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Hydroisomerization of *n*-Heptane Over Cr Promoted Pt-bearing $H_3PW_{12}O_{40}$ Catalysts Supported on Dealuminated USY Zeolite

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Abstract The Pt-bearing $H_3PW_{12}O_{40}$ (PW) catalysts, promoted by Cr or La, supported on dealuminated USY zeolite were prepared and their catalytic activities were evaluated in the hydroisomerization of *n*-heptane with an atmospheric fixed-bed reactor. The catalysts were characterized by XRD, BET, IR and H_2-chemisorption. The results showed that the dealuminated USY support retained the Y zeolite structure and the PW well kept its Keggin structure in the supported PW catalysts and the doping of Cr or La into the catalysts enhanced the dispersion of Pt on the catalyst surface. The Pt-bearing PW catalysts doped with Cr or La, especially Cr, exhibited much higher catalytic activity and selectivity than the catalysts without dopants. Both the conversion and selectivity were discussed in relation with physicochemical properties of catalysts.

Keywords 12-Tungstophoric acid · Bimetal catalyst · USY · Hydroisomerization of *n*-heptane

1 Introduction

Compared to other technologies such as blending with oxygenates and aromatics, light isoparaffins are increasingly important octane number enhancers in gasoline pool due to the more and more environmental legislations have been enacted regarding the quality of the advanced liquid fuel quality [1]. Hydroisomerization of C_5/C_6 is a commercial approach to achieve light isoparaffins, where chlorinated Pt/Al_2O_3 or Pt/mordenite has been traditionally used as catalyst [2]. Nowadays, hydroisomerization of paraffins with the chain-length longer than C_6 is highly desirable because the new standard of gasline demands to reduce the content of aromatics and olefins [1–4]. So it is of great importance to use catalytic isomerization of *n*-heptane, with a very low research octane number (RON = 0), for the production of more valuable products such as mono-branched isomers (RON = 40–65) or multi-branched isomers (RON = 80–112) [5]. However, the well-known Pt/mordenite catalyst would crack the *n*-heptane and the catalysts are easy to deactivate [3]. Therefore, many efforts have been devoted to seeking effective catalysts which can promote the selectivity of the branched paraffins in the hydroisomerization of paraffins with the chain-length longer than C_6 [2, 4]. A number of reports has described the skeletal isomerization of *n*-heptane in the presence of hydrogen over bifunctional catalysts, such as Pt–Hβ zeolite [6], Pt–Y zeolite [7], Pt or Pd promoted heteropolyacids [8, 9], WO_3/ZrO_2 catalysts [10] and SO_4^{2-}/ZrO_2 [11, 12].

Heteropolyacids (HPAs) of Keggin type possesses a strong Brönsted acidity and catalyze a wide variety of acid-catalyzed reactions [13, 14]. The major disadvantages of HPAs as catalyst lie in their low surface area (<10 m^2/g) as heterogeneous catalysts, and high solubility in a polar reaction system [15]. An immobilization of HPAs on a number of porous supports with high surface areas has therefore been extensively studied [16–19].

We have recently prepared 12-tungstophoric acid (PW) catalysts on dealuminated Y zeolite and observed that the

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secondary mesopores of Y zeolite promote the dispersion of PW on the support [8, 9, 20, 21]. Moreover, the promotion effect of PW on the hydroisomerization of *n*-heptane has been observed [8, 9]. On the other hand, bimetal catalysts are more catalytically active, stable and selective for isomerization than the catalyst containing only Pt in the isomerization of alkanes [22]. Some bimetal catalysts, such as SnPt/Al_2O_3, InPt/Al_2O_3, AlPt/HY, ZnPt/HY and NiPt/HBEA [22–24], used in the isomerization of alkane have been reported, but HPAs supported bimetal catalysts have not been reported yet. The present study initiates the investigation on Pt-bearing PW catalysts doped with Cr or La with dealuminated USY (ultra-stable Y) zeolite as the support for hydroisomerization of *n*-heptane, observing a very high conversion of *n*-heptane with high selectivity for isomerization products.

