Hydroisomerization of \( n \)-Heptane over Modified USY-Supported H\(_3\)PW\(_{12}\)O\(_{40}\) Catalysts: Effect of Hydrothermal Treatment for USY

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Abstract: We have prepared Pt-bearing modified USY-supported 12-tungstophosphoric acid catalysts from supports that were treated hydrothermally at various temperatures and time. The catalysts were characterized by XRD, IR spectroscopy, and NH\(_3\)-TPD techniques, and measured for their hydroisomerization of \( n \)-heptane in an atmospheric fixed-bed microreactor. We found that the PW-bearing catalysts showed much higher catalytic activity than do the PW-free counterparts, and that the hydrothermal conditions for the USY support could influence the catalytic activity substantially. Hydrothermal treatment at 650°C for 5 h was the optimum treatment condition; it leads to a high conversion of \( n \)-heptane (30.1%) with a very high selectivity for isomerization (98.2%). We discuss the catalytic activities in relation to the physical and chemical properties of the catalysts.

Keywords: 12-tungstophosphoric acid, USY, Hydrothermal treatment, Hydroisomerization of \( n \)-Heptane

Introduction

In modern refineries, hydroisomerization of linear alkanes to branched ones is an environmentally friendly way to increase the octane number of the gasoline pool. Chlorinated Pt/Al\(_2\)O\(_3\) and Pt/mordenite have been used traditionally as catalysts for the hydroisomerization of \( n \)-pentane and \( n \)-hexane [1], but, owing to increasingly stringent regulations regarding the advanced liquid fuel quality from the view point of the environment, it is expected that in the near future there will be a strong need to effect the hydroisomerization of the middle paraffins, from \( n \)-heptane to \( n \)-nonane, of the gasoline fraction with a thorough isomerization selectivity while minimizing cracking [2]. This demand has stimulated research interest in the hydroisomerization of \( n \)-heptane. Up to now, only a few studies have been reported in this field [3,4]. For example, Corma and coworkers [3] recently revealed that a nanocrystalline Beta zeolite-supported Pt catalyst exhibits much better \( n \)-heptane hydroisomerization selectivity than does Pt/mordenite, upon which the complete cracking of \( n \)-heptane is observed. Further research to seek suitable solid acid catalysts for hydroisomerization of \( n \)-heptane is still open.

Heteropoly acids (HPAs), which act as acid catalysts accompanied by redox properties, display high catalytic activity in various reactions [5]. 12-Tungstophosphoric acid (PW) has been the target catalyst in many reports because of its very strong acidity [6-8], but pure HPAs used as heterogeneous catalysts are hindered by their low specific surface area (< 10 m\(^2\)/g) and high solubility in polar reaction systems. To overcome this limitation, one can prepare acid salts containing large cations, such as Cs\(^+\), K\(^+\), Rb\(^+\), and NH\(_4\)\(^+\), which present surface areas in the order of 150 m\(^2\)/g [9]. On the other hand, when the use of the acid form is required, HPAs can be supported on a high-surface-area carriers [10-14], such as activated carbon, silica, silica-alumina, alumina, titania, zirconia, resin, polymer, clay, MCM-41, and HMS. In addition, zeolite Y has also been employed by several researchers as the support for HPAs [15-17] because of the existence of faujasite supercages that have diameters (1.3 nm) that are slightly larger than those of the polyanion and those of the secondary mesopores in the dealuminated Y zeolite. Y Zeolite-supported HPA catalysts have been

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evaluated in the transformation of \( m \)-xylene and the esterification of acetic acid with ethanol, but no examples exist regarding the hydroisomerization of \( m \)-paraffins over supported HPA catalysts. Very recently, we revealed [18] that, in the hydroisomerization of \( n \)-heptane, the Pt-bearing dealuminated USY-supported PW catalyst exhibited not only much higher catalytic conversion of \( n \)-heptane but also higher selectivity for isomerization than did the PW-free catalyst. This promotional effect of PW in the reaction was not observed over the unmodified USY-supported catalyst.

