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Catalytic performances of dealuminated Hβ zeolite supported Pt catalysts doped with Cr in hydroisomerization of *n*-heptane

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ABSTRACT

A series of dealuminated Hβ zeolite supported Pt catalysts doped with Cr, Ce, La or Zn were prepared via co-impregnation and characterized by X-ray diffraction (XRD), BET, NH_3-TPD, H_2-TPR, ICP, and H_2-chemisorption techniques. The catalytic performance was evaluated in hydroisomerization of *n*-heptane with an atmospheric fixed bed flow reactor. At the reaction temperature 250 °C, Hβ zeolite supported Pt catalyst showed a low selectivity to isomerized products 47.3% with a high conversion of *n*-heptane 83.9%. By dealuminating the Hβ support with steaming and acid leaching, a high selectivity to isomerized products 96.4% with considerable conversion 52.3% was observed. Moreover, by doping Cr (La or Ce) into the Pt/dealuminated Hβ catalyst, a further increase of the selectivity to isomerized products was obtained. The optimal composition for Cr-doped Pt/dealuminated Hβ catalysts was 0.4 wt% of Pt loading and 5:1 of molar ratio of Cr to Pt. This catalyst proves to be a highly efficient catalyst for the hydroisomerization of *n*-heptane, giving a very high selectivity to isomerized products 97.0% with the conversion of *n*-heptane 65.5% at the reaction temperature 270 °C. The promotion effect of Cr is discussed in relation to the catalyst acidity and the dispersion and reducibility of the supported Pt.

1. Introduction

The metal–acid bifunctional catalysts, such as γ-alumina or zeolite supported Pt catalysts, are used in hydroisomerization of light paraffins (*n*-pentane and *n*-hexane) [1,2]. Nowadays, hydroisomerization of middle paraffins from *n*-heptane to *n*-nonane in gasoline pool plays an increasingly important role in refinery due to the stringent legislations for advanced liquid fuels [3,4]. A number of reports have investigated the skeletal isomerization of *n*-heptane in the presence of hydrogen over Pt- or Pd-bearing mordenite [5,6], Y zeolite [7,8], β zeolite [6,9–11], SO_4^{2-}/ZrO_2 [12,13], and heteropolyacid catalysts [14–16]. Among them, the Pt/mordenite catalyst has been used for hydroisomerization of C_5/C_6 as a commercial approach to achieving light isoparaffins, but it readily causes cracking in the hydroconversion of C_7 [5,17]. In contrast, the Pt/Hβ catalyst is considered to be a promising candidate for hydroisomerization of *n*-heptane [6,18–20]. The unique structure of the three-dimensional interconnected channels of β zeolite is revealed to closely relate to the good catalytic performance of Pt/Hβ [20]. Moreover, the nanocrystalline β zeolite supported Pt catalyst is demonstrated to be much more selective to isomerization in *n*-heptane transformation than Pt/mordenite [5]. Nevertheless, the catalytic conversion over Pt/Hβ is still not sufficiently high simultaneously with a high selectivity to isoheptanes [10,11,20].

Attempts have been made to modify the zeolite supported Pt catalysts so as to enhance their catalytic behaviors. On the one hand, a second metal is introduced into the noble metal-supported catalysts to improve the catalytic conversion, selectivity and stability in hydroisomerization of *n*-paraffins [21–26]. For examples, Le Van Mao et al. [21,22] obtained a significantly enhanced yield for branched paraffins in the hydroisomerization of *n*-heptane by doping a small amount of Al into Pt/HY catalyst; Eswaramoorthi and Lingappan [24] observed remarkable increases in conversions of *n*-hexane and *n*-heptane, and selectivity to multi-branched isomers by the addition of Ni into Pt/HY catalyst. Recently, Wei et al. [25,26] prepared the Pt-bearing SO_4^{2-}/ZrO_2 or phosphotungstic acid/ultrastable Y zeolite catalyst for hydroisomerization of *n*-heptane and achieved a remarkable increase in both conversion and selectivity by further doping a second metal (Cr) into the catalyst. On the other hand, dealumination is an effective way to adjust the acidity of a bifunctional catalyst [27–29], and thus influences its catalytic activity. Among various zeolite supported Pt catalysts prepared by López et al. [27], Pt/Dβ (dealuminated Hβ) catalyst showed the best conversion, stability and selectivity to isopentanes in *n*-pentane hydroconversion at the reaction temperature of 300 °C. Also, Gopal and Smirniotis [30] observed an improvement in the yield for isomers in hydroisomerization of *n*-heptane due to the dealumination of the parent mordenite.

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Based on the previous studies above, it is reasonable to consider that the doping of a second metal as the promoter into dealuminated β zeolite supported Pt catalyst would be beneficial for improving its catalytic performance in hydroisomerization of *n*-heptane; however, this catalyst composition has not been reported for hydroisomerization so far. In this work, we prepare a series of Cr- (La-, Ce-, or Zn-) doped dealuminated β zeolite supported Pt catalysts for the hydroisomerization of *n*-heptane. A remarkable improved selectivity and yield for isoheptanes together with a high conversion of *n*-heptane are observed by the doping of the promoter, as well as by the dealumination treatment for β zeolite.

