研究简报

掺杂 Cr 助剂的 Pt/USY 催化剂上正庚烷异构化反应研究

魏瑞平　顾焰波　孔　岩　王　军*

(南京工业大学化学化工学院材料化学工程教育部重点实验室,南京　210009)

Hydroisomerization of *n*-Heptane over Pt/USY Catalysts Promoted by Cr Additive

WEI Rui-Ping　GU Yan-Bo　KONG Yan　WANG Jun*

(*Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and
Chemical Engineering, Nanjing University of Technology, Nanjing* 210009)

Abstract: The Pt-supported USY zeolite catalysts doped with Cr, Al or Zn were prepared by impregnation, and characterized by XRD, low temperature nitrogen physisorption, H$_2$-chemisorption and IR spectroscopy of the pyridine adsorption. Catalytic activities were evaluated via the hydroisomerization of *n*-heptane with an atmospheric fixed-bed reactor. The Pt dispersion and acidity of the Pt-supported USY catalyst were influenced by the addition of the promoters. The Pt-supported catalysts promoted by Cr, Al or Zn, especially by Cr, were catalytically much more stable and exhibited much higher catalytic activity and selectivity for isomerization of *n*-heptane than the catalysts without the dopant. Both the conversion and selectivity are discussed in relation with the physicochemical properties of catalysts.

Key words: hydroisomerization; *n*-heptane; promoter; USY; platinum

Light iso-paraffins are the increasingly important octane number enhancer in gasoline pool due to the more and more stringent environmental legislations regarding the advanced liquid fuel quality[1]. Hydroisomerization of C$_5$/C$_6$ is a commercial approach to achieve light iso-paraffins, where chlorinated Pt/Al$_2$O$_3$ or Pt/mordenite has been traditionally used as catalyst[2]. Hydroisomerizarion of paraffins with chain-length longer than C$_6$ is highly desirable to improve the octane number of gasoline without increasing the aromatic and olefin content[3,4]. Hydroisomerization of *n*-heptane is usually investigated as a model reaction because of its comparatively simple reaction products. However, the well known Pt/mordenite catalysts would crack the *n*-heptane[5]. Then many efforts have been devoted to improve the selectivity of the branched products in the hydroisomerization of *n*-heptane. The catalysts now available always involve bifunctional compositions formed by supporting platinum onto acid zeolites, such as Pt/Hβ[5], Pt/Y[6,7] and so on.

In view of the low selectivity for isomerized products over the catalysts containing only Pt metal

and the high cost of Pt, the more stable, selective and highly activive bimetallic catalysts have been studied on the conversion of hydrocarbons[8~10]. For example, Passos et al.[8] prepared Pt-Sn/Al$_2$O$_3$ and Pt-In/Al$_2$O$_3$ catalysts for the n-butane hydrogenolysis. Fabio et al.[9] used the Pt-Sn/Al$_2$O$_3$ and Pt-In/Al$_2$O$_3$ catalysts for the cyclohexane dehydrogenation and *n*-heptane convers-ion. Mao et al.[10] investigated the catalytic activity of Pt-Al/HY catalyst in the hydroisomerization of *n*-heptane and found a significantly enhanced yield of branched paraffins by the incorporation of a small amount of Al species into the HY zeolite structure. More recently, Martins et al.[11] employed Pt-Ni/HBEA as the catalyst for the hydroisomerization of n-hexane and achieved the highest conversion and selectivity, revealing a synergistic effect between Pt and Ni.

In the present study, we initiate the investigation on the USY (ultra-stable Y) zeolite supported Pt catalysts doped with Cr, Al or Zn as a promoter for hydroisomerization of *n*-heptane, observing a much higher catalytic conversion of n-heptane with higher selectivity for isomerization products.

1 Experimental

The Cr, Al or Zn promoted Pt/USY catalysts were prepared by the incipient wetness impregnation method. USY zeolite ((Si/Al=6), Zhoucun Catalyst Factory) was immersed in a mixed solution of chromium nitrate (aluminum nitrate or zinc nitrate) (0.070 mol·L^{-1}) and chloroplatinic acid (0.017 mol·L^{-1}) with the preset contents of Pt and Cr (Al or Zn), and then the composite was dried at 110 ℃ overnight, calcined at 400 °C for 3 h. The resulting catalysts are designated as mMnPt/USY, where M stands for Cr, Al or Zn, m stands for the molar ratio of M to Pt, n stands for the Pt loading in catalysts by weight percentage. In all the catalysts, the Pt loading was 0.4% or 0.8% by weight, the molar ratio of M to Pt was 1:1, 5:1, 10:1, 15:1, respectively. The nPt/USY catalyst was prepared by USY zeolite impregnation with the solution of chloroplatinic acid, followed by drying and calcination at the same conditions as for mMnPt/USY catalysts.

