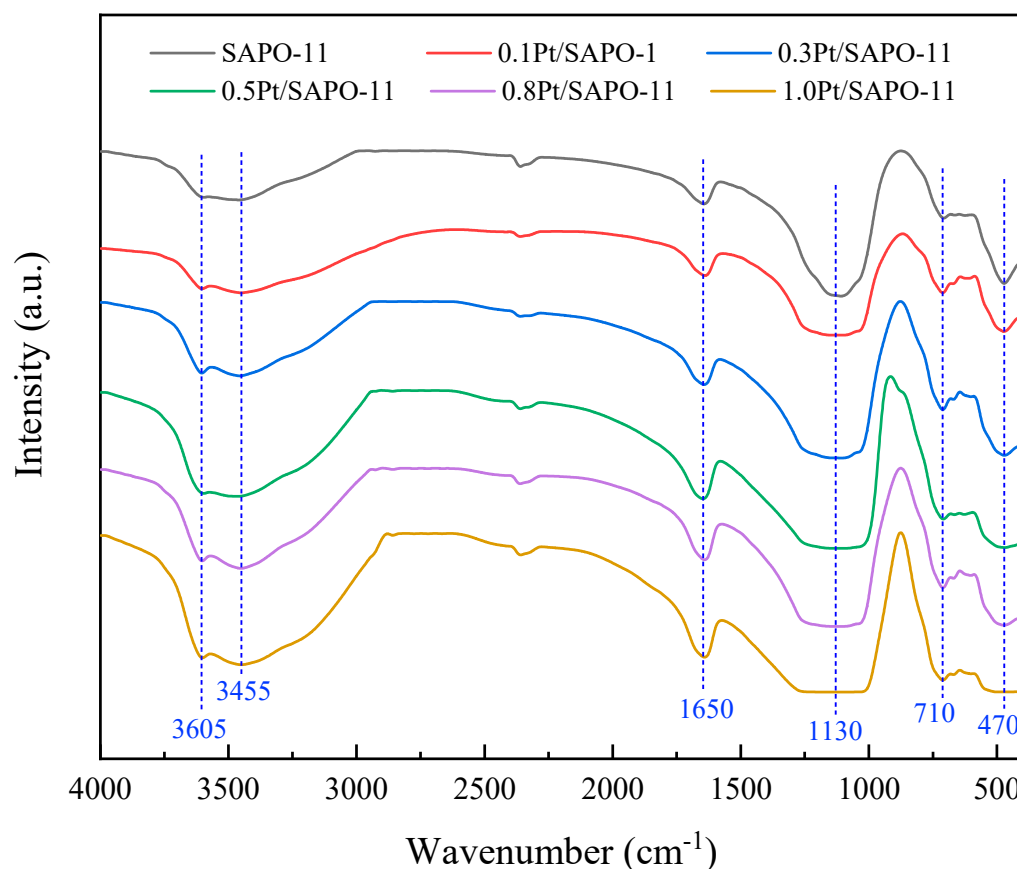


Figure 5. IRs of SAPO-11, 0.1Pt/SAPO-11, 0.2Pt/SAPO-11, 0.5Pt/SAPO-11, 0.8Pt/SAPO-11 and 1.0Pt/SAPO-11.

Pyridine molecules can access and pass through the pores of the molecular sieve; therefore, Py-IR could be used to test the types of acid sites of catalysts, as shown in Figure S10. The bands located around 1560 cm^{-1} and 1455 cm^{-1} were assigned to the Brønsted acid site and Lewis acid site, respectively, while the peak around 1500 cm^{-1} was attributed to the interaction between the Lewis and Brønsted acid sites. The density of the acid site played an important role in catalytic performance and determined the product distribution; NH_3 -TPDs were performed to test the density of the Lewis and Brønsted acid sites of SAPO-11 and xPt/SAPO-11, as shown in Figure 6. Three main NH_3 desorption peaks in the regions of $150\text{--}225\text{ }^\circ\text{C}$ (T_1), $225\text{--}300\text{ }^\circ\text{C}$ (T_2) and $300\text{--}500\text{ }^\circ\text{C}$ (T_3) were detected, which could be assigned to the desorption of NH_3 from weak, medium and strong acid sites, respectively [25]. As listed in Table 2, the sum amounts for weak, medium and strong acid sites were arranged in order as follows: $0.5\text{Pt/SAPO-11} > 0.3\text{Pt/SAPO-11} > 0.1\text{Pt/SAPO-11} > 0.8\text{Pt/SAPO-11} \approx 1.0\text{Pt/SAPO-11} > \text{SAPO-11}$. The addition of metal Pt could increase the acid sites of catalysts; however, excessive metal content could reduce acid sites [26].

Table 2. Acidity properties of SAPO-11 and xPt/SAPO-11 determined by NH_3 -TPD.

Sample	Acid Amount (mmol/g)			
	Total	Weak	Medium	Strong
SAPO-11	0.27	0.06	0.11	0.10
0.1Pt/SAPO-11	0.29	0.03	0.15	0.11
0.3Pt/SAPO-11	0.30	0.05	0.16	0.09
0.5Pt/SAPO-11	0.31	0.09	0.18	0.04
0.8Pt/SAPO-11	0.28	0.05	0.12	0.11
1.0Pt/SAPO-11	0.28	0.06	0.12	0.10