In this paper, we describe the preparation of various dealuminated USY supports for PW catalysts by hydrothermal treatment and HCl leaching; we have found that their catalytic activities in the hydroisomerization of \( n \)-heptane are influenced substantially by the treatment conditions. Catalytic activities are discussed in terms of the physical and chemical properties of the catalysts.

**Experimental**

**Preparation of Catalyst**

The modified USY support was prepared by the acid leaching of USY (Si/Al = 6.0, Fushun Petroleum Factory) with a 0.6 M aqueous HCl solution for 2 h, followed by washing with water, drying at 120°C for 10 h, and calcination at 550°C for 3 h. The obtained sample was hydrothermally treated by self-steaming with the calcination of the sample in a confined atmosphere under 100% steam at 300, 400, 550, 650, and 700°C, respectively, for 5 h, or at 650°C for 1, 2, 4, and 8 h, respectively. This process was followed by a second acid leaching as mentioned above. We denote each modified USY support as USY\( m \) (n), where \( m \) stands for the hydrothermal treatment temperature (°C), and \( n \) stands for the hydrothermal treatment time (h). Supported PW samples, PW/USY\( m \) (n), were prepared by the impregnation at room temperature with an excess of PW solution, by contacting the corresponding support with an aqueous H\(_3\)PW\(_{12}\)O\(_{40}\)·xH\(_2\)O (Shanghai Chem. Reagent Co., AR) solution under constant stirring overnight, followed by evaporation, drying, and calcination. Pt-PW/USY\( m \) (n) catalysts were obtained by the incipient wetness impregnation of PW/USY\( m \) (n) with an aqueous solution of chloroplatinate acid. This process was followed by evaporation, drying, and calcination. The weight percentages of PW and Pt in the catalysts were 10 and 0.4%, respectively.

**Characterization of Catalyst**

X-Ray powder diffraction (XRD) patterns were obtained on a Bruker D8 Advance diffractometer using Ni-filtered Cu Ka radiation at 40 kV and 20 mA. The BET surface area of samples was measured on a Micromeritics ASAP 2400 apparatus using nitrogen as the adsorbate at 77 K. The Si/Al ratio of samples was obtained using an ICP spectrometer (J.Y. Ultima C., Jobin Yvon). FTIR spectra were obtained using a Nicolet AVATAR-360 spectrometer (KBr disks) at ambient temperature. Temperature-programmed desorption of ammonia (NH\(_3\)-TPD) was carried out using a CHEMBET-3000 instrument (Quantachrome Corporation) employing helium as the carrier gas and a thermoconductor as the detector. The sample was activated at 350°C for 1 h, followed by adsorption of ammonia at 150°C, and then NH\(_3\)-TPD was performed at a heating rate of 15°C/min.

**Catalytic Activity Test**

Hydroisomerization of \( n \)-heptane was carried out in an atmospheric fixed-bed flow microreactor. The catalyst (0.5 g) in the form of granules (40-60 mesh) was charged into the stainless-steel tubular reactor. \( n \)-Heptane was injected by the micro-volume pump into the preheater, where it was vaporized and mixed uniformly with H\(_2\), and then the reactant mixture was introduced to the catalyst. The reaction started after the pretreatment of the catalyst in situ in an H\(_2\) flow at 300°C for 3 h. The reaction conditions were as follows: 250°C reaction temperature, 2 h\(^{-1}\) weight hourly space velocity, 7.9 molar ratio of H\(_2\) to \( n \)-heptane, and a 3 h reaction time on stream. The product mixture was analyzed using an on-line gas chromatograph equipped with a 50-m SE30 capillary column. The conversion of \( n \)-heptane and selectivity for products were calculated according to our previous report [18].