2. Experimental

2.1. Preparation of catalysts

The hydrogen form of β zeolite (Hβ) was prepared by the repeated ion-exchange of Naβ zeolite (Fushun No. 3 Petrochemical Factory, CNPC) with the aqueous solution of NH_4NO_3, followed by washing with deionized water, drying at 110 °C for 12 h, and calcination at 550 °C for 3 h. The dealuminated β zeolite (Dβ) was obtained by treating Hβ with a 0.5 mol L^{-1} aqueous HCl solution at 90 °C for 1 h, followed by washing, drying and calcination; the obtained solid was further steamed at 650 °C for 5 h, which was followed again by a second hydrochloride acid leaching as mentioned above. Although in previous reports when only HCl leaching was employed for the dealumination of β zeolite, 1 mol L^{-1} HCl aqueous solution was used [31,32], the combination of the two procedures (steam treatment and HCl leaching) is more critical than the HCl leaching alone, the lower concentration of 0.5 mol L^{-1} of HCl is employed in this work. The Pt/Dβ catalysts doped with Cr, La, Ce and Zn, which were designated as mMnPt/Dβ (M stands for Cr, La, Ce and Zn, m stands for the molar ratio of M to Pt, n stands for the Pt loading by weight percentage), were prepared via a co-impregnation process. Taking 5M0.4%Pt/Dβ as an example, Dβ was immersed in a mixed aqueous solution of chloroplatinic acid (0.0058 mol L^{-1}) and $Cr(NO_3)_3$ ($La(NO_3)_3$, $Ce(NO_3)_3$ or $Zn(NO_3)_2$) (0.0290 mol L^{-1}), followed by drying at 110 °C for 12 h and calcination at 400 °C for 3 h. The loadings of Pt in catalysts were 0.05–1.0% by weight and the molar ratios of M to Pt were 0:1, 1:1, 5:1, 10:1 and 15:1, respectively. During the preparation, the concentrations of M and Pt for the mixed solution were adjusted to meet the different composites of catalysts. 0.4%Pt/Hβ and 0.4%Pt/Dβ catalysts were prepared by the impregnation of Hβ and Dβ, respectively, with the aqueous solution of chloroplatinic acid, followed by drying and calcination at the same conditions as those for mMnPt/Dβ catalysts.

2.2. Characterization

X-ray diffraction (XRD) patterns were collected on a Bruker D8 ADVANCE X-ray diffractometer using Cu Kα radiation at 40 kV and 30 mA with a scan rate of 2° min^{-1} and a scanning range of 3°–50°. BET surface areas were measured using a Micromeritics ASAP2020 analyzer with nitrogen adsorption at −196 °C. The samples were pretreated at 200 °C in a vacuum of 0.01 KPa for 4 h. Temperature-programmed desorption of ammonia (NH_3-TPD), Temperature-programmed reduction of hydrogen (H_2-TPR), and Pt dispersion measurements were conducted using a JAPAN BELCAT-Analyzer. For NH_3-TPD, 200 mg of sample was pretreated at 500 °C for 2 h in a flow of helium, followed by adsorption of ammonia at 100 °C. NH_3-TPD was then performed at a heating rate of 10 °C min^{-1}. For H_2-TPR, the loaded sample in a quartz tube was pretreated at 400 °C for 1 h in a flow of oxygen followed with cooling to 60 °C and swept with argon for 20 min. While the sample was heated at a mixture of hydrogen and argon at a heating rate of 10 °C min^{-1} up to 650 °C, the temperature and consumption of hydrogen were recorded, respectively. The dispersion of Pt was determined using a pulsed technique of hydrogen chemisorption, based on 1:1 stoichiometry (H/Pt) according to the previous work [33]. 0.2 g of catalyst was reduced in hydrogen flow at 400 °C for 2 h, and then swept under argon flow at 450 °C for 0.5 h. Afterwards, the catalyst was cooled down to 50 °C and the pulse of 1 mL of the H_2/Ar mixture (10.2% H_2) was repeatedly injected into the reactor via a six-way valve until the hydrogen signals from the thermal conductivity detector were in a constant value. The volume of hydrogen chemisorbed was determined by summing the fraction of hydrogen consumed in each pulse. SiO_2/Al_2O_3 ratios of samples were obtained using a Jarrell–Ash 1100 inductively coupling plasma (ICP) spectrometer. For Hβ and Dβ zeolites, the SiO_2/Al_2O_3 ratios were 29 and 110, respectively.

2.3. Catalytic test

Hydroisomerization of *n*-heptane was carried out with an atmospheric fixed-bed flow reactor. The powder sample was first pressed at 10 MPa in a mould, and then the resulting tablet was pestled and sieved to give granular particles with a size of 0.25–0.42 mm. 0.565 g of the granular catalyst was charged in the middle of the stainless steel tubular reactor. Before the staring of the reaction at preset conditions, the catalyst was reduced in situ in H_2 flow at 300 °C for 3 h. The typical reaction conditions were as follows: 190–290 °C of reaction temperature, 2.7 h^{-1} of weight hourly space velocity (WHSV), and 7.9 of molar ratio of H_2 to *n*-heptane. The product mixture was quantitatively analyzed online by the gas chromatograph (SHIMADZU GC-2014) equipped with a SE30 capillary column (50 m × 0.25 mm × 0.3 μm) and FID. The products were qualitatively confirmed by GC–MS (ThermoFinnigan).

