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Supplementary information

Hydroisomerization of 1-octene utilizing hierarchical SAPO-11 supported Ni catalyst: Effect of alkyl chain length of mesoporogen

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Experimental section

Characterization

The SEM (Phenom manufactured by Finer, the Netherlands) were used to observe the morphology.
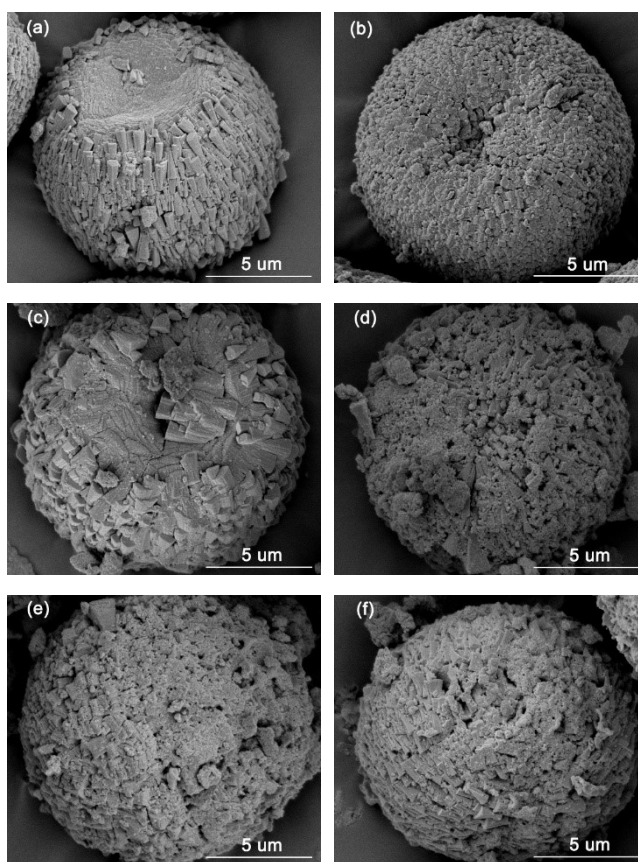

Fig.S1 SEM images of the SAPO-11 synthesized by mesoporogen with different alkyl chain length. (a) SAPO-11; (b) SAPO-11-OTAB; (c) SAPO-11-DeTAB; (d) SAPO-11-DTAB; (e) SAPO-11-TTAB; (f) SAPO-11-CTAB.

Results and discussion

Effects of properties of hierarchical SAPO-11 on 1-octene hydroisomerization

The surface area, pore volume and acidity of SAPO-11 molecular sieves are important factors affecting the selectivity of hydroisomerization. It can be seen from Figure S2(a) that the selectivity of C_8 isomer increases with the increase of S_{BET} of hierarchical SAPO-11 and the cracking selectivity decreases. It can be seen from Figure S2(b) that the larger S_{BET} not only obtains more medium-strong B acid sites[1], but also promotes the distribution of Ni nanoparticles[2], which is the reason why the increased surface area improves the olefin hydroisomerization selectivity.
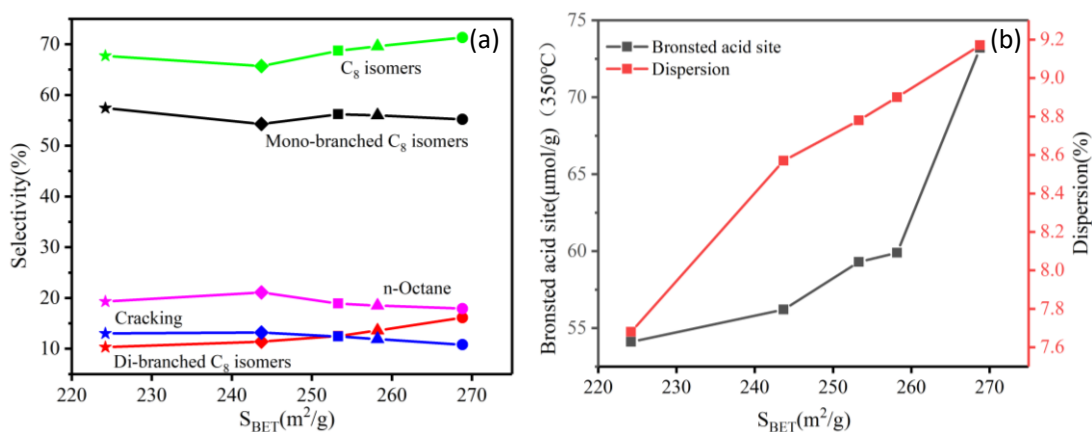