2 Experimental

2.1 Catalyst Preparation

Dealuminated USY (DUSY) was prepared by the hydrothermal treatment of USY (Zhoucun Catalyst Factory, Si/Al = 6) with the calcinations of the sample in a confined 100% steam atmosphere at 650 °C for 5 h, followed by the acid treatment in 0.5 M HCl aqueous solution at 90 °C for 2 h. And then it was washed with hot water, dried at 110 °C for 10 h and calcined at 550 °C for 5 h. The obtained sample was again processed by a second acid treatment as mentioned above.

Supported PW ($H_3PW_{12}O_{40} \cdot H_2O$, Shanghai Chem. Reagent Co., AR) samples, PW/SP, where SP stands for the support, namely, DUSY or USY, were prepared by the impregnation performed at room temperature with excess solution by contacting the corresponding support with the PW aqueous solution under constant stirring overnight, followed by evaporation at 70 °C and drying at 110 °C and calcined at 300 °C for 3 h. Subsequently, the PW/SP catalysts were immersed in the 0.017 mol L^{-1} solution of chloroplatinic acid and then dried at 110 °C, and calcined at 300 °C for 3 h. The resulting catalysts were designated as Pt-PW/SP. The bimetal catalysts were prepared by the same method. The PW/DUSY catalysts were immersed in a mixed solution of the nitrate salts of the second metal and chloroplatinic acid. The resulting catalysts are designated as nMPt-mPW/SP, where n stands for the molar ratio of promoter to Pt and M stands for the promoter as Cr or La. The PW loading was 10% and the Pt loading was 0.4% in the catalysts by weight as was not specially pointed out. The Pt/DUSY catalyst was prepared by impregnation DUSY with the solution of chloroplatinic acid. The Cr-PW/DUSY was prepared by impregnation PW/DUSY with the solution of chromium nitrate.

2.2 Catalytic Test

Hydroisomerization of *n*-heptane was carried out in an atmospheric fixed-bed flow reactor. 0.565 g of the granular catalyst (40–60 mesh) was charged in the middle stage of the stainless steel reactor. The reaction started after the pretreatment of catalyst in H_2 flow at 300 °C for 3 h. Reaction conditions were as follows: 230–310 °C of reaction temperature, 2.7 h^{-1} of weight hourly space velocity (WHSV), and 7.8 of molar ratio of H_2 to *n*-heptane. The products were qualitatively verified by GC-MS (Thermo-Finnigan). The product mixture was analyzed online by the gas chromatograph (SHIMADZU GC-2014) equipped with a SE-30 capillary column (50 m × 0.25 mm × 0.3 μm) by FID. Analysis conditions were as follows: 60 °C of column oven temperature, 150 °C of injector temperature, and 250 °C of detector temperature.

2.3 Characterization of Catalyst

The powder X-ray diffraction (XRD) patterns for catalysts were collected on a Bruker D8 ADVANCE X-ray powder diffractmeter using Cu Kα radiation at 40 kV and 30 mA, the scanning range was 3–50° with a scan rate of 2°/min. FTIR spectra of powdered samples pressed with dried KBr into discs were recorded in the range of wave numbers 1,500–800 cm^{-1} using a Thermo Nicolet NEXUS spectrometer. BET surface areas were measured on a BELSORPII equipment using nitrogen as adsorbate. The samples were pretreated under vacuum at 250 °C for 2 h before measurements. The dispersion of Pt was measured by hydrogen chemisorptions at the home-made equipment. The catalysts were pretreated in H_2 flow under 400 °C for 2 h, and then adsorbed H_2 to saturation at 100 °C. The H_2-uptake and Pt dispersion were calculated by the chemisorption of H_2.

3 Results and Discussion

3.1 Results of Characterization

3.1.1 The XRD of the Samples

Figure 1 gives the XRD patterns of USY, DUSY, pure PW and nMPt-PW/DUSY catalysts. The XRD curve of DUSY is very similar to that of USY, indicating the high comparative crystallinity of DUSY in spite of the combined treatment of steaming and HCl acid leaching. The XRD