3. Results and discussion

3.1. Characterization of various catalysts

3.1.1. XRD

XRD patterns for various catalysts are illustrated in Fig. 1. It can be seen that the diffraction curve of Dβ was almost identical to that of its parent sample Hβ, indicating a high comparative crystallinity of BEA zeolite phase after the severe dealumination for the support. Also, 0.4%Pt/Dβ and 5M0.4%Pt/Dβ showed quite similar XRD pro-

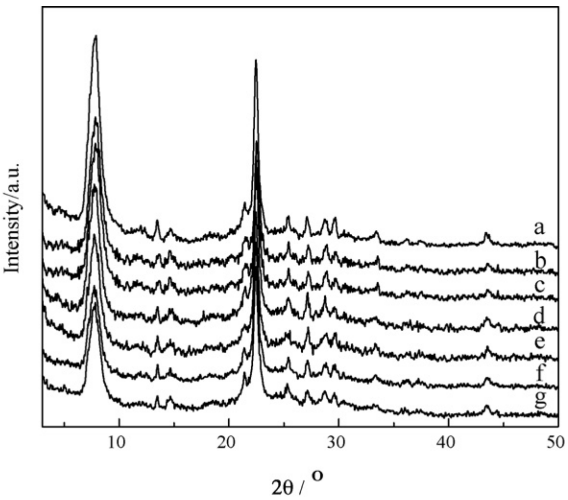

Fig. 1. XRD patterns for Hβ, Dβ and 5M0.4%Pt/Dβ catalysts. (a) Hβ, (b) Dβ, (c) 0.4%Pt/Dβ, (d) 5Ce0.4%Pt/Dβ, (e) 5Cr0.4%Pt/Dβ, (f) 5La0.4%Pt/Dβ, and (g) 5Zn0.4%Pt/Dβ.

Table 1
BET surface areas for various catalysts.

Catalyst	$S_{BET}/(m^2\ g^{-1})$	Catalyst	$S_{BET}/(m^2\ g^{-1})$
Hβ	575	5Ce0.4%Pt/Dβ	550
Dβ	578	5Cr0.4%Pt/Dβ	551
0.4%Pt/Dβ	546	10Cr0.4%Pt/Dβ	549
5Zn0.4%Pt/Dβ	574	15Cr0.4%Pt/Dβ	535
5La0.4%Pt/Dβ	521		

files to that of Dβ, which suggests that the support well retained the crystal structure of BEA zeolite after the loading of the metals.

3.1.2. *Surface area*

Table 1 lists the BET surface areas for various catalysts. It is seen that Dβ possessed a very comparable surface area (578 $m^2\ g^{-1}$) to that of Hβ (575 $m^2\ g^{-1}$). When Pt and a promoter were simultaneously supported onto Dβ, the surface areas only decreased slightly with still high data of around 540 $m^2\ g^{-1}$. On the other hand, Dβ zeolite showed a slightly larger pore volume (0.4512 $cm^3\ g^{-1}$) than Hβ (0.4317 $cm^3\ g^{-1}$), implying the creating of more mesopores in Dβ zeolite upon dealumination.

3.1.3. *NH_3-TPD*

NH_3-TPD profiles for 0.4%Pt/Hβ and mM0.4%Pt/Dβ catalysts are shown in Fig. 2. Two peaks occurred for all samples, corresponding to desorption of ammonia on weak and strong acid sites. 0.4%Pt/Hβ owned a large amount of acid sites, and in contrast, owing to the dealumination, all the Dβ supported catalysts exhibited much lowered acidity. Moreover, that decrease of acidity was much more remarkable for weak acid sites, causing the increase in the concentration of strong acidity. When Cr (Ce or La) was doped into 0.4%Pt/Dβ, an increase in acid amount was observed. And 5Cr0.4%Pt/Dβ showed a slightly larger amount of acid sites compared with 5Ce and 5La samples. 5Zn0.4%Pt/Dβ was an exception because it almost lost the strong acidity. On the other hand, when the Cr loading was raised (10Cr0.4%Pt/Dβ), the overall acid sites increased clearly and the peak for strong acidity shifted toward a higher temperature; however, too high of the Cr loading (15Cr0.4%Pt/Dβ) resulted in a decrease of acidity.