Fig.S2 Isomer selectivity of 1-octene hydroisomerization(a), medium and strong B acid sites and Ni dispersion (b) as a function of the BET surface area of hierarchical SAPO-11 molecular sieves. (In Fig.S2 (a), ■ SAPO-11-OTAB, ▲ SAPO-11-DeTAB, ● SAPO-11-DTAB, ◆ SAPO-11-TTAB, ★ SAPO-11-CTAB)

It can be seen from Figure S3(a) that with the increase of the micropore

volume of hierarchical SAPO-11, the hierarchical SAPO-11 supported Ni catalyst has no significant effect on the selectivity of the mono-branched isomer, and the selectivity of the di-branched isomer shows a trend of first increasing and then decreasing. With the increase of mesopore volume S3(b), the selectivity of both mono-branched and di-branched isomers increased, and the cracking selectivity decreased. This indicates that the existence of mesopores promotes mass transfer and reduces the residence time of isomers[3], thereby improving the selectivity of hydroisomerization and reducing the selectivity of cracking. The pore mouth and key-lock mechanism of hydroisomerization shows that the skeletal isomerization of macromolecular hydrocarbons mainly occurs near the pores of molecular sieves[4]. With the increase of the mesopore volume of the hierarchical SAPO-11, the corresponding catalyst can provide more orifices to promote the isomerization reaction and reduce the cracking reaction.
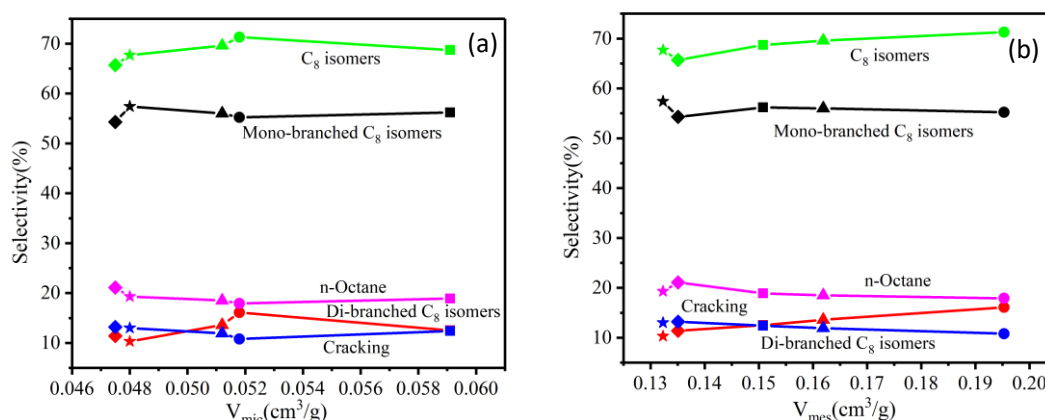

Fig.S3 Isomer selectivity of 1-octene hydroisomerization as a function of the V_{mic} (a) and V_{mes} (b) of hierarchical SAPO-11 molecular sieves. (■ SAPO-11-OTAB, ▲ SAPO-11-DeTAB, ● SAPO-11-DTAB, ◆ SAPO-11-TTAB, ★ SAPO-11-CTAB)

