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Hydroconversion of *n*-Dodecane Over Nanoporous Catalysts

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Platinum catalysts impregnated on different nanoporous materials, Meso-MFI, Si-SBA-15 and Al-SBA-15, were synthesized, and the hydroconversion of *n*-dodecane over these catalysts was performed. The catalytic characteristics were analyzed by Brunauer–Emmett–Teller surface area, X-ray diffraction, N_2-adsorption–desorption and temperature programmed desorption of NH_3. The effects of operation parameters, such as temperature and pressure, on the catalytic activities were investigated. The catalytic activities were affected considerably by the acidic properties of the catalysts, temperature and pressure. Higher acidity, high temperature and low hydrogen pressure resulted in higher hydroconversion and facilitated hydrocracking. The weak acidity, low temperature and high hydrogen pressure resulted in lower hydroconversion and higher selectivity to *i*-dodecane.

Keywords: *n*-Dodecane, Hydroconversion, Nanoporous Catalyst, Pt/Meso-MFI, Pt/Al-SBA-15.

1. INTRODUCTION

The depletion of petroleum based fossil fuels and global warming problem has highlighted the need for alternative fuel production. Biomass has attracted considerable interest owing to its carbon neutral properties in terms of CO_2 emissions as well as the dependency on fossil fuels. The biomass to liquid process (BTL) is considered one of the most promising commercial technologies to convert biomass to liquid hydrocarbons via the Fischer-Tropsch reaction of synthesis gas generated by the gasification of biomass.[1] In this process, heavy long-chain paraffinic hydrocarbons, such as higher molecular weight wax, are mainly produced and should be converted to more valuable compounds, such as iso-paraffinic hydrocarbons, to improve the oil quality. To accomplish this, hydroconversion reactions, such as hydroisomerization and hydrocracking, are the most representative process for FT-wax upgrading.

The hydroconversion reaction is generally performed over a bifunctional catalyst with acidic and metallic functions. Metal species can play a role in the hydrogenation/dehydrogenation step, and the acidic sites of the catalyst are involved in the activation of C—C and C—H bonds.[2]

Therefore, the activity, selectivity and stability of bifunctional catalyst can be modified by controlling the acidic/metallic function ratio.

Pt, Pd and Ni are useful metal species for hydroconversion, and zeolites are used mainly for acid catalysts. Zeolites possess a regular pore structure and enough acidic sites to promote the hydroconversion of *n*-paraffin, whereas their microporosity can cause intracrystalline diffusion resistance for large molecules exceeding the size of the zeolite micropores. Therefore, an acid catalyst with a large pore structure can be employed in the hydroconversion of heavy wax.[3]

Nanoporous materials, such as MCM-41, MCM-48 and SBA-15, have attracted attention in the hydroconversion of wax due to their mild acidity and well-ordered nanoporous (> 2 nm) structures. On the other hand, the few studies examined the use of nanoporous acid catalysts for hydroconversion. Moreover, these studies were limited to hydroisomerization.[4] For example, the bifunctional Pt/Al-MCM-41 catalyst exhibited higher activity for the hydroisomerization of *n*-hexane, *n*-hexadecane and wax with

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improved cold flow properties, such as viscosity, pour point and freezing point. The reaction mechanism between hydroisomerization and hydrocracking over Pt/Al-MCM-41 is dependent on the relative ratio of the metallic and acidic functions of the catalyst.[4] A Meso-MFI catalyst with a zeolite and nanoporous structure, simultaneously, was recently synthesized and employed for a range of catalytic reactions.[5] Nevertheless, to the best of our knowledge, there are no reports on the use of Meso-MFI catalysts for the hydroconversion reaction. In addition, the hydroisomerization of *n*-dodecane over Pt/Al-SBA-15 catalyst has not been reported.

This study examined the catalytic performance of two types of nanoporous catalysts (Pt/Al-SBA-15, Pt/Meso-MFI), which have distinct acidic properties, for the hydroisomerization of *n*-dodecane. The reactivity and selectivity was also investigated in terms of characteristics of the catalysts.

2. EXPERIMENTAL DETAILS

2.1. Catalyst Preparation

Si-SBA-15 and Al-SBA-15 nanoporous materials were synthesized using the procedure reported elsewhere.[6] The Si/Al ratio of Al-SBA-15 were controlled to 20, 40 and 80. A Meso-MFI with a Si/Al molar ratio of 20 was synthesized using a procedure described elsewhere.[5] Pt containing catalysts were prepared with an aqueous $Pt(NH_3)_4(NO_3)_2$ solution using the incipient wetness impregnation method and the Pt loading was 0.5 wt.%.