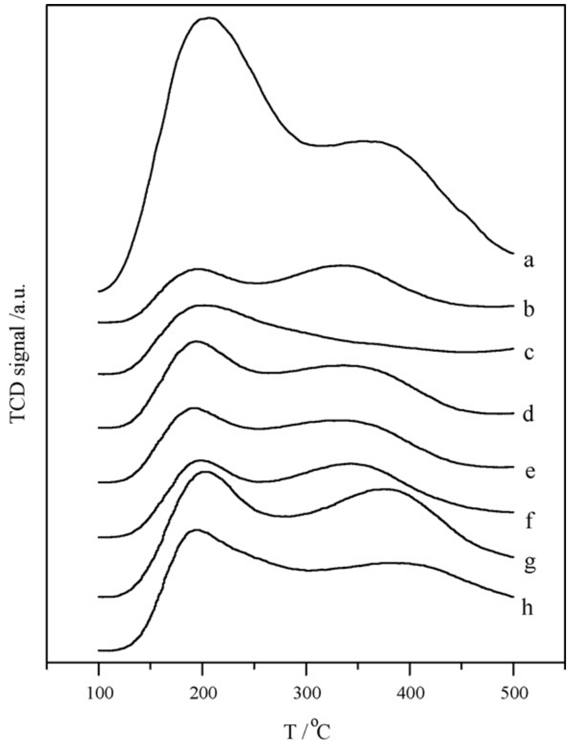

Fig. 2. NH_3-TPD profiles for 0.4%Pt/Hβ and mM0.4%Pt/Dβ catalysts. (a) 0.4%Pt/Hβ, (b) 0.4%Pt/Dβ, (c) 5Zn0.4%Pt/Dβ, (d) 5La0.4%Pt/Dβ, (e) 5Ce0.4%Pt/Dβ, (f) 5Cr0.4%Pt/Dβ, (g) 10Cr0.4%Pt/Dβ, and (h) 15Cr0.4%Pt/Dβ.

Table 2
Pt dispersions for various catalysts.

Catalyst	Pt dispersion/%
0.4%Pt/Dβ	35.7
5Zn0.4%Pt/Dβ	4.0
5La0.4%Pt/Dβ	40.7
5Ce0.4%Pt/Dβ	69.7
5Cr0.4%Pt/Dβ	42.1

3.1.4. *Pt dispersion for MPt/Dβ catalysts*

The Pt dispersion for the Pt alone sample and the second metal-doped samples are compared in Table 2. It can be seen that 0.4%Pt/Dβ showed the Pt dispersion 35.7% of and the La, Ce and Cr-doped samples gave 40.7%, 69.7%, and 42.1%, respectively. This indicates a remarkable increase of Pt dispersion by 34% upon the doping of Ce into the catalyst. However, for La and Cr-doped samples, the increase of Pt dispersion is not significant if the possible experimental error for the measurement of Pt dispersion is taken into account. Noticeably, the very low Pt dispersion of 4.0% occurred for the sample doped with Zn.

3.1.5. *H_2-TPR results for selected samples*

Fig. 3 shows H_2-TPR profiles for Cr/Dβ, 0.4%Pt/Dβ and 5Cr0.4%Pt/Dβ catalysts. 0.4%Pt/Dβ displayed a hydrogen consumption peak at around 390 °C, indicating the strong interaction between Pt^{2+} and β zeolite with the formation of $Pt\text{–}(O\text{–}Si\equiv)_y^{2-y}$ species, which are reduced at above 400 °C as described in previous literatures [34,35]. The slight difference of the reduction temperature should be relative to the dealumination of the Beta zeolite. Cr/Dβ, with the Cr loading being equal to that of 5Cr0.4%Pt/Dβ, presented a large peak at 400 °C, which is assigned to the reduction of Cr (III) species [36,37]. The bimetallic catalyst 5Cr0.4%Pt/Dβ exhibited two reduction peaks: the large one at around 395 °C and a small one at around 145 °C. It is clear that the curve for 5Cr0.4%Pt/Dβ was not a result by simply overlapping the profiles for the two monometallic samples, suggesting a strong interaction between Cr and Pt. The peak at 145 °C can be assigned to the co-reduction of Pt–Cr species [36], which implies that the reducibility of Pt species

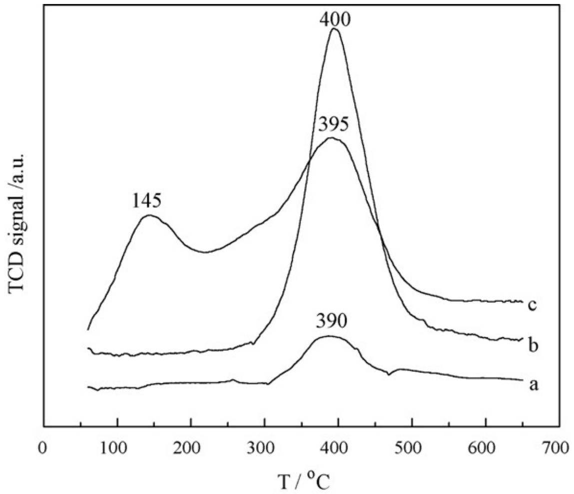

Fig. 3. H_2-TPR profiles for (a) 0.4%Pt/Dβ, (b) Cr/Dβ, and (c) 5Cr0.4%Pt/Dβ.

Table 3
Comparison of the catalytic performances between 0.4%Pt/Hβ and 0.4%Pt/Dβ for the hydroisomerization of *n*-heptane[a].