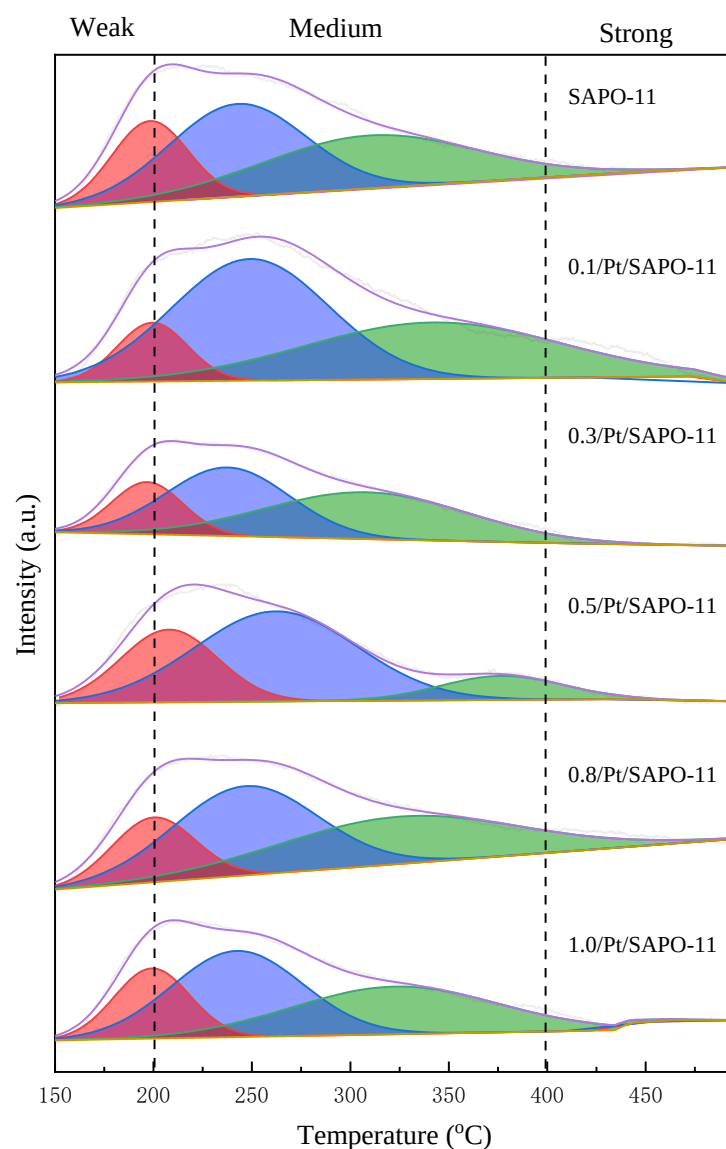


Figure 6. NH_3 -TPDs of SAPO-11, 0.1Pt/SAPO-11, 0.2Pt/SAPO-11, 0.5Pt/SAPO-11, 0.8Pt/SAPO-11 and 1.0Pt/SAPO-11.

2.5. Valence Structure

The XPS technique was employed to investigate the elemental composition and valence states of Pt species in 0.5Pt/SAPO-11 (Figure S11). The peak of Al 2p partially overlapped the peaks of Pt 4f; the Pt 4f region was divided into two pairs of peaks, namely Pt 4f_{7/2} and Pt 4f_{5/2}, indicating that 0.5Pt/SAPO-11 mainly consisted of metal Pt(0) and Pt(IV) states (Figure S11a). The peaks of Pt 4d (Figure S11b) further confirmed the existence of Pt(0) and Pt(IV) states as well as some Pt(II) state. In addition, XPS also proved the existence of C, O and Si elements in 0.5Pt/SAPO-11; relevant individual element and survey spectra are shown in Figure S11c–f.

2.6. Catalytic Properties

Because as-synthesized xPt/SAPO-11 exhibited high crystallinity, regular spherical particles, good regular dispersion, a large specific surface area and good acidity properties, it guaranteed that xPt/SAPO-11 composites would be good catalysts for the hydroisomerization reaction. xPt/SAPO-11 composites were evaluated as catalysts for *n*-heptane hydroisomerization, as shown in Figure 7. It can be seen from Figure 7a that the *n*-heptane

hydroisomerization reaction occurred within a 250 °C–340 °C temperature range and that the conversion increased with the increase in temperature. The catalytic conversion was in the order of 0.1%Pt/SAPO-11 < 0.3%Pt/SAPO-11 < 0.8%Pt/SAPO-11 $\approx$ 1.0Pt/SAPO-11 < 0.5%Pt/SAPO-11, which was consistent with the increasing order of Pt loading, and 0.5%Pt/SAPO-11 showed the highest catalytic conversion. When Pt loading continuously increased, the catalytic conversion tended to decline. This might be explained as when the metallicity of the catalyst became too strong, the coordination with the Brønsted acid functional group was destroyed, and the reaction was dominated by a cracking reaction, which was reflected in the sharp decline in the selectivity of the *n*-heptane isomerization reaction [27]. In addition, the catalytic conversion of 1.0%Pt/SAPO-11 was close to 0.8Pt/SAPO-11, which might be due to metal functional saturation [28].

