Catalytic performance of Pt/HY- β in n-octane hydroisomerization

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Abstract: A bifunctional catalyst Pt/HY- β was prepared from a bimicroporous composite zeolite Y- β . Characterization results showed that the specific surface area, pore volume, and acid amount of the catalyst Pt/HY- β all decreased compared to the original zeolite. The catalytic performance of this catalyst in n-octane hydroisomerization was investigated in a fixed bed stainless steel tubular reactor. The results showed that at a hydrogen/n-octane volume ratio of 1000, pressure of 0.6 MPa, temperature of 230 °C and LHSV of 3 h⁻¹, the conversion of n-octane, yield of liquid, hydrocracking rate and yield of iso-octane were 52.32%, 88.66%, 12.60%, 39.51%, respectively.

Key words: Composite zeolite, Pt/HY- β catalyst, n-octane, hydroisomerization

1 Introduction

Hydroisomerization of hydrocarbons is one of the basic processes in the petroleum refining industry. It produces highly valuable chemicals, diesel oil, petrol gasoline and so on (Kuznetsov, 2003). The isomerization of n-alkanes is generally carried out over bifunctional catalysts containing a noble metal for hydrogenation/dehydrogenation and acid sites for skeletal isomerization via carbenium ions (Yang et al, 2007; Ramos et al, 2007; Woltz et al, 2006). In contrast to monofunctional catalysts, a synergism exists between the two kinds of active sites in bifunctional catalysts leading to an enhanced catalytic activity, suppressed deactivation and higher yields of products with tertiary and quaternary C atoms. Zeolite-based bifunctional catalysts have been found to be effective for isomerization of alkanes to enhance the research octane number (RON). Zeolites such as ZSM-5 (Lucas et al, 2006), Y (Kuznetsov, 2003; Saberi et al, 2001; Saberi and Mao, 2003) and β zeolite (Lucas et al, 2005 a, 2005 b, 2005 c; Sánchez et al, 2006) have been playing important roles in the modern petrochemical industry due to their abundant uniform microporous structure and strong intrinsic acidities. But the catalyst based on only one zeolite could not meet the requirement of the modern industry, hence composite zeolites had received much more attention especially in the field of catalysis (Fan et al, 2004; Alsobaai et al, 2007; Zeng et al, 2005).

Since composite zeolite Y- β has two different microporous structures and modified acidity (Li et al,

2005). Pt/HY- β has higher relative crystallinity, BET surface area, pore volume and Brönsted and Lewis acid sites than Pt/Y+ β . In n-octane hydroisomerization over these impregnated catalysts at 230 °C, the catalytic performance is in the order as follows: For the conversion of n-octane, Pt/HY- β >Pt/ β >Pt/Y>Pt/Y+ β ; For the cracking ratio of n-octane, Pt/ β >Pt/HY- β >Pt/Y+ β >Pt/Y; For the yield of liquid, Pt/Y>Pt/Y+ β >Pt/HY- β >>Pt/ β ; For the yield of iso-octane, Pt/HY- β >Pt/Y>Pt/ β >Pt/Y+ β (Jin et al, 2008). Therefore, the hydroisomerization catalyst Pt/HY- β is a catalyst with two different microporous structures, and through its controllable acidity and non-unique pore size, it would probably be a new catalyst for petrochemical industry.

In this paper, a bimicroporous composite zeolite catalyst Pt/HY- β was investigated for hydroisomerization of n-octane under different conditions.

2 Experimental

2.1 Catalyst

Zeolite NaY, cetyl-trimethylammonium(CTABr), distilled water and sodium silicate were mixed and stirred and the pH was adjusted to 12 with ammonia. Bimicroporous composite zeolite Y- β was obtained by hydrothermal crystallization in a 150 mL stainless steel kettle at a temperature of 140 °C. After that, the sample was filtered, dried and calcined at 550 °C for 6 h in a muffle furnace (Li et al, 2005). HY- β support was prepared by exchanging the sodium cation (Na⁺) in its sodium composite zeolite with ammonium cation (NH₄⁺) in 1M NH₄NO₃ solution for 3 times making the Na concentration less than 0.5% by weight. The

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Received November 17, 2008

reaction product was consequently filtered, washed with distilled water and then left at 120 °C overnight and calcined at 550 °C for 3 h, and zeolite HY-β was obtained.