Catalyst	T/°C	Conversion/%	Isomerization yield/%	$Y_{\mathrm{Multi}}/Y_{\mathrm{Mono}}$[b]	Selectivity/%		
					Isomerization	Cracking	Cyclization
0.4%Pt/Hβ	190	9.4	7.6	0.09	81.1	0.7	18.2
	210	23.9	21.6	0.15	90.5	3.6	5.9
	230	50.6	41.7	0.24	82.4	15.7	1.9
	250	83.9	39.7	0.32	47.3	51.6	1.1
	270	97.3	15.7	0.47	16.1	82.8	1.1
0.4%Pt/Dβ	230	18.4	17.5	0.07	95.2	0.6	4.2
	250	52.3	50.4	0.16	96.4	2.2	1.4
	270	78.2	62.6	0.36	80.0	19.6	0.4
	290	90.6	53.6	0.48	59.2	40.6	0.2

[a] Reaction conditions: WHSV 2.7 h^{-1}; H_2/*n*-heptane (mol) 7.9; reaction time on stream 120 min.

[b] Molar ratio of the yield of multi-isoheptanes to that of mono-isoheptanes. Multi-isoheptanes include 2,2-dimethylpentane (98), 2,3-dimethylpentane (91), 2,4-dimethylpentane (83), 3,3-dimethylpentane (81) and 2,2,3-trimethylbutane (112). Mono-isoheptanes include 2-methylhexane (42), 3-methylhexane (52) and 3-ethylpentane (65). The number in parenthesis is the research octane number.

in 5Cr0.4%Pt/Dβ is dramatically improved by the doping with Cr species.

3.2. *Comparison of catalytic performances between 0.4%Pt/Hβ and 0.4%Pt/Dβ*

Before studying the effect of dopants, it is necessary to first compare the catalytic activities of 0.4%Pt/Hβ and 0.4%Pt/Dβ for the hydroisomerization of *n*-heptane. The result is shown in Table 3, where the products were online sampled when the reaction reached a steady stage after 120 min of time on stream. For both catalysts, with the increase of reaction temperature, the conversion of *n*-heptane rose quickly accompanying with a quick decrease in selectivity to isomerization. Exceptions occurred at low temperatures of 190 and 230 °C, where the selectivity to isoheptanes was low duo to the selective production of a large amount of cyclized products. Moreover, at the same reaction temperature, 0.4%Pt/Dβ gave a lower conversion of *n*-heptane and a much higher selectivity to isomerization than 0.4%Pt/Hβ did. If the selectivity to isomerization is regarded, the optimal reaction temperatures were 210 and 250 °C for 0.4%Pt/Hβ and 0.4%Pt/Dβ catalysts, respectively. In that case, the conversion of *n*-heptane and the selectivity to isomerization were substantially higher on 0.4%Pt/Dβ than those on 0.4%Pt/Hβ (52.3% vs. 23.9% in conversion, and 96.4% vs. 90.5% in selectivity). When the two catalysts were compared at a similar conversion of about 50% (230 °C for 0.4%Pt/Hβ, and 250 °C for 0.4%Pt/Dβ), both selectivity and yield for isomerized products were higher on 0.4%Pt/Dβ than those on 0.4%Pt/Hβ. What is noteworthy is that the enhanced isomerization selectivity can even be observed on 0.4%Pt/Dβ at an elevated temperature of 250 °C. It is thus concluded that 0.4%Pt/Dβ catalyst is much more selective to isomerization than 0.4%Pt/Hβ. On the other hand, for all entries, the produced mono-isoheptanes (2-methylhexane, 3-methylhexane and 3-ethylpentane) were in higher amounts than multi-isoheptanes (2,2-dimethylpentane, 2,3-dimethylpentane, 2,4-dimethylpentane, 3,3-dimethylpentane and 2,2,3-trimethylbutane).

3.3. *Influence of different dopants for MPt/Dβ catalysts*

Table 4 shows the reactivity of the hydroisomerization of *n*-heptane over 0.4%Pt/Dβ and 5M0.4%Pt/Dβ catalysts. Comparing the catalytic performance of various catalysts at same reaction conditions at the reaction temperature of 270 °C and WHSV of 2.7 h^{-1}, one can see that 0.4%Pt/Dβ displayed a very high conversion of *n*-heptane at 78.2% with a low selectivity to isomerization of 80.0%, but with the doping of Zn into the catalyst, the conversion drastically dropped to a very low level of 26.6%. However, with the doping of La, Ce, or Cr into the catalyst, only a slight decrease of conversion was observed, with the yield for isomerized products almost unaltered. One thus can draw that the slight decrease of conversion is because of the effective inhibition of the cracking products.

In order to compare the catalytic selectivity of these catalysts at a similar conversion level, WHSV was adjusted for 0.4%Pt/Dβ and 5Zn0.4%Pt/Dβ to get a conversion of around 60% (Table 4). In that case, 0.4%Pt/Dβ gave a comparative low isomerization selectivity of 89.6% and Zn-doped catalyst also showed a much lowed value of 64.3%. Nevertheless, the La, Ce, and Cr-doped catalysts exhibited much higher selectivity to isomerized products of about 96%. Furthermore, among them, 5Cr0.4%Pt/Dβ exhibited the highest selectivity (97.0%) and yield (63.5%) for isomerized products.