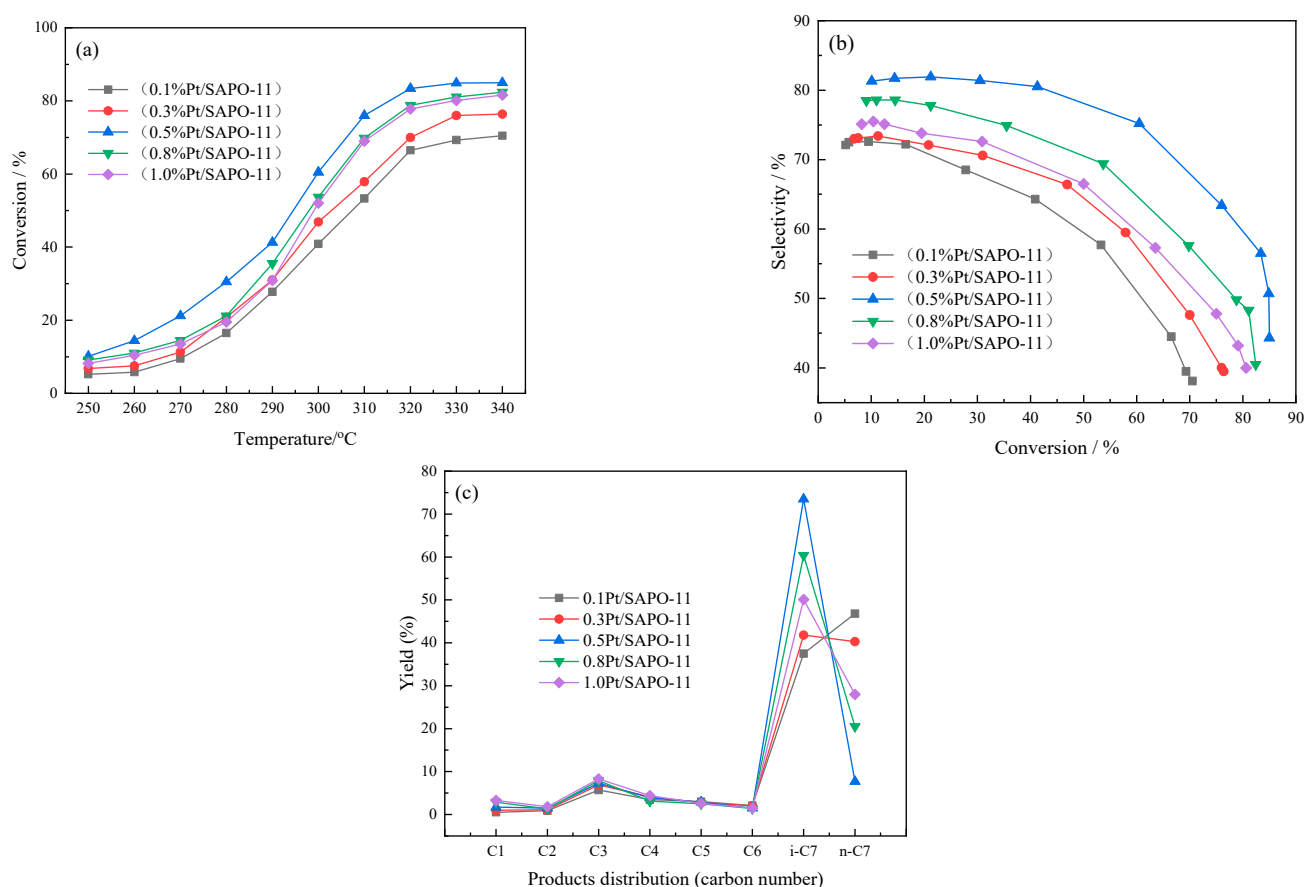


Figure 7. Catalytic performance of xPt/SAPO-11 for *n*-heptane hydroisomerization: (a) *n*-heptane conversion vs. temperature; (b) selectivity to *n*-heptane isomers as function of conversion; (c) products' distribution in hydroisomerization at atmospheric pressure, 310 °C, WHSV = 6.8 h^{−1}, H₂ flow rate = 30 mL/min, H₂/*n*-heptane (V/V) = 14.

The selectivity to isomers as a function of conversion over xPt/SAPO-11 catalysts is presented in Figure 7b. The selectivity of xPt/SAPO-11 catalysts toward isomers was in the order of 0.5Pt/SAPO-11 > 0.8Pt/SAPO-11 > 1.0Pt/SAPO-11 > 0.3Pt/SAPO-11 > 0.1Pt/SAPO-11 at the same conversion, indicating that Pt loading had a significant impact on selectivity. The isomer selectivity of 0.5Pt/SAPO-11 significantly outperformed other catalysts in the whole conversion range. Typically, the selectivity of 0.5Pt/SAPO-11 toward isomers was about 65% with a conversion of 77% at 310 °C, which was obviously higher than other xPt/SAPO-11 catalysts. The selectivity of xPt/SAPO-11 toward isomers increased with the increase in Pt loading, but if Pt loading continued to increase, the selectivity tended to decline, which might be explained by the fact that the coordination of metal Pt and the Brønsted acid function would

be destroyed due to excessive metallicity and cracking would be the main reaction, leading to greatly reduced isomer selectivity [29,30].

The good catalytic performance of xPt/SAPO-11 could be attributed to the Brønsted acids with medium and strong acidity, which had been demonstrated by the above measurements of NH₃-TPD [20,27]. Compared with 0.1, 0.3, 0.8 and 1.0Pt/SAPO-11, the Brønsted acid site of 0.5Pt/SAPO-11 could be obtained much more easily from the stable crystalline structure. In addition, the available pore structure of xPt/SAPO-11, observed from BET results, made it possible that the as-prepared catalysts synthesized by the IES and impregnation methods exhibited good catalytic properties for *n*-heptane hydroisomerization. Moreover, high conversion and activity could be due to the metal and acid sites existing in the catalysts, and the appropriate ratio of medium and strong acid sites and metal sites could facilitate the isomerization [9,21]. Wang [21] also found that superior catalytic performance was attributable to the exposure of high acid density due to little coverage of the Pt cluster on the support, the high dispersion of Pt loading to form more metal–acid bifunctional sites, and the enhanced (de)hydrogenation ability of Pt clusters. All of these could promote the effective synergy of metal sites (Pt) and acid sites. 0.5Pt/SAPO-11 has been compared with other catalysts reported in the literature, and 0.5Pt/SAPO-11 exhibited good catalytic properties, as shown in Table S1.

The yield of the products over xPt/SAPO-11 catalysts exhibited a similar trend, as shown in Figure 7c. Hydroisomerization was the dominant reaction, and 0.5Pt/SAPO-11 displayed the highest percentage of *i*-heptane and the lowest of *n*-heptane. The cracking products of *n*-heptane included C₁, C₂, C₃, C₄, C₅ and C₆ fractions, which might be due to the weak metal functionality and unsatisfactory synergistic effect between metal sites and acidic sites, resulting in the cracking of multibranched olefin intermediates [31,32]. Only a small amount of C₃ components were in the products; other cracking components were nearly undetectable. According to the above results, 0.5Pt/SAPO-11 was an effective catalyst for the isomerization of *n*-heptane, indicating that Pt loading affected the catalytic activity of catalysts in the hydroisomerization of *n*-heptane.

As 0.5Pt/SAPO-11 had good catalytic conversion and isomer selectivity, a continuous test of 0.5Pt/SAPO-11 was conducted to test the catalytic stability, as shown in Figure 8. After 6 h of testing, the catalyst still showed good activity and selectivity, indicating good catalytic stability for 0.5Pt/SAPO-11 (Figure 8a). The XRD of 0.5Pt/SAPO-11 was almost the same as that of the fresh one, suggesting the well-structured stability of 0.5Pt/SAPO-11 (Figure 8b).