2.2. Catalyst Characterization

The N_2 adsorption/desorption isotherms were obtained at −196 °C using a Micromeritics ASAP 2000. The powder X-ray diffraction (XRD, Rigaku D/MAX-III) patterns were obtained using Cu-K_α radiation. The surface acidity of the catalysts was measured using the temperature programmed desorption of ammonia (NH_3-TPD, BELCAT, BEL Japan Inc., Osaka, Japan).

2.3. Model Reaction

The hydroconversion of *n*-dodecane over a bifunctional catalyst was carried out using a batch-type reactor. The Pt containing catalyst was reduced under H_2 flow at 500 °C for 3 h. The reduced catalyst (0.5 g) was moved to a batch reactor with *n*-dodecane (75 ml) and the reaction started with stirring under high temperatures and pressures. The liquid product sampled at specific times on stream was analyzed by gas chromatography/mass spectroscopy (GC/MS, Agilent Technologies) equipped with UA-5 (Ultra ALLOY-5MS/HT; 5% diphenyl and 95% dimethylpolysiloxane, length 30 m, i.d. 0.25 mm, film thickness 0.5 μm) column.

3. RESULTS AND DISCUSSION

3.1. Characterization of Catalysts

Table I lists the textural properties of the prepared catalysts. Pt/Meso-MFI, Pt/Si-SBA-15, and Pt/Al-SBA-15 (20), (40) and (80) exhibited higher specific surface areas of 486, 571, 517, 547, and 559 m^2/g, respectively. The respective pore volumes of the catalysts were 0.70, 0.81, 0.74, 0.88, and 0.81 cm^3/g. The pore size of all catalysts was > 4 nm, which is sufficient for a large molecule like *n*-dodecane to diffuse in the catalyst. The low-angle XRD patterns of Pt/Si-SBA-15 and Pt/Al-SBA-15, (Fig. 1(a)) revealed the characteristic peaks of hexagonal nanoporous SBA-15. This suggests that the incorporation of Pt into SBA-15 does not destroy the original hexagonal mesostructures of SBA-15 itself. The high-angle XRD patterns of the Meso-MFI and Pt/Meso-MFI catalyst (Fig. 1(b)) were in accordance with conventional MFI zeolite after Pt impregnation with a slight decrease in the characteristic peak intensity.

NH_3-TPD is used to analyze the acidic properties of a catalyst. The peaks at approximately 200 °C and 400 °C are generally attributed to NH_3 desorption from the weak acid sites and strong Brönsted acid sites, respectively. The peak area means the number of acid sites of the catalyst. Figure 2 shows the NH_3-TPD curves of the Pt/Si-SBA-15, Pt/Al-SBA-15 and Pt/Meso-MFI catalysts. Both weak and strong acid sites were observed in the Pt/Meso-MFI catalyst, and the acid amount was much higher than in the other catalysts. In contrast, the Pt/Al-SBA-15 catalyst contained mainly weak acid sites and the number increased with decreasing Si/Al ratio.

3.2. Catalytic Activities

Figure 3 shows the temporal conversion and selectivity of the Pt/Si-SBA-15, Pt/Al-SBA-15 and Pt/Meso-MFI catalysts at 350 °C and 20 bar. The conversion of *n*-dodecane occurred in the order of Pt/Meso-MFI $\gg$ Pt/Al-SBA-15 (20) $>$ Pt/Al-SBA-15 (40) $>$ Pt/Al-SBA-15 (80) $>$ Pt/Si-SBA-15, which indicates higher acid strength, and the amount of the acid site of Pt/Meso-MFI catalyst plays an important role in the conversion of *n*-dodecane. In the same manner, Pt/Al-SBA-15 with a Si/Al ratio of 20 showed the highest conversion of *n*-dodecane, whereas Pt/Si-SBA-15 exhibited the lowest activity among the Pt/SBA-15 catalysts. On the other hand, the selectivity

Table I. Textural properties of catalysts.

Catalyst	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)	Si/Al
Pt/Si-SBA-15	571	0.81	7.0	–
Pt/Al-SBA-15 (20)	517	0.74	6.6	20
Pt/Al-SBA-15 (40)	547	0.88	6.6	40
Pt/Al-SBA-15 (80)	559	0.81	7.3	80
Pt/Meso-MFI	486	0.70	4.2	20