The bifunctional catalyst was prepared by the incipient wetness impregnation technique. A measured amount of H₂PtCl₆ aqueous solution was added to zeolite HY-β at room temperature. The metal-loaded sample was dried at 120 °C overnight and calcined at 350 °C in air for 3 h. Then the desired catalyst Pt/HY-β containing 0.6 wt% Pt was obtained.

2.2 Characterization of the catalysts

2.2.1 Nitrogen adsorption

The BET surface area, micropore area, total pore volume and micropore volume of the synthesized catalysts were measured by using a Micromeritics ASAP2400 surface area and porosimetry system (Micromeritics Corporation, USA). The samples were vacuum degassed for 4 h at a temperature of 300 °C before measurements were performed.

2.2.2 Temperature programmed desorption of ammonia (NH₃-TPD)

NH₃-TPD analysis was conducted on AutoChem2910 automated chemisorption analyzer (Micromeritics Corporation, USA). Prior to the measurement, 0.1 g sample was treated in helium (50 mL·min⁻¹) at 350 °C for 30 min. Then ammonia was adsorbed by the sample at 120 °C until saturation. The desorption process was monitored by a thermal conductivity detector (TCD) in a temperature range from 120 °C to 550 °C at a heating rate of 10 °C·min⁻¹. The acidic sites of the catalysts were categorized into three groups according to the temperature at the peaks of acidic sites: The peak temperatures from 150 °C to 250 °C corresponded to weak acid sites, the peak temperatures from 250 °C to 400 °C to medium acid sites and the peak temperatures from 400 °C to 500 °C corresponded to strong acid sites. The total number of the acid sites was calculated based on the amount of the desorbed ammonia at the temperature from 150 °C to 500 °C.

2.2.3 X-ray diffraction

Powder X-ray diffraction (XRD) patterns of the catalysts were obtained using a Rigaku D/max2500 X-ray diffractometer (Rigaku Corporation, Japan) with Cu Ka radiation at 40 kV and 80 mA. The spectra were recorded in a range of 5°-35° and scanned at a rate of 8°·min⁻¹.

2.3 Test on catalytic performance

The catalytic performance of the catalysts in n-octane hydroisomerization was investigated in a fixed bed stainless steel tubular reactor of 10 mm inside diameter and 300 mm length, and with a thermocouple in the centre. The catalysts were crushed and sieved to select particles with size of 40-60 mesh range to avoid diffusion effects. About 5 mL of the catalyst was added in the tubular reactor that was placed vertically inside a temperature-programmed tubular furnace with a heating rate of 5 °C·min⁻¹. Prior to reaction, the Pt-containing catalyst was pre-treated with hydrogen at 350 °C for 3 h to enhance its performance. Then the catalyst was cooled under hydrogen to reaction temperature. The reactor was connected to an online GC-8A gas chromatograph (Shimadzu Corporation, Japan). The reaction products

were analyzed by using an OV-1 capillary column of 50m×0.20mm×0.32μm and a flame ionization detector (FID). From the chromatographic data, the n-octane conversion and yields of different reaction products were calculated.

Experimental conditions were as follows: H₂ to n-octane volume ratio, 600-1200; pressure, 0.3-1.2 MPa; temperature, 200-250 °C; LHSV=1-4 h⁻¹.

The conversion (wt%) of n-octane, yield of liquid (wt%), hydrocracking rate (wt%), yield of iso-octane (wt%), selectivity of mono-branched iso-octane(wt%), selectivity of di-branched iso-octane(wt%), ratio of isomerized n-octane to cracked n-octane (I/C) and ratio of mono- to di-branched isomers (M/D) were obtained by the following equations:

$$\text{Conversion} = \frac{W_{\text{tp}} - W_{\text{un}}}{W_{\text{tp}}} \times 100\% \quad (1)$$

where W_{tp} , W_{un} are the weight of the total products and the weight of the unconverted n-octane in products, respectively.

$$\text{Yield of liquid} = \frac{W_{\text{l}}}{W_{\text{tp}}} \times 100\% \quad (2)$$

where W_{l} is the weight of the liquid in products.