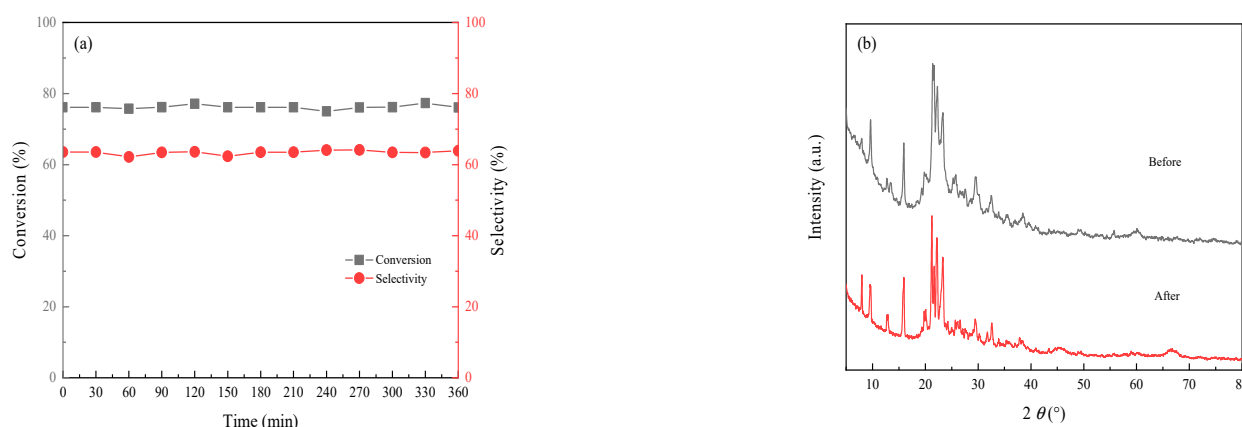


Figure 8. Long-term catalytic performance over 0.5Pt/SAPO-11: (a) conversion and selectivity at 320 °C and (b) XRD spectra before and after reaction.

2.7. Mechanism of *n*-Heptane Hydroisomerization over xPt/SAPO-11

The *n*-heptane hydroisomerization over xPt/SAPO-11 following the bifunctional metal–acid mechanism included three sequential steps: the *n*-heptane dehydrogenated to

form an *n*-heptene intermediate; the *n*-heptene intermediate diffused to the Brønsted acid site and, related the *iso*-heptene intermediate, formed through the carbocation mechanism; the *iso*-heptene intermediate diffused to Pt sites to form a corresponding isoalkane [33–35], as shown in Equations (1)–(3) and Figure 9.

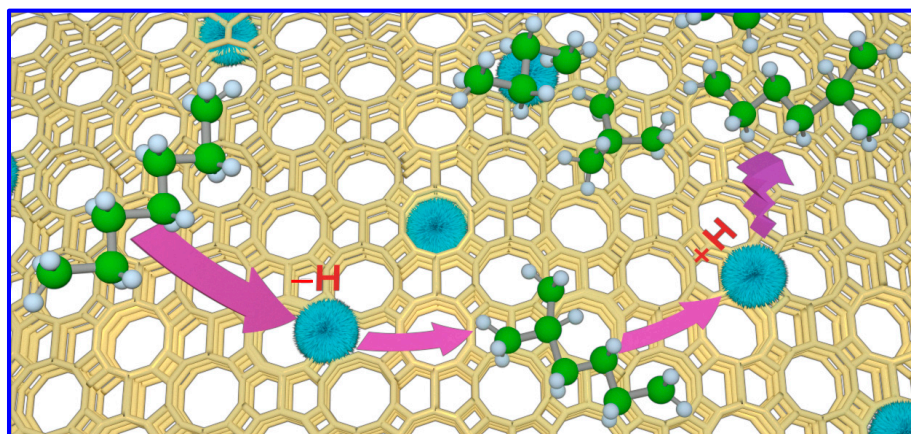
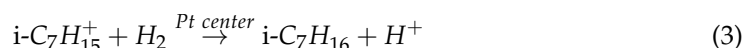
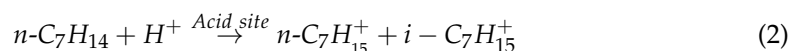
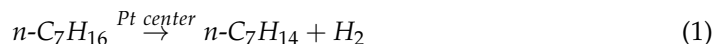


Figure 9. Scheme of *n*-heptane hydroisomerization over xPt/SAPO-11.

The isomerization mechanism of *n*-alkanes can reasonably explain the catalytic performance of xPt/SAPO-11 for *n*-heptane hydroisomerization. If sufficient active intermediates could be generated at the initial stage of the reaction, it would be conducive to the subsequent reaction. The dehydrogenation/hydrogenation function of the xPt/SAPO-11 catalysts became stronger with the increase in Pt loading, and more active intermediates could be generated during the reaction process. However, at the same time, there would be a cracking reaction accompanied by isomerization. Therefore, the Pt loading amount should be appropriate, as too high a metal content would be counterproductive [36,37].

