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Cooperative effects of secondary mesoporosity and acid site location in Pt/SAPO-11 on *n*-dodecane hydroisomerization selectivity

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ABSTRACT

Two different methods, organosilane templating and carbon templating, were used to generate secondary mesoporosity within SAPO-11. The former method produced mesoporous SAPO-11 samples with a large amount of external acidity, while the latter produced mesoporous samples containing predominantly internal acid sites. It was shown that, depending on the location of Brønsted acid sites, Pt supported on mesoporous SAPO-11 samples can exhibit widely ranging maximum isomerization yields from 13% to 84%, while solely microporous SAPO-11 showed 44% isomerization yield. The results indicate that the presence of secondary mesoporosity can be either remarkably beneficial or detrimental to hydroisomerization selectivity depending on the spatial location of the acid sites. The present results clearly showed that hydroisomerization selectivity of the catalysts can be significantly enhanced by facilitating the hydrocarbon diffusion *via* the formation of secondary mesopores while suppressing the formation of external acid sites that can non-selectively catalyze consecutive cracking reactions.

1. Introduction

The importance of hydroisomerization of long-chain normal paraffins to their branched isomers is increasing in the petroleum industry, since it is a means of improving the cold-flow properties of middle-distillate fuels and lube base oils [1–4]. Compared with catalytic cracking and solvent extraction, selective hydroisomerization can minimize the yield loss of liquid hydrocarbons [1,4]. Hydroisomerization catalysts are bifunctional, containing both a hydro-/dehydrogenation component (*e.g.*, Pt) and an acid component (*e.g.*, zeolites) [5]. It is generally accepted that a rapid hydro-/dehydrogenation equilibrium is established between alkanes and alkene intermediates in the presence of metal catalysts such as Pt. Isomerization occurs *via* the carbenium ion mechanism after protonation of reactive alkene intermediates by Brønsted acid sites. Notably, the carbenium ions can undergo not only skeletal isomerization but also C–C bond cracking (β-scission). The isomerization and cracking reactions are consecutive and highly isomerized alkanes are more susceptible to cracking [2,6,7].

It has been reported that a large-pore zeolite containing 12-membered ring structures such as Y (FAU structure) and Beta zeolite (BEA) can produce large amounts of multi-branched alkanes as well as cracked products, because there are no spatial constraints inducing shape selectivity [1,2]. In contrast, it has been reported that zeolites with 1-dimensional 10-membered ring channels, such as ZSM-22 (TON) [2,8–14], ZSM-23 (MTT) [2,13,14], and SAPO-11 (AEL) [1–4,13,15], can attain high yields of mono-branched isomers and suppress the generation of multi-branched isomers that are susceptible to cracking. To explain the high selectivity of these materials toward mono-branched isomers, especially with a mainly terminal methyl group, (i) pore mouth catalysis [9–12,15], (ii) transition state shape selectivity [13–15], and (iii) product shape selectivity [13–15] have been proposed. Which of these theories is more accurate is still under debate, but most likely multiple mechanisms may work together to different extents depending on the types of zeolite structure and reaction conditions.

Recently, zeolites containing secondary mesoporosity have been extensively studied for various acid-catalyzed reactions [16–18]. The mesoporosity can significantly increase molecular diffusion in zeolites and hence leads to a remarkable increase in activity for large molecules and resistance against coke deposition [19]. Although the positive sides of mesoporous zeolites have been mainly emphasized so far, they may exhibit deteriorated shape selectivity compared with solely microporous zeolites. The generation of secondary mesoporosity can naturally increase the number of external acid sites [20,21] that can catalyze reactions in unconstrained space and lead to the decrease of shape selectivity [21]. In this sense, selective location of acids sites mainly inside zeolite micropores while generating the secondary mesoporosity would be important to synergistically combine the original

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advantage of microporous zeolites (shape selectivity) and the fast molecular diffusion through the secondary mesopores.

In the present work, we investigated the effects of secondary mesoporosity and acid site locations in Pt/SAPO-11 on the hydroisomerization of *n*-dodecane. From the view point of hydroisomerization selectivity, both advantages and disadvantages could be expected due to the presence of secondary mesoporosity. Branched *iso*-alkanes have larger kinetic diameters than that of linear *n*-alkane. This means that the diffusion of the products in hydroisomerization (*iso*-alkanes) should be slower than that of the reactant (*n*-alkane). Long residence of *iso*-alkane in the catalyst can increase the possibility of further isomerization and consecutive cracking reactions. The presence of mesopores can facilitate the diffusion of *iso*-alkanes out of the zeolite micropores and thus can suppress the consecutive reactions. On the other hand, the generation of secondary mesoporosity can increase the number of acid sites on the external surface of the zeolite framework. The dominant presence of external acid sites can non-selectively catalyze multiple isomerization and cracking reactions in the unconstrained space.

In this work, two different methods, organosilane templating [22] and carbon templating [23], were used to generate secondary mesoporosity in SAPO-11. The former method produced mesoporous SAPO-11 with large amounts of external acidity, while the latter method produced a sample containing predominantly internal acid sites. It will be demonstrated that, depending on the location of acid sites, the mesoporous SAPO-11 samples exhibit maximum isomerization yield, ranging widely from 13% to 84%, while ordinary SAPO-11 showed 44%. The results indicate that the generation of secondary mesoporosity could be either remarkably beneficial or detrimental on hydroisomerization selectivity depending on the location of acid sites.

