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Cs salts of 12-tungstophosphoric acid supported on dealuminated USY as catalysts for hydroisomerization of *n*-heptane

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A series of Pt-bearing dealuminated USY supported Cs salts of 12-tungstophosphoric acid (PW) catalysts were prepared and their catalytic performances were measured in the hydroisomerization of *n*-heptane with an atmospheric fixed-bed flow reactor. USY was found to be a poor support for Cs salts of PW, leading to a lower catalytic activity in this reaction, but dealuminated USY supported Cs salts of PW catalysts showed very high catalytic conversion and selectivity. Among the various Cs salts of PW with different Cs/P ratios, $Cs_{2.0}PW$ was revealed to be the most effective active species. Over the dealuminated USY supported catalyst with the Pt loading of 0.4 wt.% and $Cs_{2.0}PW$ loading of 10 wt.%, the conversion of *n*-heptane was enhanced up to 76.2% with a high selectivity to isomerized products of 92.2%.

KEY WORDS: heteropoly acid; hydroisomerization of *n*-heptane; Cs salt of 12-tungstophosphoric acid; USY.

1. Introduction

In recent years, isomerization of linear alkanes is an increasingly environmentally benign method to enhance the octane number of gasoline due to the more and more stringent environmental legislations regarding the advanced liquid fuel quality [1]. Chlorinated Pt/Al_2O_3 and Pt/mordenite have been traditionally used as catalysts for the hydroisomerization of C_5/C_6 [2]. Indeed, hydroisomerization of middle alkanes, such as C_7-C_9 paraffins, is also highly desirable to improve the octane number of gasoline without enhancing the content of aromatics and olefins, and *n*-heptane is usually used as the model reactant in this study. However, the well known Pt/mordenite catalyst would crack the *n*-heptane [3]. Much effort has been devoted to seek an effective catalyst which can promote the selectivity of the branched products and minimize the cracking in the hydroisomerization of *n*-heptane. Up to now, a number of catalysts were reported in this field, such us Pt-Hβ zeolite [3], Pt-Y zeolite [4], Pt promoted heteropoly acids (HPAs) [5, 6], WO_3/ZrO_2 [7], mesoporous MoOx and Ni–MoOx catalysts [8].

On the other hand, HPAs have proved to exhibit high catalytic activity in various acid catalyzed reactions [9]. 12-Tungstophosphoric acid shows the strongest acidity among the Keggin structured HPAs [10–12]. However, their low surface area (<10 m^2/g) limit their practical utilization. In order to overcome this drawback, one method is to prepare acid salts containing cations, such as Cs^+, K^+ and $NH_4{}^+$, which can possibly enhance the surface area above 100 m^2/g, another one is to support HPAs on porous carriers, such as silica [13], silica–alumina [14], active carbon [15], MCM-41 [16], SBA-15 [17] and Y zeolite [18], and so on.

Liu *et al.* [19] reported that the mixture of Pt/Al_2O_3 and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ showed a high selectivity to isomerized products in the hydroisomerization of *n*-heptane. Miyaji *et al.* [20] found that Pt-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ supported on silica can enhance the selectivity to *iso*-heptanes with suppression of the cracking. Very recently, we revealed [21, 22] that the supported Cs salts of PW catalysts exhibited a high conversion and selectivity in the synthesis of fructone. In this work, we investigate the catalytic behaviors of Cs salts of PW catalysts supported on dealuminated USY in the hydroisomerization of *n*-heptane, and observe that the catalysts are highly efficient for this reaction to achieve the high conversion combined with the high selectivity to isomerized products.

2. Experimental

Dealuminated USY (DUSY) was prepared by the acid leaching of USY (Si/Al = 6.0, Zhoucun Catalyst Factory) with a 0.6 M aqueous HCl solution at 90 °C for 1 h, followed by washing with hot water, drying at 110 °C for 12 h, calcination at 550 °C for 3 h and hydrothermally treated at 650 °C for 5 h. The obtained sample was again treated by a second acid leaching as mentioned above.