3. Experimental Section

3.1. Materials

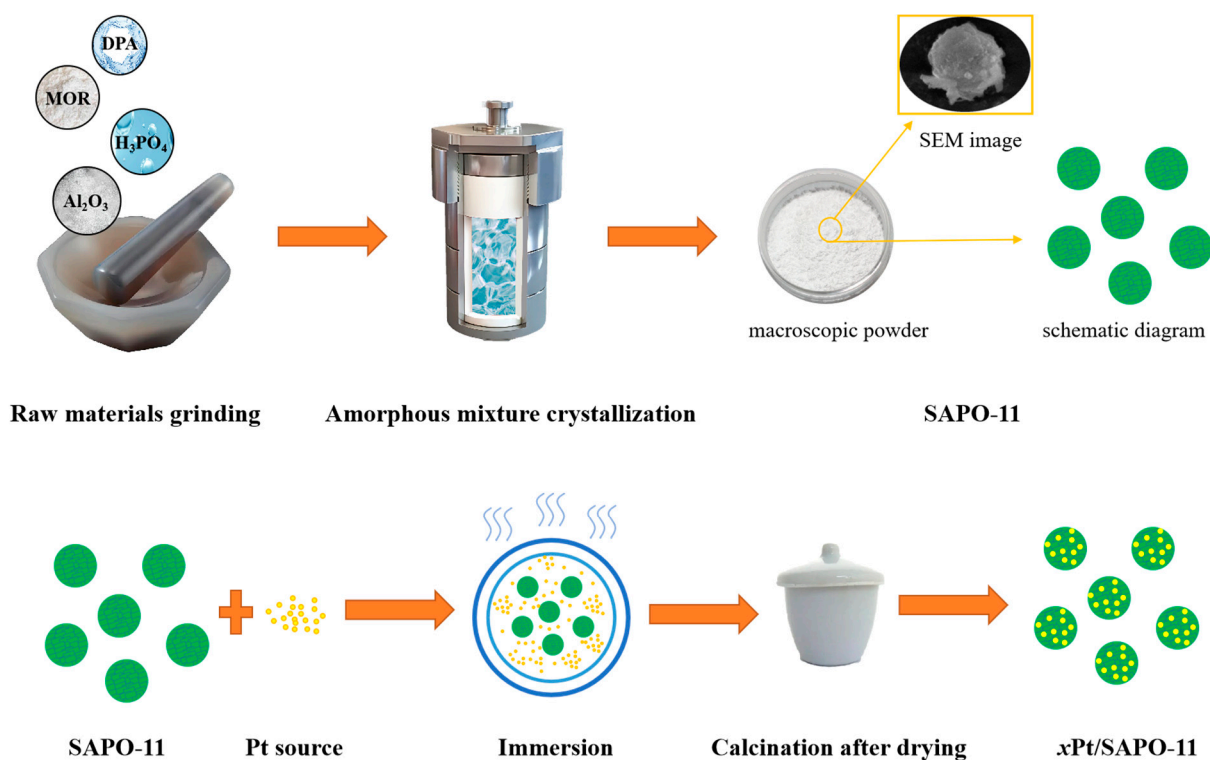
Pseudoboehmite (70.0 wt% Al₂O₃), phosphoric acid (85.0 wt% H₃PO₄), diisopropylamine ((C₃H₇)₂NH), ethyl orthosilicate (C₈H₂₀O₄Si), chloroplatinic acid (37.5 wt% H₂PtCl₆·6H₂O), *n*-heptane (*n*-C₇H₁₆) and ethanol absolute (C₂H₅OH) were purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD. Hydrogen (H₂) and nitrogen (N₂) were purchased from Daqing Xuelong Gas Co., LTD. All chemicals were used directly without purification.

3.2. Preparation

SAPO-11. The molar ratio of each raw material was about Al₂O₃:P₂O₅: template: SiO₂ = 1:1:1:0.5. The aluminum source originated from pseudoboehmite powder, the phosphorus source came from phosphoric acid, the template agent was diisopropylamine, and the silicon source was a solution of ethyl orthosilicate. The pseudoboehmite powder was placed in a mortar, and phosphoric acid, diisopropylamine and ethyl orthosilicate were added in sequence. The mixture was carefully ground to a uniform paste and then transferred into a crystallization reactor and heated at 200 °C for 1.5 h. After the crystallization time was reached, the reactor was removed and cooled to room temperature, and then the

crystallized product was washed with deionized water. When the pH value of the solution was 7, the product was filtrated and then placed in a vacuum-drying oven and dried at 80 °C for 12 h. The dried product underwent a one-step roasting process at 600 °C for 4 h to obtain the final product, an SAPO-11 molecular sieve.

xPt/SAPO-11. Pt loading catalysts, Pt/SAPO-11, were synthesized by the impregnation method. A certain amount of chloroplatinic acid and SAPO-11 zeolite were weighted according to different Pt impregnation amounts. SAPO-11 was added into deionized water containing chloroplatinic acid with continuous stirring. After standing for 5 h and drying at 80 °C for 12 h, a light-yellow solid was obtained. The product was set in a crucible and transferred into a muffle furnace, which was programmed for heating to 400 °C and kept for 6 h. As the mass proportion of Pt in SAPO-11 was separated into 0.1%, 0.2%, 0.5%, 0.8% and 1.0%, the catalysts were marked as 0.1Pt/SAPO-11, 0.2Pt/SAPO-11, 0.5Pt/SAPO-11, 0.8Pt/SAPO-11 and 1.0Pt/SAPO-11, respectively. The schematic illustration of the preparation of SAPO-11 and xPt/SAPO-11 ($x = 0.1, 0.2, 0.5, 0.8, 1.0$) with different Pt loading amounts is shown in Scheme 1.



Scheme 1. Illustration of the preparation of SAPO-11 and xPt/SAPO-11.

3.3. Characterization

X-ray diffraction (XRD) was performed on a SmartLat SE diffractometer using Cu K α radiation ($\lambda = 0.154$ nm) in the scanning range of 5–90° at 5°/min, operating at 40 kV, 30 mA. Nitrogen adsorption–desorption measurements were carried out at −196 °C with an ASAP 2460 instrument. The specific surface area was obtained with Brunauer–Emmett–Teller (BET) analysis, and the micropore and mesopore structures were separately analyzed by the Horvath–Kawazoe (HK) and Barret–Joyner–Halenda (BJH) methods. The morphologies of the samples were observed using a Zeiss SIGMA scanning electron microscope (SEM) with an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) was carried out with an FEI Talos F200X. Fourier-transform infrared spectroscopy spectra (FT-IR) were performed on a Tensor II infrared spectrometer. Fourier-transform infrared spectroscopy spectra of pyridine (Py-IR) were recorded on a Germany Brook Tensor 27 infrared spectrometer. Amounts of 0.02 g of the samples were pressed into 15 mm self-supporting disks, which were treated in a vacuum at

400 °C in an IR quartz cell for 4 h. After cooling to 50 °C, the samples were exposed to pyridine vapor for 1 h. Then, the spectra were recorded after evacuation at 150 °C. The acidic properties of the samples were tested by ammonia temperature-programmed desorption (NH₃-TPD) using an Autochem II 2920 instrument. An amount of 0.15 g of the sample was pretreated with a helium (He) gas flow of 20 mL/min at 450 °C for 0.5 h. The adsorption of NH₃ was performed at 100 °C in an NH₃-He mixture for 1 h, and TPD was performed under He flow by raising the temperature to 700 °C at a rate of 20 °C/min. The desorption amount of NH₃ was detected with a thermal conductivity detector (TCD). X-ray photoelectron spectroscopy (XPS) was performed on an EscaLab 250Xi spectrometer using Al K α radiation, and binding energies were determined with respect to the C1s peak at 284.8 eV originating from adventitious carbon.