$$\text{Hydrocracking rate} = \frac{W_{\text{cp}}}{W_{\text{tp}}} \times 100\% \quad (3)$$

where W_{cp} is the weight of the cracked products.

$$\text{Yield of iso-octane} = \frac{W_{\text{ip}}}{W_{\text{tp}}} \times 100\% \quad (4)$$

where W_{ip} is the weight of iso-octane products.

$$\text{Selectivity of mono-branched iso-octane} = \frac{W_{\text{mip}}}{W_{\text{ip}}} \times 100\% \quad (5)$$

where W_{mip} is the weight of mono-branched iso-octane products

$$\text{Selectivity of di-branched iso-octane} = \frac{W_{\text{dip}}}{W_{\text{ip}}} \times 100\% \quad (6)$$

where W_{dip} is the weight of di-branched iso-octane products.

$$\text{I/C} = \frac{W_{\text{ip}}}{W_{\text{cp}}} \quad (7)$$

$$\text{M/D} = \frac{W_{\text{mip}}}{W_{\text{dip}}} \quad (8)$$

3 Results and discussion

3.1 Physical and chemical properties of the catalysts

The physical and chemical properties of the catalysts with and without Pt are shown in Table 1. The catalyst Pt/HY-β showed lower BET surface area, micropore area,

total pore volume and micropore volume than HY- β . This is possibly because that the impregnated metal Pt both took up and plugged some of the pores, making less area available for nitrogen adsorption. But the BET surface area of the bifunctional catalyst Pt/HY- β being $635 \text{ m}^2\cdot\text{g}^{-1}$ was still great and very important for hydroisomerization reactions.

Pt/HY- β possessed fewer total acids sites, slightly fewer medium-acid sites, fewer strong-acid sites but more weak-acid sites than HY- β (see Table 1).

Table 1 Physical and chemical properties of the catalysts HY- β and Pt/HY- β

Item	HY- β	Pt/HY- β
BET surface area, $\text{m}^2\cdot\text{g}^{-1}$	706	635
Micropore area, $\text{m}^2\cdot\text{g}^{-1}$	497	456
Total pore volume, $\text{mL}\cdot\text{g}^{-1}$	0.37	0.33
Micropore volume, $\text{mL}\cdot\text{g}^{-1}$	0.20	0.18
Total acid sites, $\text{mmol}\cdot\text{g}^{-1}$	1.03	0.88
Weak, $\text{mmol}\cdot\text{g}^{-1}$	0.14	0.32
Medium, $\text{mmol}\cdot\text{g}^{-1}$	0.49	0.44
Strong, $\text{mmol}\cdot\text{g}^{-1}$	0.40	0.12

Fig. 1 presents the XRD patterns of the catalysts HY- β and Pt/HY- β . The characteristic diffraction peaks of Pt/HY- β was in agreement with that of HY- β , and it suggested that Pt had high dispersion on the catalyst.

Fig. 1 XRD patterns of the catalysts prior with and without Pt
a: XRD pattern of HY- β ; b: XRD pattern of Pt/HY- β

3.2 Catalytic properties

3.2.1 Effect of $\text{H}_2/\text{n-octane}$

The influence of $\text{H}_2/\text{n-octane}$ volume ratio on the conversion of n-octane, yield of liquid, hydrocracking rate of n-octane and yield of iso-octane was investigated. As shown in Fig. 2, the conversion and hydrocracking rate of n-octane decreased with increasing $\text{H}_2/\text{n-octane}$ (volume) ratio from 600 to 1,400, while the yield of liquid increased gradually. The yield of iso-octane reached a maximum when the $\text{H}_2/\text{n-octane}$ volume ratio was 1,000, and then decreased moderately with further increasing $\text{H}_2/\text{n-octane}$ volume ratio. This was caused by the increase of the overall ($\text{n-C}_8 + \text{H}_2$) space velocity and the partial pressure of hydrogen which was

negative for hydroconversion reactions (Holló, 2002). All these also showed the importance of H_2 in the isomerization process. The function of H_2 in isomerization could be interpreted as suppressing cracking reactions and keeping the catalytic activity by inhibiting coke formation. To maximize isomerization yield, a suitable $\text{H}_2/\text{n-octane}$ ratio should be determined, and the favorable $\text{H}_2/\text{n-octane}$ (volume) ratio range was from 1,000 to 1,200 (Fig. 2).