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Supported Cs salts of PW, $Cs_XH_{3-X}PW/SP$ (X = 1.5, 2.0 or 2.5), where SP stands for the support, namely DUSY or USY, were obtained by sequential impregnation and in situ reaction on the support according with the previous report [23]. In detail, Cs_2CO_3 was supported onto SP by the incipient wetness impregnation, followed with drying at 110 °C for 12 h and calcination at 550 °C for 4 h. After this, PW was impregnated with excess of solution by contacting the corresponding support with the PW solution under constant stirring overnight at room temperature, followed by evaporation, drying and calcination. The percentage of Cs salts of PW in catalysts was 5–20% by weight. Pt-$Cs_XH_{3-X}PW/SP$ catalysts were obtained by the incipient wetness impregnation of the $Cs_XH_{3-X}PW/SP$ with the aqueous solution of chloroplatinic acid, also followed by evaporation, drying and calcination. The $Cs_XH_{3-X}PW/SP$ and Pt-$Cs_XH_{3-X}PW/SP$ were abbreviated to be Cs_XPW and Pt-Cs_XPW/SP, respectively. The percentage of Pt in catalysts was 0.4% by weight.

Hydroisomerization of *n*-heptane was carried out in an atmospheric fixed-bed flow reactor. 0.5 g of catalyst in the form of granule (40–60 mesh) was charged in the middle stage of the stainless steel tubular reactor. The catalyst was pretreated in situ in H_2 flow at 300 °C for 3 h before reaction. Reaction conditions were as follows: 230–310 °C of reaction temperature, 2.7 h^{-1} of weight hourly space velocity, and 7.9 of the molar ratio of H_2 to *n*-heptane. The product mixture was analyzed online by the gas chromatograph (SHIMADZU GC-2014) equipped with a 50 m SE30 capillary column. The products were qualitatively verified by GC-MS (ThermoFinnigan).

The powder X-ray diffraction (XRD) patterns for catalysts were collected on a Bruker D8 ADVANCE X-ray powder diffractometer using Cu Kα radiation at 40 kV and 30 mA. BET surface areas were achieved by N_2 adsorption on the Coulter Ommisorp 100CX equipment. Temperature programmed desorption of ammonia (NH_3-TPD) was conducted in a home-made flow fixed-bed reactor. Hundred mg of sample was placed into a quartz tube and heated from room temperature to 500 °C at a heating rate of 10 °C/min in helium, and held at this temperature for 2 h. After the sample was cooled to 120 °C, ammonia was introduced into the reactor until the saturated adsorption was obtained. Subsequently, the sample was heated again from 120 to 550 °C at a heating rate of 10 °C/min.

3. Results and discussion

XRD patterns of various catalysts are illustrated in figure 1. It shows that the XRD curve of DUSY is similar to that of USY, indicating the high crystallinity of DUSY even if it was hydrothermal treated combined with acid leaching. When the Cs salt of PW is impregnated onto USY or DUSY, peaks assigned to Y zeolite are still observed, but the intensity decreases. It is clear that the crystal structure of Y zeolite is retained for catalyst supports. Figure 2 gives XRD patterns of the four catalysts with different $Cs_{2.0}PW$ loadings. The intensities of peaks assigned to the Y zeolite decreases with the increase of $Cs_{2.0}PW$ loading. When $Cs_{2.0}PW$ loading is 20%, no peaks assigned to Y zeolite are detected. This suggests the collapse of the support structure. For all XRD patterns of Pt-bearing catalysts shown in figures 1 and 2 no diffraction peak assigned to crystal Pt appears, which implies the high dispersion of Pt on the surface of catalyst. However, the diffraction peak assigned to the Cs salt of PW at around 26° is observed in Pt-Cs_XPW/DUSY, which indicates that a part of Cs salts of PW inevitably