3.4. Hydroisomerization

The hydroisomerization of *n*-heptane was performed using a continuous-flow fixed-bed stainless-steel reactor with an internal diameter of 6.0 mm. In each run, asbestos, a support rod, asbestos, quartz sand, a catalyst with 60–80 mesh and quartz were loaded in sequence into the reactor. The catalyst was activated in a hydrogen gas flow at a heating rate of 2 °C/min from room temperature to a certain temperature, with a thermocouple placed in the center of the catalyst bed measuring the reaction temperature. After the catalyst was completely activated, it was cooled to a preset temperature. *n*-Heptane was fed into the reactor with a dual plunger micropump at a predetermined flow rate to start the catalytic reaction. The product mixture was collected, and the product components were analyzed using a GC7980A gas chromatograph equipped with a hydrogen flame ionization detector.

The relevant catalytic conversion and selectivity were calculated using the following equation:

$$\text{Conversion} = \frac{\text{The amount of } n\text{-heptane asumed in the reaction (mol/h)}}{\text{The amount of } n\text{-heptane introduced in the reaction (mol/h)}} \times 100\% \quad (4)$$

$$\text{Selectivity} = \frac{\text{The amount of } n\text{-heptane isomerized products generated in the reaction (mol/h)}}{\text{The amount of } n\text{-heptane consumed in the reaction (mol/h)}} \times 100\% \quad (5)$$

4. Conclusions

In this study, xPt/SAPO-11 catalysts with trace Pt loading synthesized by the IES method and the impregnation method had high crystallinity, a high specific surface area, regular circular aggregates and a compact surface. xPt/SAPO-11 catalysts had good catalytic performance in *n*-heptane isomerization, indicating that trace Pt loading could lead to high catalytic properties. The catalytic conversion was in the order of 0.1%Pt/SAPO-11 < 0.3%Pt/SAPO-11 < 0.8%Pt/SAPO-11 $\approx$ 1.0Pt/SAPO-11 < 0.5%Pt/SAPO-11; the selectivity toward isomers was in the order of 0.5Pt/SAPO-11 > 0.8Pt/SAPO-11 > 1.0Pt/SAPO-11 > 0.3Pt/SAPO-11 > 0.1Pt/SAPO-11; and 0.5Pt/SAPO-11 displayed the highest selectivity toward *i*-heptane products, indicating that Pt loading had a significant impact on the catalytic performance. Moreover, the coordination between Pt metal sites and Brønsted acid sites was the key to enhancing the conversion of *n*-heptane and the selectivity toward *n*-heptane isomers. The mechanism of xPt/SAPO-11 catalysts for *n*-heptane hydroisomerization was proposed on the basis of references reported before and the experiment results in this manuscript.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal13101383/s1>. Figure S1: XRD of SAPO-11 and JCPDS:47-0614, Figure S2: SEM and EDS Mapping of SAPO-11, Figure S3: SEM and EDS Mapping of 0.1Pt/SAPO-11, Figure S4: SEM and EDS Mapping of 0.2Pt/SAPO-11, Figure S5: SEM and EDS Mapping of 0.5Pt/SAPO-11, Figure S6: SEM and EDS Mapping of 0.8Pt/SAPO-11,

Figure S7: SEM and EDS Mapping of 1.0Pt/SAPO-11, Figure S8: Pore diameter distributions of SAPO-11 and xPt/SAPO-11, Figure S9: Partial enlarged FT-IR spectra of samples, Figure S10: Py-IR spectra of 0.5Pt/SAPO-11, Figure S11: XPS spectra of 0.5Pt/SAPO-11, Table S1: Comparison of catalysts reported in literature. References [38–42] are cited in the Supplementary Materials.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available due to restrictions of the institution's privacy policy.