Fig. 2 Influence of hydrogen/n-octane volume ratio on hydroisomerization of n-octane
Conditions: Pt/HY- β catalyst; reaction pressure, 0.3 MPa; LHSV, 3 h^{-1} ; reaction temperature, 230°C

3.2.2 Effect of pressure

The influence of the reaction pressure on the conversion of n-octane, yield of liquid, hydrocracking rate of n-octane and yield of iso-octane was investigated at 230°C . As shown in Fig. 3, the conversion and hydrocracking rate of n-octane decreased while the yield of liquid increased gradually along with increasing pressure from 0.3 MPa to 1.2 MPa. The yield of iso-octane reached the maximum when the pressure was 0.6 MPa, and then decreased slowly with a further increasing pressure. At pressures higher than 0.6 MPa, the yield of liquid and the hydrocracking rate of n-octane were stable. These results were similar to those obtained by changing the $\text{H}_2/\text{n-octane}$ volume ratio and clearly showed the participation of H_2 which was negative in the isomerization process in the literature (Holló et al, 2002). The favorable reaction pressure was from 0.6 MPa to 0.9 MPa.

3.2.3 Effect of temperature

The conversion of n-octane, yield of liquid, hydrocracking rate of n-octane and yield of iso-octane in the reaction temperature range of $200\text{--}250^\circ\text{C}$ are shown in Fig. 4. The conversion and hydrocracking rate of n-octane increased with increasing temperature, while the yield of liquid decreased gradually. The yield of iso-octane reached a maximum (39.51%) at 230°C . So, the favorable reaction temperature range was from 230°C to 240°C .

Fig. 3 Influence of reaction pressure on hydroisomerization of octane
Conditions: Pt/HY- β catalyst; H_2 /n-octane volume ratio, 1000;
LHSV, 3 h^{-1} ; reaction temperature, $230\text{ }^\circ\text{C}$

Fig. 4 Influence of reaction temperature on hydroisomerization of octane
Conditions: Pt/HY- β catalyst; H_2 /n-octane volume ratio, 1000; reaction
pressure, 0.6 MPa ; LHSV, 3 h^{-1}

In the presence of H_2 , n-octane undergoes several reactions such as hydroisomerization, hydrocracking and even some slight dehydrocyclization. The products distribution over Pt/HY- β catalyst are listed in Table 2. The major mono-branched isomers were 2-methyl heptane (2MC_7), 3-methyl heptane (3MC_7), 4-methyl heptane (4MC_7); and the major di-branched isomers were 2,2-dimethyl hexane ($2,2\text{DMC}_6$), 2,3-dimethyl hexane ($2,3\text{DMC}_6$), 2,4-dimethyl hexane ($2,4\text{DMC}_6$), 2,5-dimethyl hexane ($2,5\text{DMC}_6$), 3,3-dimethyl hexane ($3,3\text{DMC}_6$), 3,4-dimethyl hexane ($3,4\text{DMC}_6$). No tri-branched pentane was detected in the reaction products. The trace amount of the cyclooctane products (Cyc-C_8) were observed to reach a maximum (0.44%) at $220\text{ }^\circ\text{C}$ while aromatic products had not been detected in the reaction products.

Table 2 Product distribution (wt%) and product ratios
in n-octane hydroisomerization

Product	$200\text{ }^\circ\text{C}$	$210\text{ }^\circ\text{C}$	$220\text{ }^\circ\text{C}$	$230\text{ }^\circ\text{C}$	$240\text{ }^\circ\text{C}$	$250\text{ }^\circ\text{C}$
2MC_7	4.23	5.45	7.68	9.81	8.15	5.05
3MC_7	5.36	7.34	10.54	13.41	12.23	7.60
4MC_7	2.05	2.64	3.72	4.75	3.94	2.44
$2,2\text{DMC}_6$	0.16	0.41	0.78	1.13	1.84	1.89
$2,3\text{DMC}_6$	0.44	0.93	1.43	1.67	1.89	1.40
$2,4\text{DMC}_6$	0.87	1.68	2.71	4.29	4.26	2.57
$2,5\text{DMC}_6$	0.63	1.21	1.95	3.10	3.07	1.85
$3,3\text{DMC}_6$	0.22	0.44	0.69	1.04	1.11	1.18
$3,4\text{DMC}_6$	0.28	0.29	0.30	0.32	0.37	0.28
Cyc-C_8	0.11	0.27	0.44	0.21	0.14	0.12