It is well known that, for the hydroisomerization of paraffins over metal/acid bifunctional catalysts, the paraffin transformation involves hydrogenation–dehydrogenation on metal sites, isomerization and/or cracking on acid sites, and diffusion of the olefinic intermediates from acid to metal sites and inversely. When the available metal sites are not sufficient for all the acid sites to be fed with intermediate alkenes, the hydrogenation–dehydrogenation will be the rate-determining step and more cracking products will occur. In scarcity of the acid sites, the reaction on acid sites becomes the rate-determining step, resulting in less cracking products [38]. Based on the above proposal, in this work the 0.4%Pt/Hβ catalyst possessing a large amount of acid sites (Fig. 2) is most possibly short of metallic sites, and consequently creates more cracking products and exhibits high overall conversion of *n*-heptane (Table 3). Contrarily, upon dealumination the acid amount of Pt/Dβ drops drastically, which leads to a high selectivity to isomerization coupled with a very low conversion of *n*-heptane at the reaction temperature of 230 °C (Table 3). One thus may reasonably consider that for Pt/Dβ catalyst the reaction on acid sites should be the rate-limitation step, which gifts Pt/Dβ a room for the catalyst to be operated at an elevated temperature without generating many cracking products. This is true by the result at 250 °C in Table 3 that the very high selectivity to isomerization of 96.4% with a considerable conversion of 52.3% were observed.

Also because of the slow reaction step on acid sites for Dβ supported catalysts, modifications to enhance the metal dispersion would not increase the conversion of *n*-heptane any more. This may give an interpretation for that the highest dispersion in 5Ce0.4%Pt/Dβ catalyst (Table 2) does not cause an increase of conversion (Table 4). In comparison with 5Ce0.4%Pt/Dβ and 5La0.4%Pt/Dβ, a slightly larger amount of acid sites for 5Cr0.4%Pt/Dβ is able to result in an increase of conversion with the retaining of high selectivity to isomerization (Table 4). If both metal and acid sites remarkably decrease, just as the case of 5Zn0.4%Pt/Dβ, the catalytic activity unavoidably drops to a very

Table 4
Catalytic performances of 0.4%Pt/Dβ and 5M0.4%Pt/Dβ for the hydroisomerization of *n*-heptane[a].

Catalyst	Conversion/%	Isomerization yield/%	Y_{Multi}/Y_{Mono}[b]	Selectivity/%		
				Isomerization	Cracking	Cyclization
0.4%Pt/Dβ	78.2	62.6	0.36	80.0	19.6	0.4
	63.2[c]	56.6	0.29	89.6	9.8	0.6
5Zn0.4%Pt/Dβ	26.6	20.2	0.15	75.9	21.6	2.4
	59.7[d]	38.4	0.24	64.3	34.4	1.3
5La0.4%Pt/Dβ	60.8	58.3	0.18	95.9	3.3	0.8
5Ce0.4%Pt/Dβ	63.9	61.3	0.21	95.9	3.3	0.8
5Cr0.4%Pt/Dβ	65.5	63.5	0.22	97.0	2.2	0.8

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

[b] Molar ratio of the yield of multi-isoheptanes to that of mono-isoheptanes.

[c] WHSV 4.8 h^{-1}.

[d] WHSV 0.7 h^{-1}.

low level (Fig. 3, Tables 2 and 4). Therefore, one can draw that the amounts of metal and acid sites themselves are important, however, the balance or matching between them is also significant to give a high-performance bifunctional catalyst for this reaction. Another explanation for the better performance of 5Cr0.4%Pt/Dβ is that the dramatically improved reducibility of Pt species (Fig. 3) may be favorable to the promotion of hydrogenation–dehydrogenation activity at metal sites, which again accounts for the high selectivity and conversion.

It is noticeable in Table 4 that the ratio of Y_{Multi}/Y_{Mono} was lowered in the presence of the second metal. It has been supposed for zeolite-based bifunctional catalysts that the high degree of branched carbocations produced on acid sites would facilitate the β-scission into cracked products and thus increase the rate for cracking [8,39]. So a possible interpretation for above results is that the addition of Cr, La or Ce speeds up the desorption of the branched carbocationic intermediates from the acid sites to avoid further cracking, but simultaneously, the shortened residence time for the carbocations on acid sites will reduce the chance for them to take further isomerization, which results in a lower concentration of multi-branched isomers [13,21].

It is possible to calculate the RON (research octane number) of the obtained product mixture (C_{5+} fraction, including unconverted *n*-heptane) by multiplying the volume fraction of the individual hydrocarbon with its RON, then summing up the contributions of all the compounds [23]. The RON of the product mixture obtained over 5Cr0.4%Pt/Dβ estimated by this method is 35. In practice, the octane number is generally not a linear mixing property due to the interactions between the compounds of different chemical natures and the actual RON of the mixture is likely to be different (somewhat higher) from the calculated number. However, the thus estimated RON can still be quite useful for studies [40]. In this work, the RON 35 for the product mixture is much higher than zero, the octane number of the raw material *n*-heptane. However, it is still not perfect because most of the produced isoheptanes are mono-branched ones, the RONs of which are still lower than those of the multi-branched ones.