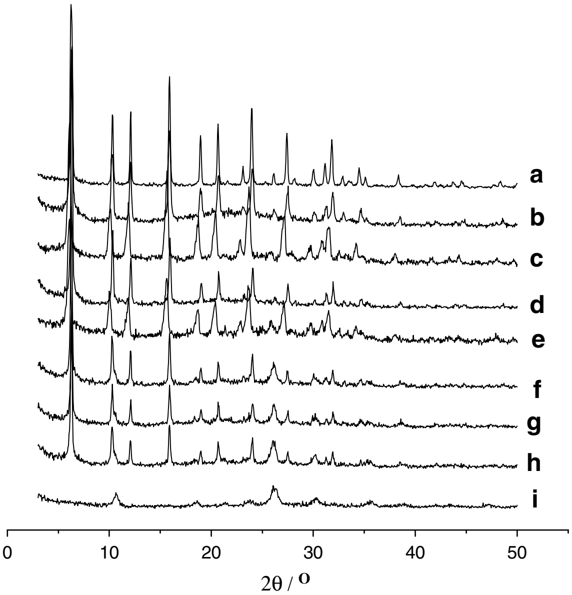

Figure 1. XRD patterns of various catalysts, (a) USY, (b) DUSY, (c) Pt/USY, (d) Pt/DUSY, (e) Pt-10%$Cs_{2.0}PW$/USY, (f) Pt-10% $Cs_{2.0}PW$/DUSY, (g) Pt-10%$Cs_{1.5}PW$/DUSY, (h) Pt-10%$Cs_{2.5}PW$/DUSY, (i) $Cs_{2.0}PW$.

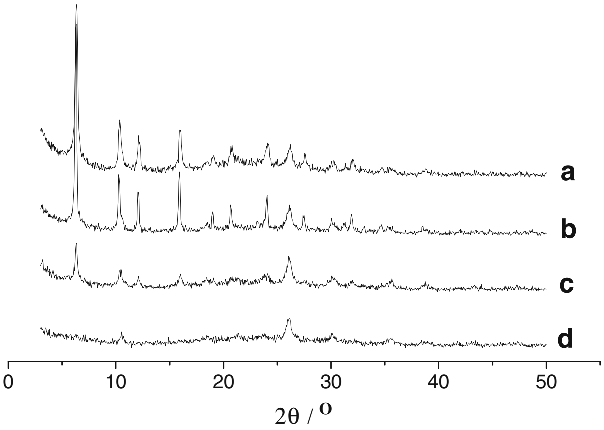

Figure 2. XRD patterns of catalysts with different $Cs_{2.0}PW$ loadings, (a) Pt-10%$Cs_{2.0}PW$/DUSY, (b) Pt-5%$Cs_{2.0}PW$/DUSY, (c) Pt-15% $Cs_{2.0}PW$/DUSY, (d) Pt-10%$Cs_{2.0}PW$/DUSY.

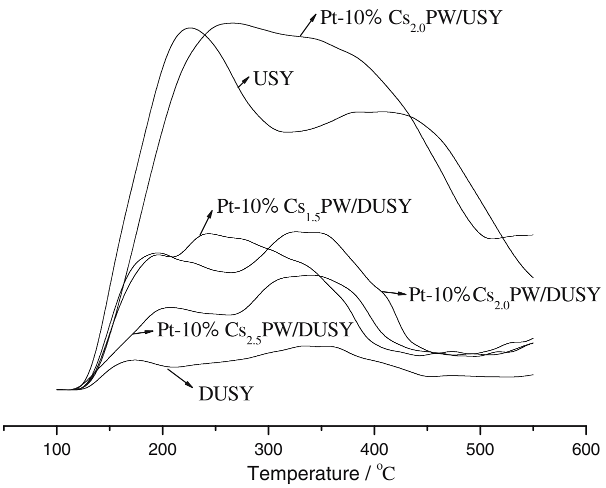

Figure 3. NH_3-TPD profiles of various catalysts.

deposit on the surface of DUSY support in form of crystal particle, the size of which is large enough to be detected by XRD.

