Selective hydroisomerization of *n*-dodecane over platinum supported on zeolites

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Abstract In this study, in order to develop catalysts for the selective isomerization of higher paraffin, the hydroisomerization reaction of *n*-dodecane was performed as a model reaction. Pt/ZSM-48, Pt/HZSM-5, Pt/HY, and Pt/SAPO-11 were examined for the selective hydroisomerization of *n*-dodecane. The catalysts were characterized via X-ray powder diffraction, N₂ adsorption, and the temperature-programmed desorption of ammonia. Among the catalysts studied, the Pt/HZSM-48 catalyst exhibited the best isomerization selectivity in the hydroisomerization reaction of *n*-dodecane, which is attributed to the moderate acid sites and medium-sized pores present in the HZSM-48. The highest iso-dodecane yield was obtained at a reaction temperature of 280 °C in the Pt/HZSM-48 catalyst. The optimal selectivity of the *n*-dodecane hydroisomerization over the Pt/SAPO-11 catalyst was obtained at approximately 300 °C, which was slightly higher than that of the Pt/HZSM-48 catalyst.

Keywords Hydroisomerization · Dodecane · Pt · HZSM-48 · SAPO-11

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Introduction

The Fischer-Tropsch (F-T) synthesis is a reaction that introduces a synthesis gas (CO/H_2) into a catalyst-charged reactor and generates a higher hydrocarbon [1, 2]. The higher hydrocarbon generated from the F-T synthesis is primarily wax, and has a low pour point. In order to improve the cold-flow characteristics (viscosity, pour point, and freezing point) of the F-T synthetic oil, a higher *n*-paraffin in the F-T oil should be converted to a higher iso-paraffin through hydroisomerization. The hydroisomerization reaction of *n*-paraffin is accompanied by a hydrocracking reaction and increases the yield of low molecular products. While multi-branched alkane is more prone to cracking, mono-branched paraffin is not. Thus, it is clear that multi-branching should be limited in order to reduce the cracking reactions.

The hydroisomerization reaction usually occurs in the dual functional catalysts, in which the hydrogenation/dehydrogenation and skeletal isomerization through carbenium ions occur at a metal active component and acid site, respectively. There has been research reported on the acid supports used in hydroisomerization catalysts as amorphous oxides and oxide compounds (HF-processed Al_2O_3 , silica-alumina, and ZrO_2/SO_4^{2-}), zeolite (Y, beta, modernite, ZSM-5, and ZSM-22), and mesoporous materials (MCM-41, AlMCM-41) [3–14]. Noble metals (Pd and Pt) and dual-metal systems (Ni/Co, Ni/W, Ni/Mo, and W/Mo in its sulfided form) have been used in the hydrogenation/dehydrogenation [3, 5, 10–12, 14].

In this study, platinum catalysts impregnated on different types of zeolites were synthesized, and the hydroisomerization reaction over the catalysts was investigated using *n*-dodecane as a model reactant. The effects of the pore size and acid characteristics of the zeolite on the catalytic performance in the *n*-dodecane hydroisomerization were analyzed. The effects of the impregnated amount of Pt on the acid characteristics and *n*-dodecane hydroisomerization over the SAPO-11 were also investigated.

Experimental

HZSM-5 and HY were purchased from Zeolyst. SAPO-11 was purchased from Tianjin Chemist Scientific Ltd. Pt/zeolite catalysts were obtained via the impregnation of the zeolite with an aqueous H_2PtCl_6 solution. After the impregnation, the materials were dried at 120 °C for 4 h, and then calcined at 480 °C for 4 h. Pt/HZSM-48 catalyst was provided from Korea Research Institute of Chemical Technology. Prior to the reaction, the catalysts were reduced in situ in hydrogen at 400 °C for 4 h.

The X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/max-2500 X-ray diffractometer fitted with Cu K α radiation (k = 1.5404 Å). The BET surface area was determined using a Micromeritics ASAP-2010 physical analyzer using N₂ adsorption at 196 °C. The NH₃–TPD was performed in helium (40 mL/min), and the ammonia was adsorbed at 100 °C [15]. The desorption process was monitored with a TCD at a temperature ramp from 100 to 600 °C with a

heating rate of 20 °C/min. The distribution of the acid sites on the zeolites was deconvolved by simulating the TPD plots through Gaussian curves.