Hydroisomerization of *n*-heptane was carried out in an atmospheric fixed-bed flow reactor. 0.5 g of the granular catalyst (0.42~0.25 μm) 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 ℃ for 3 h. Reaction conditions were as follows: 200~270 ℃ of reaction temperature, 2.7 h^{-1} of weight hourly space velocity, and 7.9 of molar ratio of H$_2$ to *n*-heptane. The product mixture was analyzed online by the gas chromatograph equipped with a SE30 capillary column (50 m × 0.25 mm × 0.3 μm) and FID. The products were confirmed by GC-MS (ThermoFinnigan). Analysis conditions were as follows: 60 ℃ of oven temperatue, 150 ℃ of injector tempera-ture, and 250 ℃ of detector temperatue.

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 with a scan rate of 2°·min^{-1}. BET surface areas were calculated by N$_2$ adsorption data from the Coulter Ommisorp 100CX equipment. The dispersion of Pt was measured by hydrogen chemisorption. The catalysts were pretreated at 400 ℃ for 2 h in hydrogen flow and then absorbed the hydrogen at 100 ℃. The acidities of the samples were measured by IR spectroscopy of the pyridine adsorption on a Thermo Nicolet NEXUS spectrometer. The self-supporting wafer of the sample was first evacuated in situ in an IR cell at 300 ℃ for 2 h under a vacuum of 1 × 10^4 Pa. After the temperature decreased to 120 ℃, pyridine was introduced into the cell until the saturated adsorption being reached. Finally desorption of pyridine was performed at 300 ℃ and the spectra were recorded.

2 Results and discussion

XRD patterns of USY and different metal promo-ted 0.4% Pt/USY catalysts are illustrated in Fig.1. It shows that the XRD patterns of all metal-bearing catalysts are very similar to that of pure USY zeolite. No diffraction peaks assigned to the crystal of Cr, Al or Zn oxide occur for all the metal-doped USY zeolite catalysts. The peak at 39.8° assigned to Pt (111) also can not be detected. Fig.2 gives the XRD patterns of

the catalysts with different Cr loadings. It can be seen that all the XRD patterns of the catalysts are similar to the USY support even when the Pt loadings is 0.8% or the molar ratio of Cr to Pt is 15:1. It could be thus deduced that the USY support well retains the pore structure of Y zeolite, and moreover, the crystal of the supported noble metal and doped metal oxide is not enough to be detected by XRD.

(a) USY, (b) 5Cr0.4%Pt/USY,
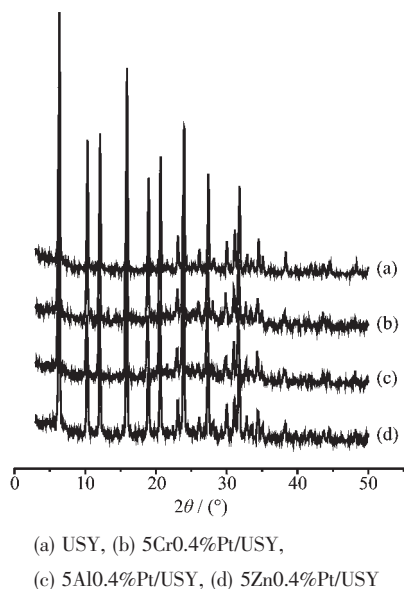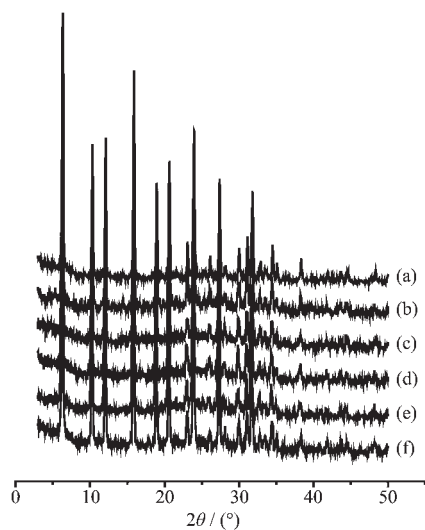
(c) 5Al0.4%Pt/USY, (d) 5Zn0.4%Pt/USY