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References

1. Tan, Y.; Hu, W.; Du, Y.; Li, J. Species and impacts of metal sites over bifunctional catalyst on long chain n-alkane hydroisomerization: A review. *Appl. Catal. A Gen.* **2021**, *611*, 117916. [\[CrossRef\]](#)
2. Wang, W.; Liu, C.; Wu, W. Bifunctional catalysts for the hydroisomerization of n-alkanes: The effects of metal–acid balance and textural structure. *Catal. Sci. Technol.* **2019**, *9*, 4162–4187. [\[CrossRef\]](#)
3. Prachee, M.; Majmutov, A.; Chen, J. Isomerization catalysts and technologies for biorefining: Opportunities for producing sustainable aviation fuels. *Fuel* **2023**, *351*, 128994.
4. Monteiro, R.R.C.; dos Santos, I.A.; Arcanjo, M.R.A.; Cavalcante, C.L., Jr.; de Luna, F.M.T.; Fernandez-Lafuente, R.; Vieira, R.S. Production of jet biofuels by catalytic hydroprocessing of esters and fatty acids: A review. *Catalysts* **2022**, *12*, 237. [\[CrossRef\]](#)
5. Li, T.; Zhang, L.; Tao, Z.; Hu, C.; Zhao, C.; Yi, F.; Gao, X.; Wen, X.; Yang, Y.; Li, Y. Synthesis and characterization of amorphous silica-alumina with enhanced acidity and its application in hydro-isomerization/cracking. *Fuel* **2020**, *279*, 118487. [\[CrossRef\]](#)
6. Wang, X.; Zhang, X.; Wang, Q. N-dodecane hydroisomerization over Pt/ZSM-22: Controllable microporous Brønsted acidity distribution and shape-selectivity. *Appl. Catal. A Gen.* **2020**, *590*, 117335. [\[CrossRef\]](#)
7. Tao, S.; Li, X.; Lv, G.; Wang, C.; Xu, R.; Ma, H.; Tian, Z. Highly mesoporous SAPO-11 molecular sieves with tunable acidity: Facile synthesis, formation mechanism and catalytic performance in hydroisomerization of n-dodecane. *Catal. Sci. Technol.* **2017**, *7*, 5775–5784. [\[CrossRef\]](#)
8. Jaroszewska, K.; Fedyna, M.; Trawczyński, J. Hydroisomerization of long-chain n-alkanes over Pt/AlSBA-15 zeolite bimodal catalysts. *Appl. Catal. B Environ.* **2019**, *255*, 117756. [\[CrossRef\]](#)
9. Mäki-Arvela, P.; Kaka khel, T.A.; Azkaar, M.; Engblom, S.; Murzin, D.Y. Catalytic hydroisomerization of long-chain hydrocarbons for the production of fuels. *Catalysts* **2018**, *8*, 534. [\[CrossRef\]](#)
10. Guo, C.; Wang, W.; Zhang, Y.; Lin, H.; Jia, G.; Li, T.; Xin, Q.; Bai, X.; Wu, W. Influences of the metal-acid proximity of Pd-SAPO-31 bifunctional catalysts for n-hexadecane hydroisomerization. *Fuel Process. Technol.* **2021**, *214*, 106717. [\[CrossRef\]](#)
11. Jin, D.; Li, L.; Ye, G.; Ding, H.; Zhao, X.; Zhu, K.; Coppens, M.O.; Zhou, X. Manipulating the mesostructure of silicoaluminophosphate SAPO-11 via tumbling-assisted, oriented assembly crystallization: A pathway to enhance selectivity in hydroisomerization. *Catal. Sci. Technol.* **2018**, *8*, 5044–5061. [\[CrossRef\]](#)
12. Yadav, R.; Sakthivel, A. Silicoaluminophosphate molecular sieves as potential catalysts for hydroisomerization of alkanes and alkenes. *Appl. Catal. A Gen.* **2014**, *481*, 143–160. [\[CrossRef\]](#)
13. Lv, G.; Wang, C.; Chi, K.; Liu, H.; Wang, P.; Ma, H.; Qu, W.; Tian, Z. Effect of Pt site distribution on the catalytic performance of Pt/SAPO-11 for n-dodecane hydroisomerization. *Catal. Today* **2018**, *316*, 43–50. [\[CrossRef\]](#)
14. Wu, Q.; Yuan, J.; Guo, C.; Liu, Z.; Li, X.; Liu, Z.; Wang, W.; Wu, W. The hydroisomerization of n-hexadecane over Pd/SAPOs bifunctional catalysts with different opening size: Features of the diffusion properties in pore channels and the metal-acid synergistic catalysis. *Fuel Process. Technol.* **2023**, *244*, 107692. [\[CrossRef\]](#)
15. Wang, Y.; Tao, B.; Wu, B.; Chen, H.; Xu, J.; Yang, Y.; Li, Y. Shape-controlled synthesis of Pt particles and their catalytic performances in the n-hexadecane hydroconversion. *Catal. Today* **2016**, *259*, 331–339. [\[CrossRef\]](#)
16. Lucas, A.; Sánchez, P.; Dorado, F.; Ramos, M.; Valverde, J. Effect of the metal loading in the hydroisomerization of n-octane over beta agglomerated zeolite based catalysts. *Appl. Catal. A Gen.* **2005**, *294*, 215–225. [\[CrossRef\]](#)
17. Batalha, N.; Pinard, L.; Bouchy, C.; Guillon, E.; Guisnet, M. n-Hexadecane hydroisomerization over Pt-HBEA catalysts. Quantification and effect of the intimacy between metal and protonic sites. *J. Catal.* **2013**, *307*, 122–131. [\[CrossRef\]](#)