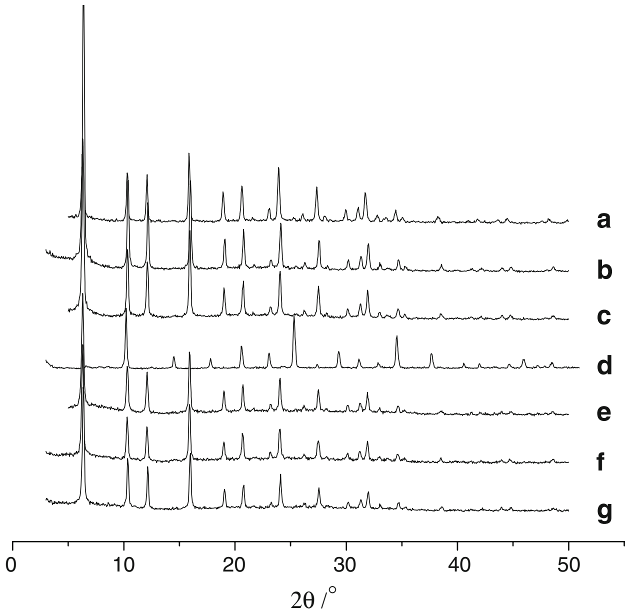

Fig. 1 XRD patterns of different catalysts. (**a**) USY, (**b**) DUSY, (**c**) Pt/DUSY, (**d**) PW, (**e**) Pt-PW/DUSY, (**f**) 5CrPt-PW/DUSY, (**g**) 5LaPt-PW/DUSY

curve does not change when noble metal Pt is impregnated onto DUSY. When PW and metals are impregnated onto DUSY, no diffraction peaks assigned to the crystal of the metal oxide and PW occur for all the bimetal-doped PW supported on DUSY zeolite catalysts. It could be deduced that the crystal size of the supported noble metal, doped metal oxide or PW is not large enough to be detected by XRD. On the other hand, peaks assigned to Y zeolite are still observed, but the intensity decreases. This might be caused by the dealumination of the DUSY when PW was introduced onto the support and the decrease of the mass fraction of the support [25].

Figure 2 gives the XRD patterns of the nCrPt-PW/DUSY catalysts with different Cr loadings. It can be seen that all the XRD patterns of the catalysts are similar to the USY support and no diffraction peaks assigned to the crystal of the metal oxide occurs even when the molar ratio of Cr to Pt is 15:1 (15CrPt-PW/DUSY). It could be thus deduced that the metal oxides are highly dispersed on the DUSY support.

The power XRD patterns of catalysts with various PW loadings are illustrated in Fig. 3. No characteristic peaks of bulk crystal PW appear in nCrPt-PW/DUSY materials with the PW loading up to 40%, indicating the high dispersion of PW on the surface of DUSY. On the other hand, the intensities of characteristic peaks for Y zeolite in the samples decrease with increasing of PW loadings. This implies that the octahedral structure of DUSY support is somewhat distorted upon the supporting of PW on its

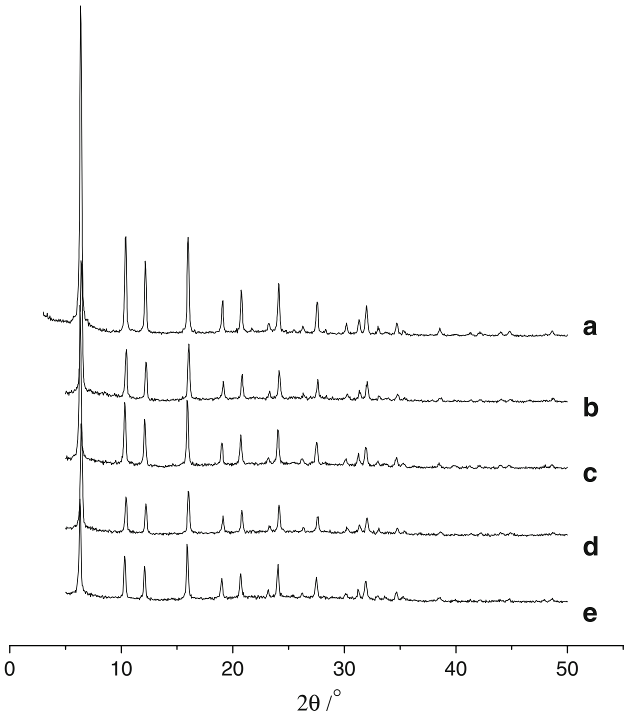

Fig. 2 XRD patterns of catalysts with different Cr loading. (**a**) DUSY, (**b**) CrPt-PW/DUSY, (**c**) 5CrPt-PW/DUSY, (**d**) 10CrPt-PW/DUSY, (**e**) 15CrPt-PW/DUSY