Fig.1　XRD patterns of Cr, Al and Zn promoted catalysts

(a) USY, (b) 1Cr0.4%Pt/USY, (c) 5Cr0.4%Pt/USY,

(d) 10Cr0.4%Pt/USY, (e) 15Cr0.4%Pt/USY, (f) 5Cr0.8%Pt/USY

Fig.2　XRD patterns of various catalysts with different Cr loadings

Table 1 lists the BET surface area of catalysts doped with Al, Zn and Cr. It can be seen that the USY exhibits a high surface area of 687 $m^2 \cdot g^{-1}$. When

the Pt was supported onto the USY, the surface area drops to 672 $m^2 \cdot g^{-1}$. The surface area of catalysts further decreases with the addition of the promoters Al, Zn and Cr, but it varies slightly when the value of nCr/nPt is higher than 10. The Pt dispersion of various catalysts is also displayed in Table 1. The dispersion of Pt for 0.4%Pt/USY catalyst is 21%, and it can be promoted to more than 30% by the addition of a second metal (Al, Zn or Cr). Moreover, the dispersion of Pt increases with the increasing of Cr loadings.

Table 1　BET surface areas and Pt dispersions of various catalysts

Catalyst	Surface area / $(m^2 \cdot g^{-1})$	Pt dispersion / %
USY	687	—
0.4%Pt/USY	672	21
5Al0.4%Pt/USY	654	40
5Zn0.4%Pt/USY	638	35
1Cr0.4%Pt/USY	647	27
5Cr0.4%Pt/USY	636	31
10Cr0.4%Pt/USY	610	33
15Cr0.4%Pt/USY	610	44

Fig.3 gives the IR spectra for the 0.4% Pt/USY catalyst and the catalysts promoted by Cr, Al and Zn adsorbing pyridine in the region of 1 390~1 600 cm^{-1}. Three strong bands at 1 540, 1 490 and 1 450 cm^{-1} can be seen for 0.4% Pt/USY, 5Cr0.4% Pt/USY and
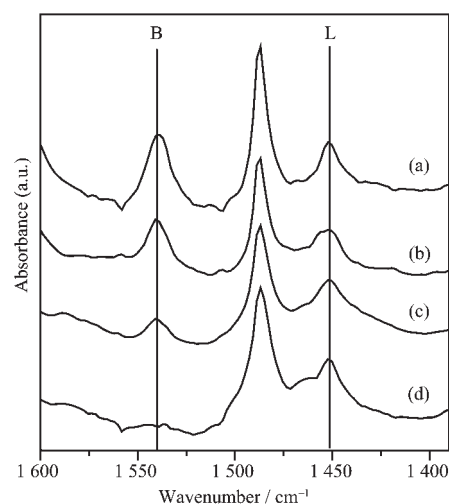
(a) 0.4%Pt/USY, (b) 5Cr0.4%Pt/USY,

(c) 5Al0.4%Pt/USY (d) 5Zn0.4%Pt/USY

Fig.3　IR spectra for adsorbed pyridine on various catalysts

5Al0.4%Pt/USY. In general, the band at 1 450 cm^{-1} for adsorbed pyridine is assigned to the adsorption of pyridine on Lewis acid sites, and the band at 1 540 cm^{-1} is associated with Brönsted acid sites. It is thus obvious that both Lewis and Brönsted acid sites exist in the three catalysts. Moreover, 5Cr0.4% Pt/USY catalyst has less Lewis and Brönsted sites than 0.4% Pt/USY catalyst, but has more sites than 5Al0.4%Pt/USY. While the spectrum of the 5Zn0.4% Pt/USY catalyst gives two strong bands at 1 490 cm^{-1} and 1 450 cm^{-1}, the band at 1 540 cm^{-1} is very weak. This means that the 5Zn0.4%Pt/USY catalyst possesses dominantly Lewis acid sites.