**Results and Discussion**

During the catalytic test, we observed stabilized after about 2 h reaction time. Table 1 shows the influence that the hydrothermal treatment temperature for USY supports has on the stabilized activity of Pt-PW/USY\( m \) (5) catalysts in the hydroisomerization of \( n \)-heptane. It is evident that the PW-free catalysts are almost inactive in the reaction, whereas the catalytic conversion of \( n \)-heptane can be enhanced remarkably by introducing PW into the catalyst. This finding is in agreement with our previous results [18]. Upon increasing the hydrothermal treatment temperature from 300 to 400°C, we observed no remarkable change of the conversion on PW-bearing catalysts, but when the temperature was increased up to 550°C, a sharp increase in the conversion was observed (conversion: 22.8%). Furthermore, we achieved the maximum conversion of 30.1% at a hydrothermal treatment temperature of 650°C; further increases of temperature led to a substantial decrease of conversion. This change of conversion as a function of hydrothermal treatment temperature was not observed on the PW-free catalyst. Table
Table 1. Comparison of the Reactivity of n-Heptane Hydroisomerization Over the Catalysts Supported on Modified USY Carriers with Various Hydrothermal Treatment Temperatures

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Al</th>
<th>Conversion of n-heptane %</th>
<th>Product selectivity/%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Isomerization</td>
</tr>
<tr>
<td>Pt/USY300(5)</td>
<td>13.2</td>
<td>3.1</td>
<td>100</td>
</tr>
<tr>
<td>Pt/USY650(5)</td>
<td>31.8</td>
<td>2.5</td>
<td>100</td>
</tr>
<tr>
<td>Pt-PW/USY300(5)</td>
<td>13.2</td>
<td>14.6</td>
<td>100</td>
</tr>
<tr>
<td>Pt-PW/USY400(5)</td>
<td>15.3</td>
<td>12.6</td>
<td>97.0</td>
</tr>
<tr>
<td>Pt-PW/USY550(5)</td>
<td>26.5</td>
<td>22.8</td>
<td>95.4</td>
</tr>
<tr>
<td>Pt-PW/USY650(5)</td>
<td>30.8</td>
<td>30.1</td>
<td>98.2</td>
</tr>
<tr>
<td>Pt-PW/USY700(5)</td>
<td>34.1</td>
<td>17.6</td>
<td>98.8</td>
</tr>
</tbody>
</table>

a See experimental section for reaction conditions, b Si/Al ratio for the dealuminated USY support.

Table 2. Comparison of the Reactivity of n-Heptane Hydroisomerization Over the Catalysts Supported on USY650(n) with Various Hydrothermal Treatment time

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Al</th>
<th>Conversion of n-heptane %</th>
<th>Product selectivity/%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Isomerization</td>
</tr>
<tr>
<td>Pt-PW/USY650(1)</td>
<td>10.6</td>
<td>13.2</td>
<td>98.7</td>
</tr>
<tr>
<td>Pt-PW/USY650(2)</td>
<td>14.4</td>
<td>16.2</td>
<td>98.8</td>
</tr>
<tr>
<td>Pt-PW/USY650(4)</td>
<td>21.1</td>
<td>12.5</td>
<td>98.3</td>
</tr>
<tr>
<td>Pt-PW/USY650(5)</td>
<td>30.8</td>
<td>30.1</td>
<td>98.2</td>
</tr>
<tr>
<td>Pt-PW/USY650(8)</td>
<td>39.7</td>
<td>27.6</td>
<td>98.1</td>
</tr>
</tbody>
</table>

a See experimental section for reaction conditions, b Si/Al ratio for the dealuminated USY support.

1 also shows that whatever the conversion, the selectivity for isomerization was always > 95%. Table 2 compares the catalytic activities of Pt-PW/USY650(n) catalysts, with respect to different hydrothermal treatment times for their USY supports, in hydroisomerization of n-heptane. We observe in Table 2 that increasing the hydrothermal treatment time from 1 to 4 h gives, more or less, the same conversion at a comparatively low level. Nevertheless, the conversion increases by a very large margin, from 12.5 to 30.1%, when the treatment time increases from 4 to 5 h, and a slight decrease of conversion is observed upon increasing the treatment time to 8 h. In Table 2, we also observe that the selectivity for isomerization is at least 98%, even though the conversions are different for each different catalysts. On the other hand, Tables 1 and 2 indicate that, upon increasing the hydrothermal treatment temperature or treatment time, the Si/Al ratio of modified USY increases substantially, which testifies that high steaming temperatures or times facilitate the dealumination. The catalytic conversion does not relate directly, however, to the extent of dealumination.