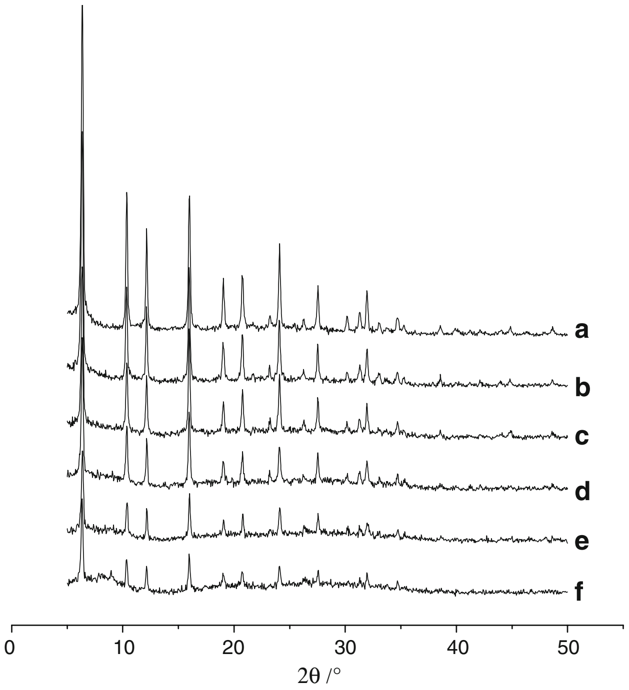

Fig. 3 XRD patterns of catalysts with different PW loading. (**a**) DUSY, (**b**) Pt-10%PW/DUSY, (**c**) 5CrPt-10%PW/DUSY, (**d**) 5CrPt-20%PW/DUSY, (**e**) 5CrPt-30%PW/DUSY, (**f**) 5CrPt-40%PW/DUSY

Table 1 BET surface area, H_2-uptake and Pt dispersion of various catalysts

Catalyst	Surface area (m^2 g^{-1})	H_2-uptake (mmo g^{-1})	Pt dispersion (%)
USY	687	–	–
DUSY	713	–	–
PW	6	–	–
Pt/DUSY	692	0.62	61
Pt-PW/DUSY	651	0.60	59
5LaPt/PW/DUSY	625	0.74	72
1CrPt-PW/DUSY	636	0.61	60
5CrPt-PWDUSY	617	0.77	76
10CrPt-PW/DUSY	604	0.87	85
15CrPt-PW/DUSY	565	1.07	104

surface, but it still keeps its structure even when the PW loading is as high as 40%.

3.1.2 BET Surface Areas, H_2-uptakes and Pt Dispersions of the Samples

Table 1 lists the BET surface area of various catalysts. It can be seen that pure PW exhibits a very low surface area of 6 m^2/g and the DUSY exhibits a higher surface area than USY. All of the supported PW catalysts possess rather high surface areas because the secondary structured mesopores are created during the dealumination of USY, which is beneficial for the high dispersion of PW on the support [26]. The surface areas of the supported catalysts are lower than the support and decrease with the increasing of the metal loading. The H_2-uptake over various catalysts and the Pt dispersions are also displayed in Table 1. The dispersion of Pt for Pt/DUSY catalyst is 61%, and it decreases a little with the addition of PW due to the decrease of surface area. The dispersion can be promoted by the addition of a second metal Cr, moreover, it increases with the increasing of Cr loadings. When the molar ratio of Cr to Pt reaches 15:1, the dispersion of Pt exceeds 100. This maybe because of the H_2-spillover, however, some investigation showed that the spillover H_2 is also beneficial for the isomerization of paraffin [27].

3.1.3 IR Spectra of the Samples

FTIR spectra of the various typical catalysts are presented in Fig. 4. Pure PW shows the typical IR bands at ca. 810 and 890 (W–O–W) cm^{-1}, 981 (terminal W = O), 1,080 cm^{-1} (P–O in the central tetrahedron), asymmetric vibrations associated with the typical Keggin anions [19].