Conditions: Pt/HY- β catalyst; H_2 /n-octane volume ratio: 1000; reaction pressure: 0.3 MPa ; LHSV: 3 h^{-1}

The composition of the iso-octane fraction versus the reaction temperature is shown in Fig. 5. It was clear that the hydroisomerization products consisted of 81.78% mono-branched isomers at low temperature ($200\text{ }^\circ\text{C}$). With the reaction temperature increasing, the selectivity of di-branched isomers increased up to 37.79% in the isomerization products, but in all cases the mono-branched isomers were the major products. These results strongly suggested that the di-branched isomers were mostly formed in successive reactions from mono-branched heptane, and they appeared largely at high temperature. At low temperature, the conversion of n-octane to di-branched isomers and to cracking products was very slow, which was in agreement with the literature (Roussel et al, 2005).

Fig. 6 shows the yield of different products versus temperature over Pt/HY- β catalyst. The hydroconversion products consisted of both isomerization and cracking products even at low temperature. For the isomerization products, the maximum yield of mono-branched isomers and di-branched isomers were 27.97% at $230\text{ }^\circ\text{C}$ and 12.54% at $240\text{ }^\circ\text{C}$, respectively. Mono-branched isomers were the major isomers. This product distribution was in good agreement with the classical hydroisomerization mechanism. The hydroisomerization reactions proceeded successively through mono-, di-, and tri-branched intermediates formed by type A (methyl shift) and type B [via protonated cyclopropane (PCP)] isomerization mechanism (Blomsma et al, 1996; Zhang and Panagiotis, 1999). Isomerization via PCP intermediates was responsible for the formation of the di-branched isomers. The cracking products appeared with moderate conversions because skeletal isomerization of carbenium ion intermediates competed against the cracking reactions at high temperatures.

Fig. 5 Hydroisomerized products distribution of n-octane
Conditions: Pt/HY- β catalyst; H_2 /n-octane volume ratio, 1000;
reaction pressure, 0.6 MPa; LHSV, 3 h^{-1}

Fig. 6 Influence of reaction temperature on products yield
(monobranched, di-branched and cracked products)
Conditions: Pt/HY- β catalyst; H_2 /n-octane volume ratio, 1000;
reaction pressure, 0.6 MPa; LHSV, 3 h^{-1}

3.2.4 Effect of LHSV

The effect of reactant flow rate, LHSV, (liquid hourly space velocity defined as $1/\text{contact time}$) on conversion of n-octane, yield of liquid, hydrocracking rate of n-octane and yield of iso-octane was studied at 230°C , for a H_2 to n-octane volume ratio (H_2 /n- C_8 ratio) of 1000:1. As shown in Fig. 7, with increasing LHSV, the contact time of n-octane on the Pt/HY- β catalyst decreased, thus, both the conversion and the hydrocracking rate of n-octane decreased, while the yield of liquid increased gradually. The yield of iso-octane reached

its maximum when the LHSV was 3 h^{-1} , and then decreased with further increase of LHSV. Both the conversion and the hydrocracking rate of n-octane decreased sharply with the LHSV increasing from 1 h^{-1} to 2 h^{-1} . These results showed that low flow rates were favorable to hydrocracking reactions. The favorable LHSV range was from 2 h^{-1} to 3 h^{-1} .