NH_3-TPD curves are shown in figure 3. For supports, USY possesses much larger acid amounts than DUSY. When $Cs_{2.0}$PW is impregnated onto USY, no apparent increase of acid amount is observed. However, by introducing Cs_XPW species onto DUSY, it can be obviously seen that the acid amount of supported catalysts is much higher than that of DUSY alone, but is still significantly lower than that of USY. For Pt-Cs_XPW/DUSY ($X = 1.5$, 2.0 or 2.5) catalysts, the acid amounts of Pt-10%$Cs_{1.5}$PW/DUSY and Pt-10%$Cs_{2.0}$PW/DUSY are higher than that of Pt-10%$Cs_{2.5}$PW/DUSY.

Table 1 shows BET surface areas of catalysts with different loadings of Cs_XPW supported on DUSY. USY possesses a high surface area of 687 m^2/g, and after dealumination, it decreases to 571 m^2/g for DUSY. By impregnating Pt and/or Cs salts of PW onto DUSY, the surface area further decreases. Pt/DUSY has a high BET surface area of 560 m^2/g, and the area decreases remarkably with the increase of $Cs_{2.0}$PW loading. For the same loading (10%) of Cs salts of PW, the BET surface area decreases with the increase of the substitute number of Cs^+, which are in good agreement with the previous report [24]. Generally speaking, the supported samples still possess rather high surface areas due to the dispersion effect of the porous carrier, except for the Pt-20%$Cs_{2.0}$PW/DUSY sample, which lost the porous structure of Y zeolite in its support.

Table 1
BET surface areas of various DUSY supported catalysts

Catalyst	$S_{BET}/m^2\ g^{-1}$
USY	687
DUSY	571
Pt/DUSY	560
Pt-10%$Cs_{1.5}$PW/DUSY	500
Pt-10%$Cs_{2.0}$PW/DUSY	478
Pt-10%$Cs_{2.5}$PW/DUSY	463
Pt-5%$Cs_{2.0}$PW/DUSY	483
Pt-15%$Cs_{2.0}$PW/DUSY	263
Pt-20%$Cs_{2.0}$PW/DUSY	162

Table 2 displays the stabilized conversion of *n*-heptane, yield and selectivity to isomerized products at a reaction temperature of 270 °C over various catalysts. For Pt/USY, a considerable conversion of *n*-heptane of 41.9% with a very low isomerization selectivity of 64.2% is observed, and moreover, the conversion drops to 35.7% with a low selectivity of 68.6% by introducing $Cs_{2.0}$PW into the catalyst. It thus suggests that Pt/USY alone is not a selective catalyst for the reaction and USY is not a suitable support for $Cs_{2.0}$PW. As for Pt/DUSY, only a very low conversion of 7.6% is observed. In contrast, when Cs salts of PW are introduced onto DUSY support, the conversion of *n*-heptane increases drastically, and Pt-10%$Cs_{2.0}$PW/DUSY shows a maximum conversion of 41.4% among the three DUSY supported Cs salts of PW catalysts with different Cs/P ratios. Furthermore, very similar conversions are observed over Pt/USY and Pt-10%$Cs_{2.0}$PW/DUSY (41.9% vs. 41.4%), but with significantly different isomerization selectivities (64.2% vs. 98.8%). This demonstrates that DUSY is a very effective support for Cs salts of PW, and $Cs_{2.0}$PW is a very active acidic species for the hydroisomerization of *n*-heptane.

The hydroisomerization of *n*-paraffins over metal/acid bifunctional catalysts can be explained by the classical bifunctional mechanism [25, 26] including the dehydrogenation and hydrogenation on the metal sites and isomerization (cracking, condensation or cyclization) via carbonium ions as reaction intermediates on the acid site. Therefore, the acidic properties of catalysts would influence the catalytic behavior in a large range.