The conversion of *n*-heptane in the hydroisomerization of *n*-heptane at 230 ℃ over different metal doped Pt-supported USY catalysts as a function of reaction time on stream is compared in Fig.4. It can be seen that on 0.4%Pt/USY catalyst, the conversion of *n*-heptane is comparatively low and decreases with the time on stream when the time on stream is less than 80 min. The addition of a second metal (Cr, Al or Zn) promotes the initial catalytic activity. However, the conversion of *n*-heptane on the 5Zn0.4% Pt/USY catalyst decreases drastically within 40 min, and is almost equal to that on 0.4% Pt/USY after 100 min. For 5Al0.4% Pt/USY and 5Cr0.4% Pt/USY, it seems that the catalytic stability is improved, and 5Cr0.4% Pt/USY also gives a much stable high conversion. As
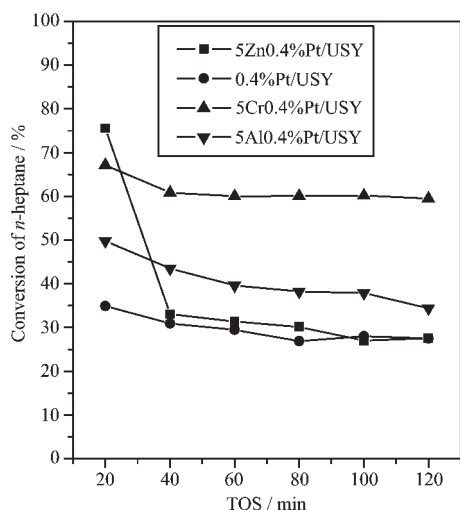

Fig.4　Conversion of *n*-heptane as a function of TOS (reaction time on stream) over different catalysts

shown in Fig.3, 5Zn0.4%Pt/USY possesses dominantly Lewis acidic sites, so it can be deduced that Brönsted acid sites may be essential to maintain the stable activity. Fig.5 gives the influence of the Cr loading on the conversion of *n*-heptane. It shows that the catalytic stabilities increase with the increase of the Cr loading. Fig.4 and 5 indicate that the addition of Cr and Al can improve the catalytic stability in the hydroisomerization of *n*-heptane compared to the catalysts containing only Pt, but Zn can not, even it shows a very high initial activity.
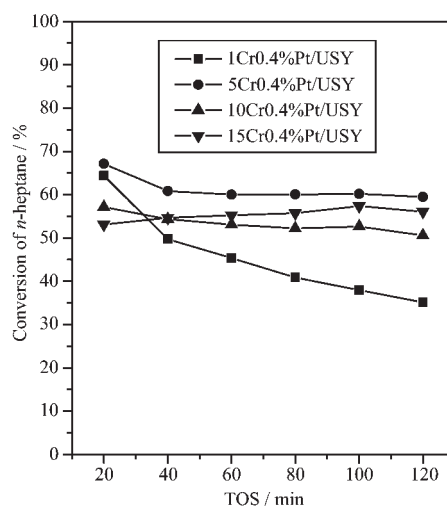

Fig.5　Conversion of *n*-heptane as a function of TOS (reaction time on stream) over catalysts with different Cr loadings

Table 2 gives the stable conversion of *n*-heptane, isomerization yield and selectivity at 230 ℃ and 120 min on stream over various catalysts. The catalytic conversion of 27.5% is obtained over 0.4% Pt/USY catalyst but with a very low selectivity of 59.9% for isomerization products. For the 0.8% Pt/USY catalyst, the isomerization selectivity is improved to 73.0%, while the conversion of the *n*-heptane drops to 20.0%. If the 0.4% Pt/USY catalyst is doped with a second metal (Cr, Al or Zn) with a 5∶1 molar ratio of M/Pt, both the isomerizaion selectivity and *n*-heptane conversion can be improved, especially for 5Cr0.4% Pt/USY. Moreover, comparing with 0.4%Pt/USY, all of the mCr0.4%Pt/USY catalysts show higher isomerization yield, which increases with the increase of Cr loading. Both 5Cr0.8% Pt/USY and 15Cr0.4%Pt/USY exhibit the isomerization selectivity around 80.0%, but

15Cr0.4%Pt/USY catalyst has a higher conversion of *n*-heptane.

Table 3 shows the effect of the reaction temperature on the catalytic activities of three supported catalysts. Over all the catalysts, the conversion of *n*-heptane increases drastically with the increasing of reaction temperature, while the rapid decrease of the selectivity for isomerization products is observed. The maximum yield of the isomerization products is found at 230 ℃. From Table 3, it is possible to compare the selectivity for the isomerization products over the 0.4%Pt/USY, 5Cr0.4%Pt/USY and 15Cr0.4%Pt/USY catalysts at a similar conversion of around 40.0%. Over 0.4%Pt/USY catalyst at the conversion of 41.5%, a very low selectivity of 22.2% for isomerization

products is obtained and a high reaction temperature of 250 ℃ is needed, while over 5Cr0.4%Pt/USY and 15Cr0.4% Pt/USY at the conversions of 41.6% and 40.5%, the high selectivies for isomerization products of 85.4% and 87.1%, respectively, are observed at a lower reaction temperatures of 220 ℃. Thus the addition of Cr dopant can remarkably improve the selectivity of the isomerization products while with much high activity.