For the Pt-PW/DUSY and 5CrPt-PW/DUSY samples, the four vibration bands can be clearly observed, whereas the intensity of the peaks decrease and the vibration band of W = O shifts from 981 cm^{-1} to 960 cm^{-1} because of the interaction of PW and DUSY support. This unambiguously demonstrates that the primary structure of PW Keggin anions is preserved, and the results are consistent to the report [28].

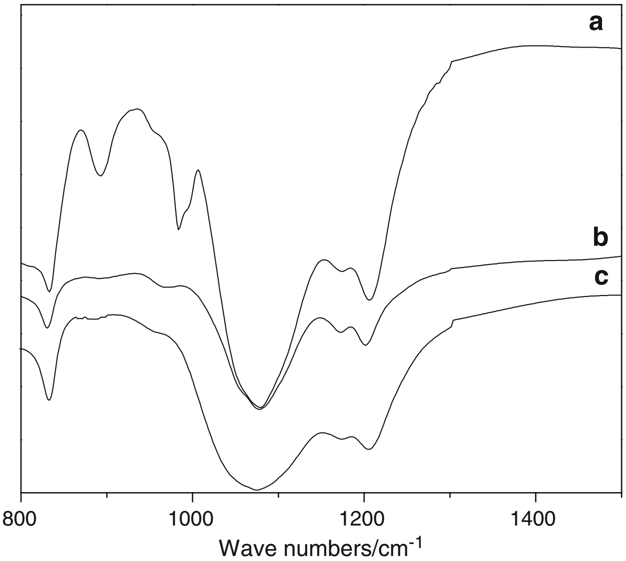

Fig. 4 IR spectra of typical catalysts. (**a**) PW, (**b**) Pt-PW/DUSY, (**c**) 5CrPt-PW/DUSY

3.2 The Effect of Catalyst Component on the Catalytic Activity

3.2.1 Catalytic Activities of Various Catalysts at 250 °C

Table 2 displays the stabilized conversion of *n*-heptane, mono- and multi-branched products yields and selectivity to branched products at 250 °C and 120 min on stream over various catalysts. The multi-branched products are preferred to get more because of their higher octane numbers. From Table 2, it can be seen that on the Cr-PW/DUSY catalyst, a very low catalytic activity is obtained and the main products are cyclizations. The Pt/USY catalyst have a conversion of 41.5%, but mainly is cracking product. The isomerization selectivity is improved over the Pt/DUSY catalyst but the conversion of the *n*-heptane drops to 22.5%, and only the mono-branched products are improved obviously. The conversion of *n*-heptane can be improved to 29.9% with the isomerization selectivity of 87.0% over the Pt-PW/DUSY catalyst because of the addition of PW but the promotion effect is not very obvious. If the Pt-PW/DUSY catalyst is doped with a second metal (Cr or La) with a 5:1 molar ratio of M/Pt, both the isomerization selectivity and *n*-heptane conversion can be improved, especially for 5CrPt-PW/DUSY. Over the

Table 2 Catalytic activities of various catalysts on the hydroisomerization of *n*-heptane

Catalyst	Conversion (%)	Mono-iso[a] yield (%)	Multi-iso[b] yield (%)	Selectivity (%)		
				Iso	Cra	Cyc
Pt/USY	41.5	5.6	3.6	22.2	77.8	0
Pt/DUSY	22.5	15.8	3.9	87.5	9.7	2.9
Pt-PW/USY	34.9	12.4	4.0	46.2	51.8	2.1
Pt-PW/DUSY	29.9	20.7	5.6	87.7	9.2	3.0
Cr-PW/DUSY	3.0	1.4	0.3	56.7	20.1	22.3
5CrPt-PW/DUSY	50.3	37.2	9.3	92.4	6.1	1.5
5LaPt-PW/DUSY	43.5	32.3	7.9	92.3	6.0	1.5

Reaction temperature: 250 °C, H_2/n-C_7: 7.8 mol mol^{-1}, WHSV: 2.7 h^{-1}, time on stream: 120 min

[a] Mono-branched products include 2-methylhexane (42), 3-methylhexane (52) and 3-ethylpentane (65)

[b] Multi-branched products include 2, 2-dimethylpentane (98), 2,3-dimethylpentane (91), 2,4-dimethylpentane (83), 3,3-dimethylpentane (81) and 2,2,3-trimethylbutane (112). The number in parenthesis is the research octane number

5CrPt-PW/DUSY catalyst, the conversion of *n*-heptane can be improved to 50.3% with a high isomerization selectivity of 92.4%, and moreover the yield of multi-branched product improved obviously with a decrease of the cyclization selectivity. Thus the addition of Cr or La dopant can remarkably improve the selectivity of the isomerization products while with much high activity.