3.4. *Effect of Cr and Pt loading for CrPt/Dβ catalysts*

Fig. 4 shows the conversion of *n*-heptane and selectivity to isomerization as a function of Cr loading for *m*Cr0.4%Pt/Dβ (*m* = 0–15) catalysts. The conversion of *n*-heptane was at the high level when the Cr loading was very low (*m* = 1). Generally speaking, the conversion decreased with the increase of Cr loading (*m* from 1 to 15), and meanwhile, the selectivity to isomerized products increased gradually. The notable decrease of conversion at the very high Cr loading (*m* = 15) may be ascribed to the decrease of strong acid sites (Fig. 2). Although 5Cr0.4%Pt/Dβ and 10Cr0.4%Pt/Dβ showed a very similar result, for economical considerations, 5:1 is the preferred molar ratio of Cr/Pt for mCr0.4%Pt/Dβ catalysts.

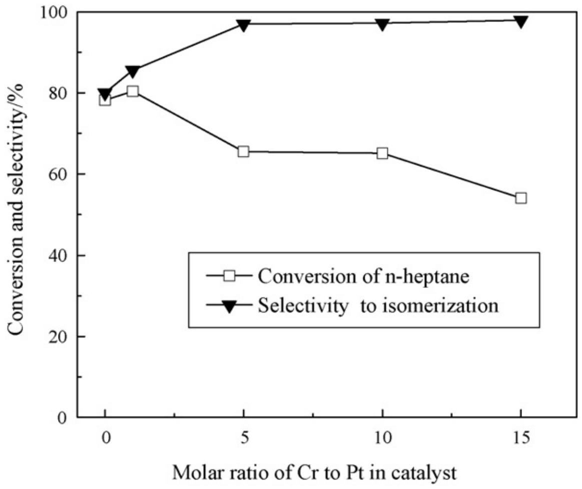

Fig. 4. Conversion of *n*-heptane and selectivity to isomerization over *m*Cr0.4%Pt/Dβ catalysts with different Cr loadings. Reaction conditions: reaction temperature 270 °C; WHSV 2.7 h^{-1}; H_2/*n*-heptane (mol) 7.9; reaction time on stream 120 min.

Fig. 5 gives the influence of Pt loading for CrnPt/Dβ catalysts with a fixed Cr loading (the weight percentage of Cr_2O_3 was 1.6%, the same value in 5Cr0.4%Pt/Dβ catalyst) on the catalytic conver-

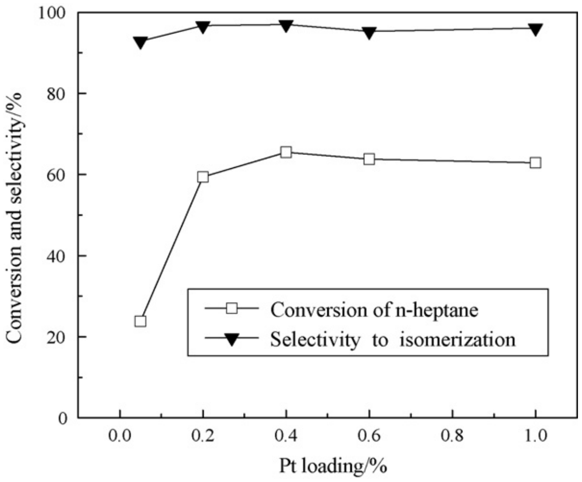

Fig. 5. Conversion of *n*-heptane and selectivity to isomerization over the CrnPt/Dβ catalysts with different Pt loadings. Reaction conditions: reaction temperature 270 °C; WHSV 2.7 h^{-1}; H_2/*n*-heptane (mol) 7.9; reaction time on stream 120 min.

sion and selectivity. At low Pt loadings, the conversion of *n*-heptane increased quickly with the increase of supported Pt, and it reached a constant value of around 64% when the Pt loading was up to 0.4%. When the Pt loading exceeded 0.2%, the isomerization selectivity amounted to a high level of around 97.0%. This result is in agreement with the expectation of the classical bifunctional reaction mechanism for the hydroisomerization of paraffins, which tells that the acid and metal functions should match well with each other to get a high conversion and selectivity [41–43]. And the optimal Pt loading of 0.4% for the Cr-doped Dβ zeolite can be proposed from Fig. 5.

3.5. Effect of reaction temperature and WHSV

The influence of reaction temperature on the catalytic behavior of 5Cr0.4%Pt/Dβ catalyst in the hydroisomerization of *n*-heptane is shown in Fig. 6. It can be seen that with the increase of reaction temperature, the conversion of *n*-heptane always increased very quickly. At high temperatures the selectivity to isomerization decreased gradually because of creating of more and more cracking products, but at low temperatures it increased slowly due to the gradual disappearance of cyclized products. Compared to 0.4%Pt/Dβ (Table 3), 5Cr0.4%Pt/Dβ exhibited a rather high and constant selectivity to isomerization at a wider window of reaction temperature 230–290 °C. However, 5Cr0.4%Pt/Dβ showed a much lower conversion of *n*-heptane than 0.4%Pt/Dβ when they are compared at the reaction temperature of 250 °C, the optimal one for the latter catalyst. Nevertheless, Fig. 6 indicates that the optimal reaction temperature for 5Cr0.4%Pt/Dβ is 270 °C, at which, the very high selectivity to isomerized products (97.0%) coupled with a rather high conversion of *n*-heptane (65.5%) were obtained. These results are better than those of 0.4%Pt/Dβ at 250 °C. On the other hand, the yields of mono- and multi-branched heptanes also increased with the increase of the reaction temperature, and the high temperature seemed more beneficial for the creation of multi-branched heptanes.