The hydroisomerization of the *n*-dodecane as a model reaction was undertaken at atmospheric pressure in a continuous-flow, fixed-bed stainless-steel reactor with an H_2/n - C_{12} molar ratio of 15 and WHSV of 2 h⁻¹. The amount of catalyst was 0.24 g. The products were analyzed using an online gas chromatograph (YL 6100 GC) equipped with FID and a HP-5 (capillary 30 m × 0.32 mm).

Results and discussion

Pt/zeolite catalysts

Figure 1 shows the NH₃-TPD results of the zeolite supports and the 0.5 wt% platinum catalysts impregnated on HY, HZSM-5, and HZSM-48. Peaks were observed in the NH₃-TPD of HZSM-5 catalysts at 250 and 430 °C, which correspond to the weak and strong acid sites, respectively. The NH₃-TPD pattern of the Pt/HZSM-5 catalyst was similar to that of the HZSM-5 catalyst with only a difference in terms of the reduced amount of the acid sites. There were two peaks in the NH₃-TPD of HY catalysts at 230 and 350 °C, which correspond to the weak and medium strength acid sites, respectively [16]. The amount of acid sites slightly decreased in the Pt/HY catalysts when compared with the HY catalysts. There were two peaks in the NH₃-TPD of Pt/HZSM-48 catalyst at 220 and 360 °C, which is similar to the NH₃-TPD of Pt/HY catalyst. There were fewer acid sites of the Pt/HZSM-48 catalyst than in the Pt/HZSM-5 and Pt/HY catalysts. The acid site characteristics of the Pt/HZSM-48 catalyst, however, were more developed at the medium strength acid site of 350 °C than at the weak acid site of 220 °C.

Figure 2 shows the n-dodecane conversion, selectivity of the iso-dodecane, and yield of the iso-dodecane in the n-dodecane hydroisomerization reaction under



Fig. 1 NH₃-TPD curves of the catalysts



Fig. 2 a Conversion of *n*-dodecane, **b** selectivity to iso-dodecane, and **c** yield of iso-dodecane over the catalysts (reaction condition: H_2/n -dodecane = 2, reaction pressure 1 atm, and WHSV 40 h⁻¹)

conditions of a H₂/*n*-dodecane of 2, a reaction pressure of 1 atm, and a WHSV of 40 h⁻¹. The *n*-dodecane conversion increased in all catalyst systems according to the rising temperature regardless of the zeolite carriers. The *n*-dodecane conversion occurred in the order of Pt/HZSM-48 > Pt/HY(12) > Pt/HY(60) > Pt/HZSM-5. The findings of the effects of the reaction temperature on the selectivity to iso-

Table 1Effect of platinum loading on the N_2 adsorption analysis results of the samples		$S_{\rm BET}~({\rm m^2/g})$	$V_{\rm total}~({\rm cm}^3/{\rm g})$
	SAPO-11	121	0.15
	SAPO-11 Pt 0.2 (wt%)	82	0.13
	SAPO-11 Pt 0.5 (wt%)	92	0.13
	SAPO-11 Pt 0.8 (wt%)	43	0.11



Fig. 3 Effect of platinum loading on the XRD of the SAPO-11

dodecane indicate that the Pt/HZSM-48 and Pt/HY catalysts had a temperature range within the optimal selectivity. In particular, the Pt/HZSM-48 catalysts recorded a very high selectivity of 80% or more in the range of 230–280 °C. As a result, the highest yield of the iso-dodecane (60 wt%) was obtained with the Pt/HZSM-48 catalyst at 280 °C.

Efficient catalysts for *n*-dodecane hydroisomerization are only possible through the minimization of the cracking reactions. A cracking reaction lowers the selectivity of the iso-dodecane that decomposes the *n*-dodecane into light products. Selectivity in the iso-dodecane usually depends on the balance between the metal and acidity of the catalyst: the appropriate balance plays a decisive role in determining the reactivity and selectivity of dual functional catalysts [3]. The catalysts of high hydrogenation ability and low acidity can be optimal for maximum hydroisomerization reactions. Because it contains strong acid sites, HZSM-5 is more prone to cracking reactions than the isomerization reaction of *n*-dodecane. The HZSM-48 catalyst has fewer acid sites than other zeolites and contains only weak and medium strength acid sites without strong acid sites, thus being rarely subject to cracking reactions when compared with other zeolites. Although the Pt/HY catalysts have similar acid site strengths to those of the Pt/HZSM-48 catalyst, the iso-dodecane selectivity was much lower than that of the Pt/HZSM-48 catalyst.