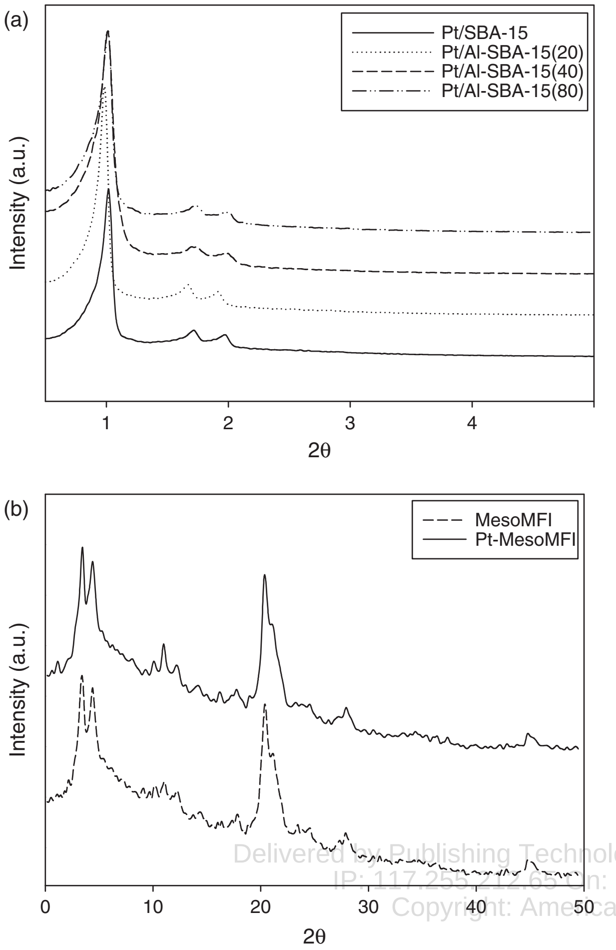

Fig. 1. (a) Low angle, and (b) high angle XRD patterns of prepared catalysts.

to iso-dodecane over the Pt/Al-SBA-15 catalysts was much higher than that over the Pt/Meso-MFI catalyst. As shown in Figure 2, the highest *n*-dodecane conversion and extremely low selectivity of iso-dodecane of the Pt/Meso-MFI catalyst was attributed to its strong acidic characteristics, resulting in dominant hydrocracking instead of hydroisomerization. In case of the Pt/Si-SBA-15 catalyst with fewer acid sites, the iso-dodecane yield was much lower than those of the other catalysts owing to its lowest conversion, irrespective of the higher selectivity of iso-dodecane. The Pt/Al-SBA-15 catalyst is more prone to the hydroisomerization of *n*-dodecane because of its weak acidic properties with respect to conversion and selectivity. Liquid products obtained from the Pt/Meso-MFI catalyst consisted of hydrocarbons whose carbon chain length was <11, primarily in the range of C_5 and C_8. From these results, it can be suggested that the acid properties of the bifunctional catalyst play a decisive role in determining the reactivity and selectivity for *n*-paraffin hydroconversion. The balance between the Pt metal and acidity with moderate acid strength and the acid levels might secure the optimum activity for hydroisomerization. Pt/Al-SBA-15 (20) showed the best performance of the Pt/Al-SBA-15 catalysts examined.

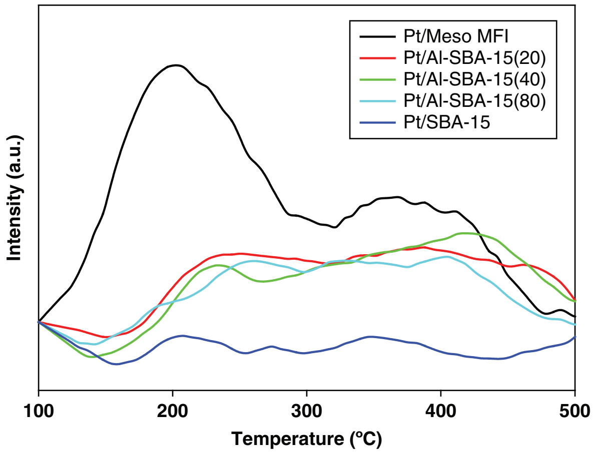

Fig. 2. NH_3 TPD of various catalysts.