Fig. 7 presents the influence of WHSV on the catalytic behavior of 5Cr0.4%Pt/Dβ. The conversion of *n*-heptane and yields for mono- and multi-branched products decreased slowly with the increase of WHSV, whereas the selectivity to isomerization increased gradually at low WHSV and then stayed at very high level of 97.0% when WHSV was beyond 2.7 h^{-1}. Additionally, the cracking selectivity was lowered with the increase of WHSV, but it held a very low level at high values of WHSV. Only trace amount of cyclized products was observed at those conditions. Therefore, from Fig. 7 one can propose that 2.7 h^{-1} of WHSV is the preferred selection for a good catalytic performance of 5Cr0.4%Pt/Dβ.

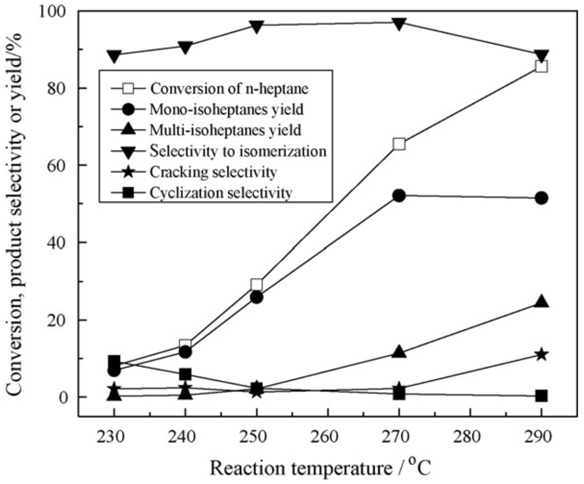

Fig. 6. Influence of reaction temperature on the catalytic performance of 5Cr0.4%Pt/Dβ in the hydroisomerization of *n*-heptane. Reaction conditions: WHSV 2.7 h^{-1}; H_2/*n*-heptane (mol) 7.9; reaction time on stream 120 min.

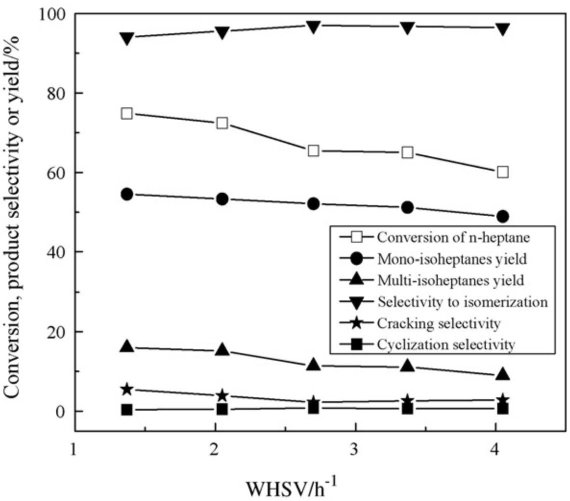

Fig. 7. Influence of WHSV on the catalytic performance of 5Cr0.4%Pt/Dβ in the hydroisomerization of *n*-heptane. Reaction conditions: reaction temperature 270 °C; H_2/*n*-heptane (mol) 7.9; reaction time on stream 120 min.

4. Conclusions

In the hydroisomerization of *n*-heptane, the dealuminated Hβ zeolite (Dβ) supported Pt catalyst (0.4%Pt/Dβ) exhibits the much higher selectivity to isomerized products and the conversion *n*-heptane at 250 °C of reaction temperature than the non-dealuminated catalyst (0.4%Pt/Hβ). Upon doping the promoter (Cr, La, or Ce) into the catalyst 0.4%Pt/Dβ, the catalytic performance is further improved. For CrPt/Dβ catalysts, the optimal Pt loading is 0.4% by weight and the preferred molar ratio of Cr to Pt is 5:1. Over this catalyst, the high conversion of *n*-heptane (65.5%) and the very high selectivity to isomerized products (97.0%) are obtained at the reaction temperature of 270 °C, WHSV of 2.7 h^{-1}, and molar ratio of H_2 to *n*-heptane of 7.9. This demonstrates that 5Cr0.4%Pt/Dβ is a highly efficient catalyst for hydroisomerization of *n*-heptane. The dealumination for the catalyst support β zeolite largely decreases the acid number, which leads to a better balance between metal and acid sites and enables the bifunctional catalyst to show high conversion while creating only slight of cracking products even at a comparatively high reaction temperature. The promotion effect of Cr is suggested to arise from the increased number of strong acid sites, the improved Pt dispersion, and the enhanced reducibility of supported Pt.

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