It is known that USY is prepared from $NH_4{}^+Y$ by hydrothermal treatment, during which secondary structured mesopores are created by removing Al from zeolite framework, but the extra-framework Al species still retain in the secondary mesopores. The retained Al species may show basicity, and facilitate the partial decomposition of Cs salts of PW on USY [27]. Figure 3 also does not indicate a significant change in acid amount by supporting $Cs_{2.0}$PW onto USY. Thus it is understandable that no improvement of activity of Pt-$Cs_{2.0}$PW/USY can be observed in Table 2. In the dealumination of USY through hydrothermal treatment and twice acid leaching, not only more secondary mesopores are created but also the extra-framework Al species are removed from the zeolite crystal [28]. As a consequence, a much lower acid amount for the DUSY support is observed in figure 3. This may cause a much lower conversion of 7.6% over the Pt/DUSY catalyst in Table 2. It seems that the high acid density for USY and Pt-$Cs_{2.0}$PW/USY is favorable to cracking reactions, and the low acid amount facilitates isomerization products but with a very low activity.

Table 2
Catalytic activities of various catalysts in the hydroisomerization of *n*-heptane[a]

Catalyst	Conversion /%	Mono-branched product yield /%[b]	Multi-branched product yield /%[c]	Isomerization selectivity /%
Pt/USY	41.9	20.2	6.3	64.2
Pt-10%$Cs_{2.0}$PW/USY	35.7	18.7	5.8	68.6
Pt/DUSY	7.6	7.3	0.3	100
Pt-10%$Cs_{1.5}$PW/DUSY	27.2	22.2	3.9	95.8
Pt-10%$Cs_{2.0}$PW/DUSY	41.4	34.3	6.6	98.8
Pt-10%$Cs_{2.5}$PW/DUSY	12.8	11.7	1.1	100

[a] Reaction temperature: 270 °C; WHSV: 2.7 h^{-1}; H_2/*n*-heptane(mole): 7.9; catalyst amount: 0.5 g; reaction time on stream:120 min.

[b] Mono-branched products include 2-methylhexane, 3-methylhexane and 3-ethylpentane.

[c] Multi-branched products include 2,2-dimethylpentane, 2,3-dimethylpentane, 2,4-dimethylpentane, 3,3-dimethylpentane and 2,2,3-trimethylbutane.

Many researchers have revealed that Cs salts of PW possess very strong acidity, which could be ascribed to solid superacid [24, 29]. When Cs salts of PW are supported onto DUSY, they tend to interact with the hydroxyl groups in the surface of secondary pores and thus disperse on the surface of the mesopores [30], because of which the acid strength of supported catalysts is not as strong as that of pure heteropoly compounds [31]. Furthermore, the acid amounts of Pt-Cs_xPW/DUSY catalysts are improved substantially compared with DUSY due to the introducing of Cs salts. It is therefore suggested that the obviously increased activity over Pt-Cs_xPW/DUSY combined with the high selectivity to isomerization may associate closely with their medium acid amounts. For $Cs_{2.5}$PW/DUSY catalyst, its acid amount is comparatively lower than those of $Cs_{1.5}$PW/DUSY and $Cs_{2.0}$PW/DUSY, which leads to a lower conversion of 12.8% in Table 2. A maximum activity is observed over the DUSY supported $Cs_{2.0}$PW sample among Cs salts of PW with different Cs/P ratios. Travers *et al.* [32] found a similar result in the *n*-C_6 conversion over the $Cs_{2.0}$PW catalyst. This might arise from the medium acid amount and high BET surface area.

Table 3 lists the stabilized conversion of *n*-heptane, yield and selectivity to isomerized products at 270 °C over four catalysts with different $Cs_{2.0}$PW loadings. From Table 3, it can be seen that the conversion increases with the increase of the $Cs_{2.0}$PW loading up to 10%, then decreases with a further increase of the $Cs_{2.0}$PW loading. The optimum $Cs_{2.0}$PW loading is 10%, leading to the high conversion of *n*-heptane of 41.4% with the very high isomerization selectivity of 98.8%. Actually, the increase of $Cs_{2.0}$PW loading should improve the catalyst acidity, which seems favorable to a high catalytic activity. However, figure 2 indicates that the crystal structure of support is destroyed when $Cs_{2.0}$PW loading is 20%. In addition, as shown in Table 1, the BET surface area decreases remarkably with the increase of $Cs_{2.0}$PW loading. This could explain the lowed activity of the catalyst with the high $Cs_{2.0}$PW loading.