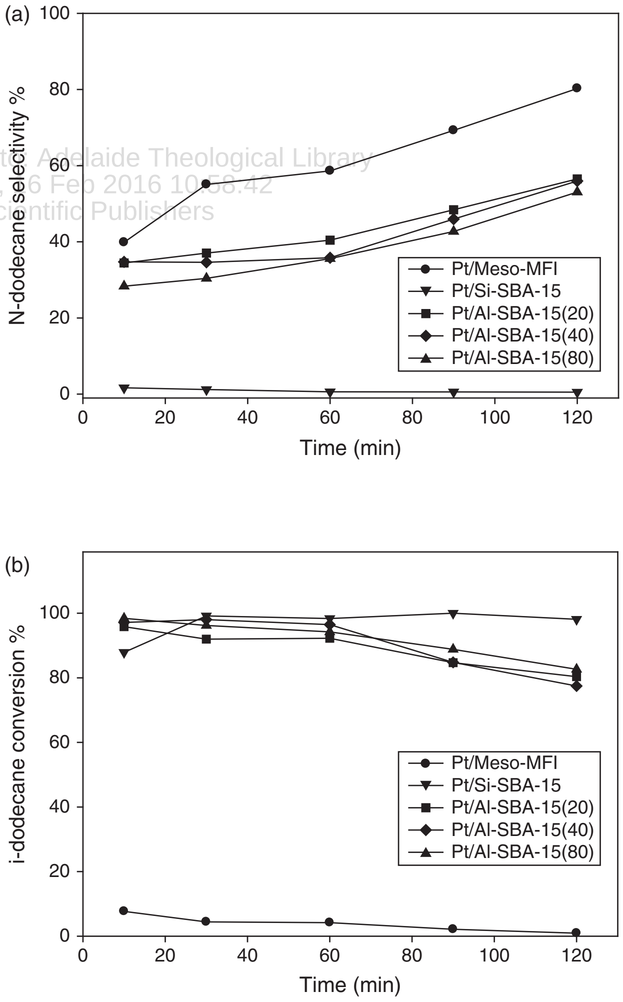

Fig. 3. Temporal conversion and selectivity over catalysts at 350 °C and 20 bar (a) *n*-dodecane conversion (b) isomer selectivity.

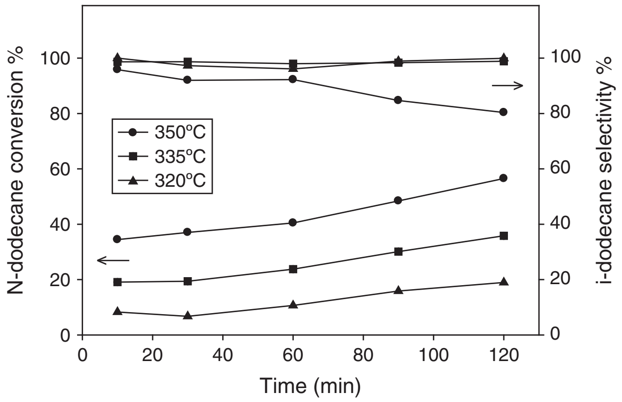

Fig. 4. Effect of reaction temperature on *n*-dodecane conversion and isomer selectivity.

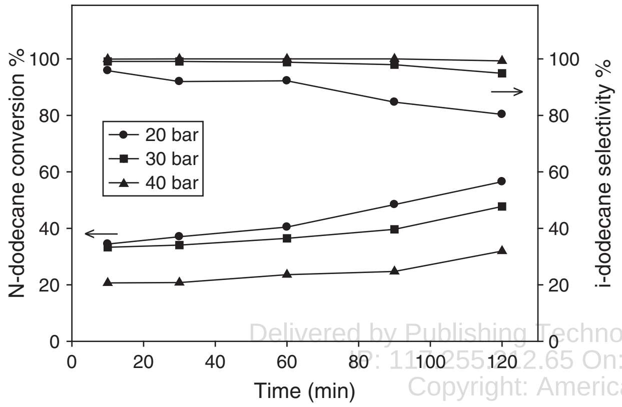

Fig. 5. Effect of reaction pressure on *n*-dodecane conversion and isomer selectivity.

Figure 4 shows the catalytic activity of Pt/Al-SBA-15 (20) at different reaction temperatures between 320 °C and 350 °C at fixed pressure of 20 bar. The hydroconversion of *n*-dodecane increased with increasing temperature, whereas the selectivity of iso-dodecane decreased due to the enhanced hydrocracking reaction at higher temperatures.

The effect of the operating pressure on the catalytic activity was investigated at 350 °C (Fig. 5). The hydroconversion activity decreased with increasing pressure under isothermal conditions. Hydrogen and *n*-dodecane competitively adsorbed on the active sites of the catalyst. On the other hand, with increasing pressure (increase in hydrogen partial pressure), hydrogen can adsorb on catalyst more easily than *n*-dodecane, resulting in a decrease in the hydrocracking reaction with a concomitant increase in iso-dodecane selectivity. Zhang et al. reported that an increase in the total reaction pressure resulted in low conversion with high selectivity, indicating a negative reaction order with respect to hydrogen in *n*-hexadecane isomerization using a Pt/WO_3/ZrO_2 catalyst.[7]

4. CONCLUSION

Pt/Si-SBA-15, Pt/Al-SBA-15, and Pt/Meso-MFI catalysts were applied to the catalytic hydroconversion of *n*-dodecane. Pt/Meso-MFI with strong acid sites exhibited higher activity for the hydroconversion reaction, whereas Pt/Al-SBA-15 with sufficient weak acid sites enhanced the hydroisomerization reaction. The effect of the reaction temperature and pressure on the activity of the Pt/Al-SBA-15 catalyst was also investigated. With increasing temperature from 320 °C to 350 °C, the hydrocracking reaction became superior to the hydroisomerization reaction. The hydroconversion activity decreased with increasing reaction pressure.

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