Fig. 7 Influence of LHSV on hydroisomerization of n-octane
Conditions: Pt/HY- β catalyst; H_2 /n-octane volume ratio, 1000;
reaction pressure, 0.6 MPa; reaction temperature, 230°C

As shown in Fig. 8, the ratio of the isomerized to cracked n-octanes (I/C) increased with increasing LHSV (decreasing contact time). This result confirmed that n-octane was converted into isomers first, and then into cracking products, as the following products sequence: n- $C_8 \rightarrow$ mono-branched isomers $\rightarrow$ di-branched isomers $\rightarrow$ cracking products, which was in agreement with that reported in literature (Sánchez, 2006). Furthermore, the ratio of mono- to multi-branched isomers (M/D) was also increased with increasing LHSV, indicating that the isomerization first led to mono-branched isomers, and then to multi-branched ones.

3.2.5 Time on stream

The effect of the time on n-octane conversion, yield of liquid, hydrocracking rate of n-octane and yield of iso-octane was studied at 230°C over Pt/HY- β . As shown in Fig. 9, with increasing time, the conversion and the hydrocracking rate of n-octane decreased while the yields of liquid and iso-octane increased slowly within 1h. Then the n-octane conversion, yield of liquid, hydrocracking rate of n-octane and yield of iso-octane changed very little.

3.2.6 Contrast experiment

The performance of n-octane hydroisomerization over the mono-functional catalyst HY- β was also investigated at H_2 /n-octane volume ratio of 1000, pressure of 0.6 MPa, temperature of 230°C and LHSV of 3 h^{-1} . The results showed that the conversion of n-octane, yield of liquid, hydrocracking rate of n-octane and yield of iso-octane were 9.24%, 95.3%, 5.47%, 3.77%, respectively, indicating that the bifunctional

Fig. 8 Ratio of the formation rates of the isomerized/cracked (I/C) and of the mono-/di-branched isomers (M/D) vs. LHSV
Conditions: Pt/HY- β catalyst; H₂/n-octane volume ratio, 1000; reaction pressure, 0.6 MPa; reaction temperature, 230 °C

Fig. 9 Influence of reaction time on hydroisomerization of octane
Conditions: Pt/HY- β catalyst; H₂/n-octane volume ratio, 1000; reaction pressure, 0.6 MPa; LHSV, 3 h⁻¹; reaction temperature, 230 °C

catalyst Pt/HY- β had higher isomerization activity to n-octane than HY- β . Especially, the conversion of n-octane and yield of iso-octane over Pt/HY- β were 5.66 and 10.48 times that respectively over HY- β over HY- β under the same conditions. It was clear that the high activity and selectivity of the Pt-containing catalyst (Pt/HY- β) can be attributed to not only the high dispersion but also its great hydrogenating-dehydrogenating capacity in the hydroisomerization processes (Zhang and Panagiotis, 1999; Fúnez et al, 2008). The results of HY- β was possibly caused by the higher number of strong acid sites which was available to the cracking reactions on the surface of HY- β . Furthermore, di-branched isomers were not detected in the process of n-octane hydroisomerization over catalyst HY- β . The results encourage the use of Pt/HY- β as a new hydroisomerization catalyst for treatment of heavy alkanes to produce their isoalkanes.

4 Conclusions

The specific surface area, pore volume, acid amount and

crystallinity of the catalyst Pt/HY- β were all lower than those of catalyst HY- β . Under the favorable conditions of hydrogen/n-octane volume ratio of 1000, pressure of 0.6 MPa, temperature of 230 °C and LHSV of 3 h⁻¹, the conversion of n-octane, yield of liquid, hydrocracking rate of n-octane and yield of iso-octane were 52.32%, 88.66%, 12.60%, 39.51%, respectively. Especially, the conversion of n-octane and yield of iso-octane over Pt/HY- β catalyst were 5.66 and 10.48 times that respectively over HY- β under the same conditions. The hydroconversion of n-octane over Pt/HY- β catalyst produce both isomerization and cracking products. And it was suggested that the di-branched isomers were mostly formed in successive reactions from mono-branched heptane at high reaction temperature, and n-octane was converted into isomers first, then into cracking products successively. For the isomerization products, the maximum yield of the mono-branched isomers and di-branched isomers were 27.97% at 230 °C and 12.54% at 240 °C, respectively.

Acknowledgements

This work is a project sponsored by China Petroleum and Chemical Corporation (No.: 090701). Meanwhile, we also thank Fushun Research Institute of Petroleum and Petrochemicals of Sinopec for generous help.

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(Edited by Zhu Xiuqin)