The XRD patterns of Pt-PW/USYm(n) catalysts are compared with those of the pure PW and USY samples in Figure 1. All the XRD curves of Pt-PW/USYm(n) catalysts, except for that of Pt-PW/USY650(8), are similar to that of USY, which indicates the high crystallinity of the hydrothermally treated USY supports. A clear decrease of the crystallinity for USY650(8) can be verified by the decrease of its peak intensity relative to that of USY. When PW is impregnated onto modified USY supports, not all the peaks assigned to the PW crystal can be detected (Figure 1). This finding demonstrates that PW

Figure 1. XRD patterns of samples of (a) pure PW, (b) USY, (c) Pt-PW/USY550(5), (d) Pt-PW/USY650(5), (e) Pt-PW/USY700(5), (f) Pt-PW/USY650(4), and (g) Pt-PW/USY650(8).
Table 3. BET Surface Areas of USY, USY650(5), and Pt-PW/USY650(5) Samples

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area /m²g⁻¹</th>
<th>Micropore ¹</th>
<th>Mesopore ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>USY</td>
<td>775</td>
<td>524</td>
<td>251</td>
</tr>
<tr>
<td>USY650(5)</td>
<td>734</td>
<td>438</td>
<td>296</td>
</tr>
<tr>
<td>Pt-PW/USY650(5)</td>
<td>602</td>
<td>417</td>
<td>185</td>
</tr>
</tbody>
</table>

¹ Micropore refers to < 2.0 nm pores, ² Mesopore refers to > 2.0 nm pores.

Figure 2. FTIR spectra of (a) Pt-PW/USY650(5), (b) USY, and (c) pure PW samples.

must be highly dispersed on the surface of the support. Moreover, when a small amount of Pt is impregnated onto PW/USYm(n), no detectable signals assigned to Pt can be found for the Pt-bearing samples, which implies that Pt is also highly dispersed on the catalyst surface. This finding is in agreement with previous results [18,19]. Table 3 shows the BET surface area of USY, USY650(5) and Pt-PW/USY650(5) samples. We see that after hydrothermal treatment and acid leaching, the surface area of USY650(5) decreases slightly, but the concentration of mesopores increases substantially which could provide evidence for the generation of secondary-structured mesopores during dealumination. After supporting PW, the catalyst surface area clearly decreases and, moreover, this decrease arises mainly from the decrease of the mesopore surface area. The result implies the possibility that PW mostly disperses well on the surface of the mesopores of the catalyst, rather than in the micropores. This suggestion seems reasonable when considering that the diameter of the main channel of Y zeolite (0.74 nm) is narrower than that of PW anions (ca. 1.0 nm) [15].

Figure 2 shows FTIR spectra of Pt-PW/USY650(5), USY650(5), and pure PW samples. Four peaks, at 1080, 982, 892, and 789 cm⁻¹, are clearly observed in Figure 2(c). These peaks are typical absorption bands for PW having a Keggin structure, with the lines at 1080 and 982 cm⁻¹ corresponding to stretching vibrations of P-O and W=O groups, respectively, and the other two reflecting W-O-W vibrations [20]. Compared with Figure 2(b), the background lines for USY in Figure 2(a) of Pt-PW/USY650(5) have decreased sharply. Moreover, a weak, but clear, band at 959 cm⁻¹ is found in Figure 2(a), which could be assigned to W=O in PW. It is noteworthy of that the W=O band for Pt-PW/USY650(5) catalyst shifts to a lower wavenumber compared to that for pure PW; this observation implies the occurrence of weak interactions between PW and hydroxyl groups on the surface of the USY650(5) support. Although the line at 1080 cm⁻¹ for PW in Figure 2(a) cannot be distinguished, because of overlap with the very strong lines of the modified USY support, the weak lines for PW at 789 and 896 cm⁻¹ can be detected. This observation confirms that the supported PW has retained the Keggin structure. This result agrees well with those of other authors [21,22].