Fig. 4 Effect of the platinum loading on the NH₃-TPD of the SAPO-11

The Y zeolite pores, which are formed via a 12-membered ring, have a relatively large diameter of 7.4 Å. The inner cavity has a diameter of 12 Å. The ZSM-48 zeolite has a ten-membered ring channels with a one-dimensional pore system and medium pore size (5.3-5.8 Å) [17]. The Pt/HY catalysts have large pore openings and accordingly produce multi-branched iso-paraffin relatively easily, which is highly prone to cracking. The pore opening of the Pt/HZSM-48 catalysts is sufficiently small compared to that of the Pt/HY catalysts, which means that the Pt/HZSM-48 catalysts deter large iso-paraffins from reacting at acid sites inside the pores and have superior selectivity in the *n*-dodecane conversion compared to the Pt/HY catalysts. Consequently, the Pt/HZSM-48 catalysts have weak acid sites and small pore sizes, thus being effective for producing iso-dodecane in hydroisomerization reactions.

Pt/SAPO-11 catalysts

Table 1 presents the effect of the platinum loading on the N_2 adsorption analysis results of the SAPO-11, and it can be seen that the BET surface area of the SAPO-11 decreased with increasing amounts of platinum. The effects of the platinum loading on the XRD of the SAPO-11 samples are shown in Fig. 3. There are no



Fig. 5 Effect of the platinum loading on **a** the conversion of *n*-dodecane, **b** the selectivity to iso-dodecane, and **c** the yield of iso-dodecane over the SAPO-11 (reaction conditions: H_2/n -dodecane = 2, reaction pressure 1 atm, and WHSV 40 h⁻¹)

significant changes to the XRD patterns of the SAPO-11 until the Pt loading increases to 0.8 wt%, which indicates that the SAPO-11 structure is not significantly affected by the Pt loading.

In the results of the NH_3 -TPD analysis shown in Fig. 4, two peaks at weak acid site near 160 °C and a medium strength acid site near 240 °C can be observed over

the Pt/SAPO-11 catalysts. While increasing the Pt loading had little impact on the peak near 160 °C, the maximum temperature at the medium strength acid site increased slightly to highest 280 °C for the Pt 0.8 wt%/SAPOI-11 catalyst. These findings indicate that the increasing Pt loading causes a slight increase in the acid strength of a medium strength acid site and does not significantly reduce the amount of acid sites despite the apparently reduced BET surface area.

The *n*-dodecane conversion in hydroisomerization was very low over the SAPO-11, as shown in Fig. 5. With an increasing Pt loading, the *n*-dodecane conversion increased by approximately 40–60% over a catalyst loading of 0.2–0.8 wt% Pt at a reaction temperature of 300 °C and of \geq 90% at 350 °C. Selectivity to the iso-dodecane reaches its highest value in the range of 230–300 °C. The results demonstrate that the iso-dodecane yield achieved its highest value at 300 °C. The iso-dodecane yield was not significantly influenced by the Pt loading in the range of 0.2–0.8 wt% and reached its highest near 40%. The structure of the SAPO-11 consists of a one-dimensional ten-membered ring channel system with a pore size of 3.9 × 6.4 Å [18]. The Pt/SAPO-11 catalyst, which did not contain strong acid sites but had small pore sizes, exhibited excellent activity and selectivity in the hydroisomerization reaction of the *n*-dodecane.

Conclusions

Among the catalysts that use zeolites as support, the Pt/HZSM-48 catalyst exhibited the best isomerization selectivity in the hydroisomerization reaction of *n*-dodecane, which is attributed to the moderate acid sites and medium-sized pores of the HZSM-48. The highest iso-dodecane yield was obtained at a 280 °C reaction temperature in the Pt/HZSM-48 catalyst. The Pt/SAPO-11 catalyst showed remarkable performance in the *n*-dodecane hydroisomerization reaction of the *n*-dodecane due to its small pore size and lower acidity. The optimal selectivity of the *n*-dodecane hydroisomerization over the Pt/SAPO-11 catalyst was obtained at approximately 300 °C, which was slightly higher than that of the Pt/HZSM-48 catalyst.

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