2. Experimental

2.1. Synthesis of microporous SAPO-11

In a typical synthesis of ordinary SAPO-11, 36.7 g aluminum isopropoxide (Aldrich, ⩾98%) was hydrolyzed in 77.8 g deionized water under stirring for 2 h. 20.7 g of phosphoric acid (Junsei, 85%) was added to the mixture and homogenized for 1 h. 10.9 g of dipropylamine (DPA, TCI, >99%) was added to the mixture, followed by the addition of 3.75 g of tetraethyl orthosilicate (TEOS, Aldrich, 98%). The mixture was homogenized under stirring for 5 h and then was heated at 363 K for 1 h to remove the isopropanol produced from the hydrolysis of aluminum isopropoxide. The final molar composition of the synthesis gel was 1.0 Al_2O_3:1.0 P_2O_5:1.2 DPA:0.2 TEOS:50 H_2O. The synthesis gel was transferred into a Teflon-lined stainless steel autoclave and hydrothermally crystallized at 458 K for 2 days under tumbling (30 rpm). The resultant product was filtered, washed with deionized water, and dried at 373 K. The sample was calcined at 823 K under a continuous flow of dry air (200 cm^3 min^{-1}) for 10 h by using a plug-flow reactor.

2.2. Synthesis of mesoporous SAPO-11 by organosilane templating

Mesoporous SAPO-11 samples were synthesized by using dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride (ODAS, 42 wt% in methanol, Aldrich) as a mesopore-directing agent. The basic synthesis procedure for mesoporous SAPO-11 is similar to that mentioned for ordinary SAPO-11 synthesis except for the addition of ODAS into the final synthesis gel mixture. Because ODAS includes Si-moiety, a silicoaluminophosphate framework can be derived even without the addition of TEOS as a silica precursor. Here, two mesoporous SAPO-11 samples were prepared by the organosilane templating method, without and with the addition of TEOS as a secondary silica precursor. The molar compositions were 1.0 Al_2O_3:1.0 P_2O_5:1.2 DPA:0.1 ODAS:50 H_2O and 1.0 Al_2O_3:1.0 P_2O_5:1.2 DPA:0.1 ODAS:0.1 TEOS:50 H_2O, respectively. After the hydrothermal crystallization, the resultant samples were collected, dried, and calcined following the same procedure used for the synthesis of microporous SAPO-11. The product synthesized from the former composition was denoted as S-SAPO-11, while the product from the latter composition was denoted as ST-SAPO-11 (‘S’ indicates ODAS silane and ‘T’ indicates TEOS).

2.3. Synthesis of mesoporous SAPO-11 by carbon templating

Mesoporous SAPO-11 samples were also synthesized by using carbon black (FW-200, Evonik) as a mesopore-directing agent. The basic synthesis procedure for mesoporous SAPO-11 is similar to that mentioned for ordinary SAPO-11 synthesis except for the addition of carbon black into the final synthesis gel mixture. Two samples were prepared by adding two different amounts of carbon black. The synthesis gel compositions were 1.0 Al_2O_3:1.0 P_2O_5:1.2 DPA:0.2 TEOS:50 H_2O:9.5, and 19 C. After the hydrothermal crystallization, the resultant samples were collected, dried, and calcined following the same procedure used for the synthesis of microporous SAPO-11. The sample synthesized by using the smaller amount of carbon black (9.5 C) is denoted as C1-SAPO-11, while the one synthesized by using the larger amount of carbon black (19 C) is denoted as C2-SAPO-11.

2.4. Catalyst preparation

1.0 wt% Pt was supported on the calcined SAPO-11 samples *via* the incipient wetness impregnation method using an aqueous solution of $Pt(NH_3)_4(NO_3)_2$ (Aldrich). After impregnation, the samples were dried for 5 h at 373 K and calcined in dry air at 673 K for 3 h.

2.5. Characterization

The elemental compositions of the synthesized SAPO-11 samples were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using Thermo elemental iCAP-6000 apparatus. X-ray diffraction (XRD) patterns were recorded using a Bruker D2-phaser diffractometer operated at 30 kV and 10 mA, with Cu Kα radiation and LYNXEYE detector. The data were collected with a resolution of 0.01° and a count time of 2.5 s at each point. Scanning electron microscopy (SEM) images were obtained with a Magellan 400 instrument operating at 1 kV in back-scattered mode (BSE) without metal coating. Transmission electron microscopy (TEM) images were taken with a Tecnai F30 S-Twin operating at 300 kV after mounting the samples on a carbon-coated copper grid (300 mesh) using ethanol dispersion. N_2 adsorption–desorption isotherms were measured using a BELSorp-max volumetric analyzer (BEL Japan) at the liquid N_2 temperature (77 K). Before the measurement, all samples were degassed under vacuum for 3 h at 673 K. The micropore surface area (S_{micro}), external surface area (S_{ext}), and micropore volume (V_{micro}) of the samples were determined using *t*-plot analysis. The total pore volumes were estimated at $P/P_0 = 0.98$ and the mesopore volumes (V_{meso}) were calculated by subtracting the micropore volume (V_{micro}) from the total pore volume.

The number of total Brønsted acid sites and external Brønsted acid sites was analyzed by using FT-IR spectra after adsorption of pyridine (Py) and 2,6-ditertbutyl pyridine (2,6-DTBPy), respectively [20]. FT-IR spectra were collected on a Thermo Nicolet NEXUS instrument. A self-supporting wafer consisting of a 15 mg sample was placed in an in situ IR cell with a CaF_2 window and