Figure 3 shows the NH₃-TPD curves for the USY650(5) support and various Pt-PW/USYm(n) catalysts. Two very weak ammonia desorption peaks appear at 230 and 410°C for the support, indicating a very low acid number on the support. This phenomenon arises from the hydrothermal and acid treatments for the USY sample being accompanied with dealumination [23]. By contrast, Figure 3 also reveals much higher amounts of acid on the PW-bearing catalysts than on the support alone, with the acid strength almost unaltered.

Figure 3. NH₃-TPD profiles of samples of (a) USY650(5), (b) Pt-PW/USY550(5), (c) Pt-PW/USY650(5), (d) Pt-PW/USY700(5), (e) Pt-PWUSY650(4), and (f) Pt-PW/USY650(8).
It is well known that the hydroisomerization of \( n \)-paraffins over metal/solid acid catalysts can be explained on the basis of a classical bifunctional mechanism [24-27] with the metal being the active center for dehydrogenation and hydrogenation and the acid being the active center for isomerization (cracking, condensation, or cyclization) via carbenium ions as reaction intermediates. In case of the highly dispersed Pt on the catalyst surface, as shown in Figure 1, we deduce that the catalyst’s acidity could control the catalytic activity over a large range. Therefore, it is most likely that the remarkable improvement of the amount of acid for Pt-PW/USY\( \text{m(} n \text{)} \) catalysts could account for their substantially increased conversions, as shown in Tables 1 and 2. However, the observation of more-or-less similar amounts of acid for the PW-bearing catalysts in Figure 3 does not allow us to explain the large discrepancies of their conversions in Tables 1 and 2, which result from the different hydrothermal treatment conditions for the USY support.

Previous results have shown that in addition to the acidity, the catalyst pore structure also exerts significant impact on the catalytic activity in the hydroisomerization of paraffins [1,3]. When H-Y or NH\( _x \)-Y zeolite is subjected to hydrothermal treatment, secondary mesopores that have diameters of 15-20 nm could be created [28,29] with the removed amorphous Al species filling the insides of the secondary pores. The main effect of acid leaching, as far as the textural properties are concerned, is to extract the amorphous material from the secondary pores created by the hydrothermal treatment without creating a large quantity of new secondary pores [28]. Recently, using positron annihilation spectroscopy, Zhu and coworkers [30] revealed that both the number and diameter of the secondary mesopores are influenced remarkably by the hydrothermal treatment temperature and time. The authors indicated that more secondary mesopores were generated upon increasing either the hydrothermal treatment time or temperature, but that much higher temperatures and/or long treatment times could result in a decrease of the number of secondary mesopores. This finding has been confirmed [31]. Based on the above considerations, one can infer that is by altering the pore structure of the catalyst support of USY that the hydrothermal treatment conditions influence remarkably the catalytic activity of Pt-PW/USY\( \text{m(} n \text{)} \) in this reaction. When USY is hydrothermally treated at low temperature or for a short time, only a small number of secondary mesopores form. A hydrothermal treatment temperature of 650°C and time of 5 h are proposed to be the optimum conditions to create a large number of secondary mesopores, which can encapsulate and disperse PW anions; on the other hand, these conditions could decrease the diffusion limitations of the reactants and products and, thus, enhance the catalytic activity of hydroisomerization.

**Conclusions**

Pt-PW/USY\( \text{m(} n \text{)} \) catalysts show much higher catalytic activity than their PW-free counterparts, which might be due to the remarkable improvement of the amount of acid upon introducing PW into the catalysts. More significantly, the hydrothermal treatment conditions for the USY support can influence the catalytic activity substantially by altering the catalyst pore structure. We found that hydrothermal treatment at 650°C for 5 h is the optimum treatment condition; it leads to the high conversion of \( n \)-heptane (30.1%) with a very high selectivity for isomerization (98.2%).

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