3.2.2 *Catalytic Activities of Catalysts with Different Cr Loading*

Table 3 gives the catalytic activities over nCrPt-PW/DUSY catalysts with different Cr loadings. It can be seen that the yields of mono- and multi-products, and the conversion of *n*-heptane increase with the increase of Cr loading and find their highest values when the molar ratio of Cr to Pt is 5:1. The isomerization selectivity increases with increase of Cr and the change is not obvious when the molar ratio of Cr to Pt is larger than 5:1. The isomerization selectivities of nCrPt-PW/DUSY catalysts are higher than the catalyst without promoter, especially over the 5CrPt-PW/DUSY catalyst which has much higher multi-branched product yield of Pt-PW/DUSY catalyst with only half of cracking selectivity. Thus the addition of Cr dopant can remarkably improve the catalytic activity of isomerization of *n*-heptane, especially the yield of multi-branched products with high octane numbers and suppress cracking and cyclization. The optimum value of the molar ratio of Cr to Pt is 5:1.

3.2.3 *Catalytic Activities of Catalysts with Different PW Loading*

Stabilized conversion and selectivity in *n*-heptane hydroisomerization over catalysts with different PW loading are compared in Table 4. The catalytic conversion of *n*-heptane of 25.5% is observed over the 5CrPt/DUSY catalyst with a comparatively high selectivity for isomerization products of 90.5%. Comparing the isomerization activity of Pt/DUSY as shown in Table 2, it can be seen that the promotion effect of Cr additive on the DUSY supporting Pt catalyst is not much obvious owing to the decrease of acid sites during the dealumination of USY. It is noteworthy that the conversion can be remarkably improved by introducing suitable amount of PW (not over 10%) into the catalyst. The conversion reaches the maximum value of 50.3% when PW loading is 10%, with an isomerization selectivity as high as 92.4%. The further increasing of the PW loading results in a decease of conversion and selectivity for isomerization. It is mostly possible that the substantial increase of conversion of *n*-heptane on supported PW catalysts could associate with the improvement of catalyst acidity originated from the

Table 3 Influence of Cr loadings in nMPt-PW/USY catalysts on the hydroisomerization of *n*-heptane

Catalyst	Conversion (%)	Mono-iso yield (%)	Multi-iso yield (%)	Selectivity (%)		
				Iso	Cra	Cyc
Pt-PW/DUSY	29.9	20.7	5.6	87.7	9.2	3.0
1CrPt-PW/DUSY	31.0	21.4	5.2	85.7	12.3	2.0
5CrPt/PW/DUSY	50.3	37.2	9.3	92.4	6.1	1.5
10CrPt-PW/DUSY	47.5	35.8	8.8	93.8	4.6	1.6
15CrPt-PW/DUSY	24.2	17.6	4.3	90.4	6.7	2.9

Reaction temperature: 250 °C, H_2/n-C_7: 7.8 mol mol^{-1}, WHSV: 2.7 h^{-1}, time on stream: 120 min

Table 4 Influence of PW loadings in nMPt-PW/USY catalysts on the hydroisomerization of *n*-heptane

Catalyst	Conversion (%)	Mono-iso yield (%)	Multi-iso yield (%)	Selectivity (%)		
				Iso	Cra	Cyc
5CrPt/DUSY	25.5	18.9	4.1	90.5	7.7	1.8
5CrPt-5%PW/DUSY	39.8	14.2	1.0	94.2	0	5.8
5CrPt-10%PW/DUSY	50.3	37.2	9.3	92.4	6.1	1.5
5CrPt-20%PW/DUSY	24.2	16.7	4.1	85.9	11.3	2.7
5CrPt-30%PW/DUSY	23.3	14.3	3.6	76.7	20.5	2.9
5CrPt-40%PW/DUSY	27.2	14.0	3.7	65.2	32.3	2.4

Reaction temperature: 250 °C, $H_2/n\text{-}C_7$: 7.8 mol mol^{-1}, WHSV: 2.7 h^{-1}, time on stream: 120 min

strong acidity of PW. However, this strong acidity of PW might also be responsible for the increase of cracking products as compared with the PW-free catalyst.