From figure S4, it can be seen that the increase of medium-strong B acid sites of the hierarchical SAPO-11 promotes the production of C_8 isomers[5], especially the mono-branched isomers, while the cracking selectivity decreases slightly; the effect of B/L on the isomerization selectivity consistent with the medium-strong B acid sites[6]. Studies have shown that olefin hydroisomerization first forms a carbonium ion at the B acid center of the molecular sieve, and the carbonium ion generates a single branched chain isomerization intermediate through skeletal isomerization, and the single branch chain isomerization intermediate can continue to undergo isomerization reaction to generate double branched chain isomer, and more medium-strong B acid sites is more conducive to the improvement of isomerization selectivity. According to the PCP isomerization mechanism, increasing B acid sites provides more protonated cyclopropane intermediates required for rearrangement of protonated alkylene carboniums, and the presence of mesopores facilitates mass transfer and reduces the residence time of intermediates, so that the medium-strong B acid sites is beneficial to the improvement of the hydroisomerization selectivity rather than the cracking selectivity, which is also well proved by the experimental results.
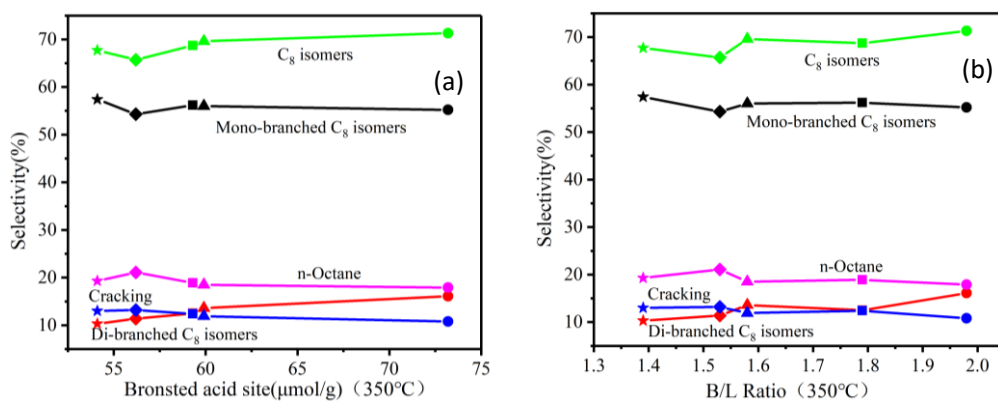
Fig.S4 Isomer selectivity of 1-octene hydroisomerization as a function of the medium-strong B acid sites (a) and B/L (b) of hierarchical SAPO-11 molecular sieves. (■ SAPO-11-OTAB, ▲ SAPO-11-DeTAB, ● SAPO-11-DTAB, ◆ SAPO-11-TTAB, ★ SAPO-11-CTAB)

The dispersion of Ni nanoparticle is also an important factor affecting olefin hydroisomerization on bifunctional catalysts. It can be seen from Figure S5 that the selectivity of isomers increases with the increase of the dispersion of Ni nanoparticles, and the selectivity of both mono-branched isomers and di-branched isomers increases. This shows that better dispersion of Ni nanoparticles is very important to improve the selectivity of isomer products[7].
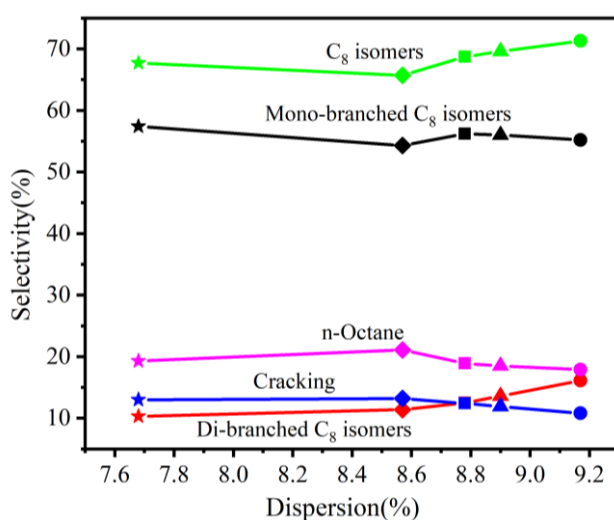

Fig.S5 Isomer selectivity of 1-octene hydroisomerization as a function of the Ni dispersion of hierarchical SAPO-11 catalysts. (■ SAPO-11-OTAB, ▲ SAPO-11-DeTAB, ● SAPO-11-DTAB, ◆ SAPO-11-TTAB, ★ SAPO-11-CTAB)

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