18. Sun, N.; Wang, H.; Luo, A.; Yang, Z.; Wang, Y.; Kang, L. Synthesis and hydrogen isomerization performance of ordered mesoporous nanosheet SAPO-11 molecular sieves. *J. Solid State Chem.* **2022**, *309*, 122972. [\[CrossRef\]](#)
19. Dang, T.T.H.; Bartoszek, M.; Schneider, M.; Hoang, D.L.; Bentrup, U.; Martin, A. Chloride-free Cu-modified SAPO-37 catalyst for the oxidative carbonylation of methanol in the gas phase. *Appl. Catal. B* **2012**, *122*, 115–122. [\[CrossRef\]](#)
20. Du, Y.; Feng, B.; Jiang, Y.; Yuan, L.; Huang, K.; Li, J. Non-solvent synthesis and n-hexadecane hydroisomerization performance of SAPO-11 catalyst. *Eur. J. Inorg. Chem.* **2018**, *22*, 2599–2606. [\[CrossRef\]](#)
21. Wang, D.; Liu, J.; Cheng, X.; Kang, X.; Wu, A.; Tian, C.; Fu, H. Trace Pt clusters dispersed on SAPO-11 promoting the synergy of metal sites with acid sites for high-effective hydroisomerization of n-alkanes. *Small Methods* **2019**, *3*, 1800510. [\[CrossRef\]](#)
22. Song, X.; Bai, X.; Wu, W.; Kikhtyanin, O.V.; Zhao, A.; Xiao, L.; Su, X.; Zhang, J.; Wei, X. The effect of palladium loading on the catalytic performance of Pd/SAPO-11 for n-decane hydroisomerization. *Mol. Catal.* **2017**, *433*, 84–90. [\[CrossRef\]](#)
23. Wang, X.; Guo, S.; Niu, Z. Synthesis of a ZSM-5 (core)/SAPO-11 (shell) composite zeolite and its catalytic performance in the methylation of naphthalene with methanol. *RSC Adv.* **2023**, *13*, 2081–2089. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Mériaudeau, P.; Tuan, V.A.; Nghiem, V.T.; Lai, S.Y.; Hung, L.N.; Naccache, C. SAPO-11, SAPO-34, and SAPO-41 molecular sieves: Synthesis, characterization, and catalytic properties in n-octane hydroisomerization. *J. Catal.* **1997**, *169*, 55–66. [\[CrossRef\]](#)
25. Nie, R.; Lei, H.; Pan, S.; Wang, L.; Fei, J.; Hou, Z. Core-shell structured CuO–ZnO@H-ZSM-5 catalysts for CO hydrogenation to dimethyl ether. *Fuel* **2012**, *96*, 419–425. [\[CrossRef\]](#)
26. Yang, Z.; Liu, Y.; Liu, D.; Meng, X.; Liu, C. Hydroisomerization of n-octane bimetallic Ni–Cu/SAPO-11 catalysts. *Appl. Catal. A Gen.* **2017**, *543*, 274–282. [\[CrossRef\]](#)
27. Qin, H.; Feng, N.; Lv, Q.; Wan, H.; Guan, G. Pt Single Atom-Anchored CeO_x/SAPO-11 for Highly Efficient Hydroisomerization of n-Heptane. *Fuel Process. Technol.* **2023**, *241*, 107604. [\[CrossRef\]](#)
28. Niu, P.; Xi, H.; Ren, J.; Lin, M.; Wang, Q.; Jia, L.; Hou, B.; Li, D. High selectivity for n-dodecane hydroisomerization over highly siliceous ZSM-22 with low Pt loading. *Catal. Sci. Technol.* **2017**, *7*, 5055–5068. [\[CrossRef\]](#)
29. Kim, M.Y.; Lee, K.; Choi, M. Cooperative effects of secondary mesoporosity and acid site location in Pt/SAPO-11 on n-dodecane hydroisomerization selectivity. *J. Catal.* **2014**, *319*, 232–238. [\[CrossRef\]](#)
30. Ma, J.; Liu, X.; Yuan, H. In situ synthesis of mesoporous Pt/SAPO-11 for the preparation of biological aviation kerosene. *J. Porous Mat.* **2022**, *29*, 1387–1398. [\[CrossRef\]](#)
31. Souverijns, W.; Martens, J.A.; Froment, G.F.; Jacobs, P.A. Hydrocracking of isoheptadecanes on Pt/H-ZSM-22: An example of pore mouth catalysis. *J. Catal.* **1998**, *174*, 177–184. [\[CrossRef\]](#)
32. Geng, L.; Gong, J.; Qiao, G.; Ye, S.; Zheng, J.; Zhang, N.; Chen, B. Effect of metal precursors on the performance of Pt/SAPO-11 catalysts for n-dodecane hydroisomerization. *ACS Omega* **2019**, *4*, 12598–12605. [\[CrossRef\]](#) [\[PubMed\]](#)
33. Shamanaeva, I.A.; Parkhomchuk, E.V.; Bukhtiyarova, G.A. Hydrodeoxygenation isomerization of methyl palmitate over SAPO-11-supported Ni-phosphide catalysts. *Catalyst* **2022**, *12*, 1486. [\[CrossRef\]](#)
34. Yuan, Z.; Cheng, Y.; Ma, S.; Jiang, Z.; Zhou, Y.; Wang, Y.; Zhang, W.; Suo, Y. Instant exactness synthesis and n-heptane hydroisomerization of high performance Ni/SAPO-11 catalyst. *J. Porous Mat.* **2020**, *5*, 1455–1466. [\[CrossRef\]](#)
35. Yang, H.; Du, X.; Lei, X.; Lei, X.; Zhou, K.; Tian, Y.; Li, D.; Hu, C. Unraveling enhanced activity and coke resistance of Pt-based catalyst in bio-aviation fuel refining. *Appl. Energy* **2021**, *301*, 117469. [\[CrossRef\]](#)
36. Cui, X.; Liu, Y.X.; Liu, X.M. Controlling acidic sites to improve hydroisomerization performance of Pt/SAPO-11 catalysts. *Catal. Lett.* **2015**, *145*, 1464–1473. [\[CrossRef\]](#)
37. Lyu, Y.C.; Yu, Z.M.; Yang, Y.; Liu, Y.X.; Zhao, X.X.; Liu, X.M.; Mintova, S.; Yan, Z.F.; Zhao, G.F. Metal and acid sites instantaneously prepared over Ni/SAPO-11 bifunctional catalyst. *J. Catal.* **2019**, *374*, 208–216. [\[CrossRef\]](#)
38. Jin, D.; Ye, G.; Zheng, J.; Yang, W.; Zhu, K.; Coppens, M.O.; Zhou, X. Hierarchical silicoaluminophosphate catalysts with enhanced hydroisomerization selectivity by directing the orientated assembly of premanufactured building blocks. *ACS Catal.* **2017**, *7*, 5887. [\[CrossRef\]](#)
39. Pastvova, J.; Kaucky, D.; Moravkova, J.; Rathousky, J.; Sklenak, S.; Vorokhta, M.; Brabec, L.; Pilar, R.; Jakubec, I.; Tabor, E.; et al. Effect of Enhanced Accessibility of Acid Sites in Microporous Mordenite Zeolites on Hydroisomerization of n-Hexane. *ACS Catal.* **2017**, *7*, 5781. [\[CrossRef\]](#)
40. Yang, Z.; Liu, Y.; Zhao, J.; Gou, J.; Sun, K.; Liu, C. Zinc-modified Pt/SAPO-11 for improving the isomerization selectivity to dibranched alkanes. *Chin. J. Catal.* **2017**, *38*, 509–517. [\[CrossRef\]](#)
41. Zhang, F.; Liu, Y.; Sun, Q.; Dai, Z.; Gies, H.; Wu, Q.; Pan, S.; Bian, C.; Tian, Z.; Meng, X.; et al. Hybridization chain reactions on silica coated Qbeads for the colorimetric detection of multiplex microRNAs. *Chem. Commun.* **2017**, *53*, 4954.
42. Wang, Y.; Tao, Z.; Wu, B.; Xu, J.; Huo, C.; Li, K.; Chen, H.; Yang, Y.; Li, Y. Effect of metal precursors on the performance of Pt/ZSM-22 catalysts for n-hexadecane hydroisomerization. *J. Catal.* **2015**, *322*, 1–13. [\[CrossRef\]](#)

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