3.3 The Effect of Reaction Conditions on the Catalytic Activity

3.3.1 Effect of Reaction Temperatures on Catalytic Activity

Table 5 presents the effect of the reaction temperature on the catalytic activities of two supported catalysts. For both the catalysts, the conversion of *n*-heptane increases drastically with the increase of reaction temperature, which leads to the decrease of selectivity of isomerization products and cyclization, while the selectivity for cracking products increase. At the same reaction temperature, the selectivity of isomerization over 5CrPt-PW/DUSY catalyst is higher than that over Pt-PW/DUSY catalyst. From Table 5, it is possible to compare the selectivity for isomerization products at a same conversion level of around 50.0%. Over Pt-PW/DUSY catalyst at the conversion of 54.2%, a low selectivity of 63.2% for isomerization products is obtained and a high reaction temperature of 290 °C is needed, while over the 5CrPt-PW/DUSY catalyst, at conversions of 50.3%, the high selective for isomerization products of 92.4% is achieved, and comparatively low reaction temperatures of 250 °C is employed. Thus it is obvious that the catalysts promoted by Cr are more active and selective than the catalyst without the Cr promoter. Table 5 also shows that the optimum reaction temperature over 5CrPt-PW/DUSY is 250 °C.

3.3.2 Effect of WHSV on Catalytic Activity

The effect of WHSV on the catalytic activities is presented in Fig. 5. It can be seen that the conversion of *n*-heptane and cracking selectivity decrease with the increase of WHSV, whereas the isomerization selectivity increase slightly. At low WHSV, the decrease of isomerization selectivity might be caused by the long stay time leading to cracking. The optimum WHSV should be 0.7 h^{-1}, at this WHSV value, the conversion of *n*-heptane, selectivies for isomerization, yield of mono- and multi-products can reach 75.3%, 91.3%, 51.9% and 16.7%, respectively.

Over zeolite supported noble metal bifunctional catalysts, the hydroisomerization of *n*-heptane can be explained by the classical bifunctional mechanism with the metal sites being the active center for dehydrogenation and hydrogenation and the acid sites being the active center for isomerization (cracking, condensation or cyclization) via carbenium ions as reaction intermediates [29, 30]. It is clear that both the metal and acid sites could control the catalytic activity to a great extent. Over the USY supports

Table 5 Influence of reaction temperature on the hydroisomerization of *n*-heptane over various catalysts

Catalyst	T (°C)	Conversion (%)	Mono-iso yield (%)	Multi-iso yield (%)	Selectivity (%)		
					Iso	Cra	Cyc
Pt-PW/DUSY	230	16.6	12.0	2.7	88.5	6.6	5.0
	250	29.9	20.7	5.6	87.7	9.2	3.0
	270	42.8	24.3	7.2	73.4	23.6	3.0
	290	54.2	26.6	7.9	63.2	35.9	0.4
	310	65.4	27.5	8.3	54.7	45.1	0.2
5CrPt-PW/DUSY	230	24.2	19.8	2.9	94.3	2.0	3.8
	250	50.3	37.2	9.3	92.4	6.1	1.5
	270	69.1	43.7	13.9	83.3	16.1	0.6
	290	78.1	42.2	14.9	73.0	26.7	0.3
	310	86.6	33.6	13.5	54.5	45.6	0