Over metal/acid bifunctional catalysts, the hydroisomerization of *n*-paraffins can be explained by the classical bifunctional mechanism[12,13], which includes the de-hydrogenation and/or hydrogenation on the metal site and isomerization (cracking, condensation or cyclization) via carbenium ions on the acid site.

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

Catalyst	Conversion / %	Mono−branched product yield / %	Multi−branched product yield / %	Isomerization selectivity / %
0.4%Pt/USY	27.5	12.7	3.8	59.9
0.8%Pt/USY	20.0	11.1	3.5	73.0
5Al0.4%Pt/USY	38.2	17.9	6.4	63.8
5Zn0.4%Pt/USY	26.4	13.8	4.6	69.7
1Cr0.4%Pt/USY	35.1	14.9	4.4	55.1
5Cr0.4%Pt/USY	59.5	25.8	10.1	60.4
10Cr0.4%Pt/USY	50.6	26.4	9.3	70.6
15Cr0.4%Pt/USY	55.7	33.0	11.2	79.3
5Cr0.8%Pt/USY	48.7	29.5	9.9	80.9

Table 3 Comparison of the reactivities of hydroisomerization of *n*-heptane over selected catalysts at different reaction temperatures

Catalyst	T / ℃	Conversion / %	Mono-branched product yield / %	Multi-branched product yield / %	Isomerization selectivity / %
0.4%Pt/USY	230	27.5	12.7	3.8	59.9
	250	41.5	5.6	3.6	22.2
	270	51.1	5.0	3.2	16.0
5Cr0.4%Pt/USY	200	20.8	15.6	3.8	93.6
	210	32.2	22.0	6.4	88.2
	220	41.6	26.9	8.7	85.4
	230	59.5	25.8	10.1	60.4
	250	75.7	19.1	9.0	37.3
	270	87.7	11.5	6.3	20.3
15Cr0.4%Pt/USY	210	25.5	19.4	4.6	94.0
	220	40.5	27.1	8.1	87.1
	230	55.7	33.0	11.2	79.3
	260	77.9	25.1	10.9	46.3
	270	82.4	18.3	8.5	32.6

Therefore, the features of both acid and metal sites would exert a significant impact on the catalytic activity. Iso-paraffins, especially the multi-branched ones, are desired products owing to their very high octane number. Fig.3 tells that 5Cr0.4%Pt/USY and 5Al0.4%Pt/USY catalysts possess a less acid amount than 0.4%Pt/USY. This decreased acid amount may cause a less cracking reaction of carbenium ions on acid sites, and thus benefits for the selectivity for isomerization (see Tables 2 and 3). However, 5Zn0.4% Pt/USY almost losses its Brönsted acidity, and shows a poor catalytic stability. On the other hand, Pt dispersion can be improved by the addition of the second metal (Cr, Al and Zn) (see Table1) and it increases with the increase of loading of Cr, which is suggested to play an important role in improving both the selectivity for isomerization and the overall activity of the bimetallic catalysts. Mao et al.[10] hypothesized a new "desorption-transfer promoting site" added to the bifunctional catalytic site by the promoter, whose main role was to speed up desorption of the olefinic species from the acid site and transfer them to the metallic Pt site. In such a way, the residence time of the branched carbenium ions on the acid site is much shorter, and then avoiding from the further cracking. Therefore, it is mostly possible that the so called "desorption-transfer promoting site" is also created due to the addition of Cr (Al or Zn) species into Pt/ USY catalyst, which is one of the reasons for the enhanced isomerization selectivity.

3　Conclusion

The Pt-bearing USY zeolite catalysts promoted by Cr, Al or Zn are more catalytically active, stable and selective for isomerization than the catalyst containing only Pt. The catalyst promoted by Cr shows the highest n-heptane conversion and selectivity of isomerization products. Over the 0.4%Pt/USY catalyst at a reaction temperature of 250 ℃, the conversion of n-heptane is 41.5% with a very low selectivity of 22.2% for isomerization products, while over the 5Cr0.4%Pt/USY catalyst, the conversion of n-heptane is 41.6% with the selectivity for isomerization products as high as 85.4%, while the reaction temperature is only 220 ℃. The high activity and selectivity of the 5Cr0.4% Pt/USY catalyst is associated with the increased Pt dispersion and the slightly decreased acid amount, as well as the creation of the "desorption-transfer promoting site", due to the introduction of Cr into the catalyst.

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