The catalytic activities of Pt/DUSY and Pt-10% $Cs_{2.0}$PW/DUSY at different reaction temperatures are shown in Table 4. For both catalysts, it can be seen that the conversion of *n*-heptane increases rapidly with the increase of reaction temperature, while the selectivity to isomerized products decreases. At the similar level of conversion of 7.6%, at 270 °C for Pt/DUSY and at 230 °C for Pt-10%$Cs_{2.0}$PW/DUSY, the two catalysts give the same isomerization selectivity of 100%. This suggest that the advantages of introduction of the Cs salt of PW are on the one hand to lower the reaction temperature, i.e., to enhance the activity, and on the other hand to maintain the high selectivity to isomerized products. In this work, we employed a low Pt loading (0.4%) in Pt-10%$Cs_{2.0}$PW/DUSY catalyst, and at 310 °C of reaction temperature, it exhibits a very high convertion of *n*-heptane of 76.2% with a high selectivity of 92.2%, moreover, the yield of multi-branched products amounts to a high value of 19%, which is more

Table 3
Comparison of the reactivity of hydroisomerization of *n*-heptane over catalysts with different $Cs_{2.0}$PW loadings[a]

Catalyst	Conversion /%	Mono-branched product yield/%	Multi-branched product yield/%	Isomerization selectivity/%
Pt-5%$Cs_{2.0}$PW/DUSY	10.6	9.1	1.2	97.2
Pt-10%$Cs_{2.0}$PW/DUSY	41.4	34.3	6.6	98.8
Pt-15%$Cs_{2.0}$PW/DUSY	18.8	15.5	2.6	96.3
Pt-20%$Cs_{2.0}$PW/DUSY	8.1	5.1	0.9	74.1

[a] Reaction temperature: 270 °C; WHSV: 2.7 h^{-1}; H_2/*n*-heptane(mole): 7.9; catalyst amount: 0.5 g; reaction time on stream: 120 min.

Table 4
Comparison of the reactivity of hydroisomerization of *n*-heptane over various catalysts at different reaction temperatures[a]

Catalyst	T/°C	Conversion /%	Mono-branched product yield/%	Multi-branched product yield/%	Isomerization selectivity/%
Pt/DUSY	230	1.6	1.6	0.0	100
	250	2.8	2.8	0.0	100
	270	7.6	7.3	0.3	100
	290	15.9	14.9	0.9	99.6
	310	35.4	30.0	4.8	98.3
Pt-10%$Cs_{2.0}$ PW/DUSY	230	7.6	7.3	0.3	100
	250	22.8	20.6	2.2	100
	270	41.4	34.3	6.6	98.8
	290	65.4	48.1	14.5	95.7
	310	76.2	51.3	19.0	92.2

[a] WHSV: 2.7 h^{-1}; H_2/*n*-heptane(mole): 7.9; catalyst amount: 0.5 g; reaction time on stream:120 min.

valuable for improving the octane number of gasoline poor than mono-branched ones. These results verify that Pt-10%$Cs_{2.0}$PW/DUSY is a highly efficient catalyst for the hydroisomerization of *n*-heptane.

4. Conclusions

DUSY, prepared from USY zeolite by the hydrothermal treatment combined with twice acid leaching, is revealed to be a suitable support for Cs salts of PW in the hydroisomerization of *n*-heptane. The Pt-10%$Cs_{2.0}$PW/DUSY catalyst shows a high catalytic activity, which is comparable to Pt/USY, but the former couples with a much higher selectivity to isomerized products. Also, this catalyst is much more active than Pt/DUSY, suggesting that the Cs salt is essentially the very active acidic species. At the reaction temperature of 270 °C, Pt-10%$Cs_{2.0}$PW/DUSY catalyst gives a considerable conversion of *n*-heptane of 41.4% with very high isomerization selectivity of 98.8%, and at 310 °C, it exhibits a very high convertion of 76.2% with a high selectivity of 92.2%.

Acknowledgments

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