$H_2/n\text{-}C_7$: 7.8 mol mol^{-1}, WHSV: 2.7 h^{-1}, time on stream: 120 min

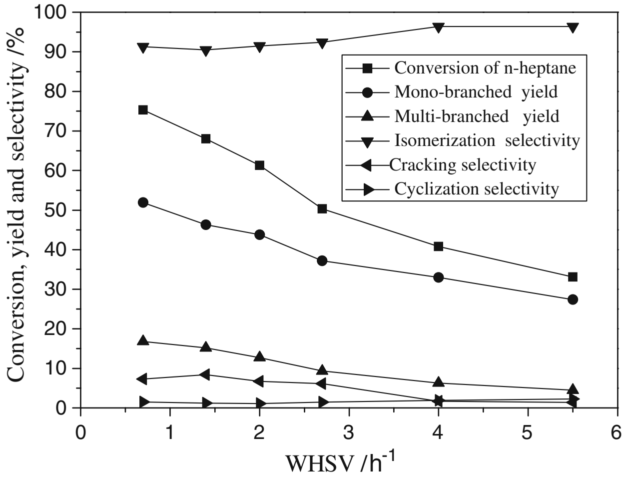

Fig. 5 Hydroisomerization of *n*-heptane over 5CrPt-PW/DUSY at different WHSV. Reaction temperature: 250 °C, H2/n-C7: 7.8 mol mol^{-1}, time on stream: 120 min

noble metal Pt (Pt/USY) catalyst, the products are mainly cracking because of the lots of acid sites (both Brönsted and Lewis acid site) on the USY (see Table 2). The acid sites of DUSY will decrease during the dealumination of USY [20], and as a result, the conversion of *n*-heptane decrease and the selectivity of isomerization increase. However, with addition of both PW and bimetal as 5CrPt-PW/DUSY catalyst, the catalytic activity is improved obviously under a comparative low reaction temperature as shown in Tables 2 and 5. In our previous study for the hydroisomerization of *n*-heptane over the USY supported bimetal catalysts, we have found that both the conversion of *n*-heptane and the isomerization selectivity will be improved by the increase of Brönsted acid sites [31]. It is well known that PW posses a strong Brönsted acidity, the DUSY has a plenty of secondary mesopores, which is favorable to the dispersion of PW over the support with the PW structure being maintained as we have investigated before [20, 21]. It is supposed that the improvement of the catalytic activity over the hydroisomerization of *n*-heptane may relate to the strong Brönsted acidity of PW. On the other hand, compared to the catalysts containing only Pt, bimetallic catalysts are more stable, more selective, and showed higher activity in the conversion of hydrocarbons. A change of bond strength between chemisorbed hydrocarbons and Pt surface atoms due to electron transfer from the promoter to Pt (electronic effect) and a dilution of the Pt surface atoms to decrease the ensemble size by the second metal (geometric effect) have been proposed as reasons for the beneficial effect of the promoter [22]. Table 1 shows that the dispersion of Pt can be obviously improved by addition of dopants, and then improves the catalytic activity. This finding has also been confirmed by others [22–24]. A few researchers hypothesized a new "desorption-transfer promoting site" added to the bifunctional catalytic site by the promoter [23], whose main role was to quicken desorption of the olefinic species from the acid site and transfer them to the Pt site. In this way, the residence time of the branched carbocations on the acid site is much shorter, and then avoids further cracking. Therefore, it is mostly possible for the substantial increase of selectivity for isomerization. Initially, the increase of the Pt and promoter loadings can give more chance for the *n*-heptane adsorbed on the metal sites and then easy to dehydrogenate, at the same time, give more opportunities for the branched alkenes to hydrogenate on the metal sites, which can promote the conversion of *n*-heptane and the selectivity of isomeriazation. However, when loading of the metal reach to a certain value, the speed of dehydrogenate on the metal sites is faster than the speed of isomerization or cracking on the acid sites, and then the promotion effect is not obvious with the substantial increase of metal loadings, this phenomenon can be seen from Table 3. It can be deduced that the molar ratio of dopants to Pt have optimal values to give a high isomerization activity.

4 Conclusions

The Pt-PW/DUSY catalysts promoted by Cr or La, especially by Cr, are more catalytically active, stable and selective for isomerization than the catalyst containing only Pt. The optimum value of the molar ratio of Cr to Pt is 5:1 with the Pt loading of 0.4%. Over the 5CrPt-PW/DUSY catalyst at a reaction temperature of 250 °C, WHSV of 0.7 h^{-1} and molar ratio of H_2 to *n*-heptane of 7.8, the conversion of *n*-heptane is 75.3% with the selectivity for isomerization products as high as 91.3%, the mono-branched product yield of 51.9% and the multi-branched product yield of 16.7%. The high activity and selectivity of the 5CrPt-PW/DUSY catalyst is associated with the improvement of PW, the increased Pt dispersion and the creation of the "desorption-transfer promoting site" due to the introduction of Cr into the catalyst.

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