

Alkane isomerization over promoted zirconia-based catalysts

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The skeletal isomerization of alkanes catalyzed by a solid-acid plays an important role in industrial processes of petroleum chemistry. Comparing with liquid acid catalysts, zirconia-based catalysts, sulfated zirconia and tungstated zirconia, have the advantage of environmental friendliness.

With mesoporous zirconia and dense-phase zirconia as the precursors, the Al- and Ga-promoted sulfated zirconia (ASZ and GSZ), Al- and Ga-promoted sulfated zirconia on MCM-41 (ASZ/MCM-41 and GSZ/MCM-41), Al-promoted mesoporous sulfated zirconia (AS/m-ZrO₂), Al- and Ga-promoted tungstated zirconia (AWZ and GWZ) and Al-promoted mesoporous tungstated zirconia (AW/m-ZrO₂) were prepared. The catalysis of alkanes isomerization (C₄-C₆) over these catalysts was studied, compared and correlated to the catalyst characterizations.

In compared to sulfated zirconia, the Al or Ga-promoted catalysts showed much improved activity and selectivity for isomerization of n-butane, n-pentane and n-hexane. Both Al and Ga not only helped to retard the phase transformation of ZrO₂ from tetragonal to monoclinic, but also retained more sulfur content. The mesostructure of S/m-ZrO₂ catalysts was stabilized by Al and Ga doped. Characterization of acidity showed no significant difference in strength distribution of acid sites over the SZ systems. In the Al case, the pyridine adsorption DRIFT spectra provided the evidence of increased Brønsted acid sites and XPS found the content of weak Brønsted acid sites become the highest while the Al-promoted catalyst gives the highest activity. This implies that these weak Brønsted acid sites play an important role in the catalytic reaction.

Tungstated zirconia catalysts have been offered a potential alternative to SZ because of its stable and inorganic nature, which ensures WZ less tendency to decompose during oxidation-reduction environments. The catalytic activity for n-butane isomerization was greatly improved over Al- and Ga-promoted dense-phase tungstated zirconia at the reaction temperature of 300°C. The catalytic performance was further improved over AW/m-ZrO₂. At the identical conversion of n-butane, the reaction temperature is 250°C over AW/m-ZrO₂, much lower than AWZ. Both AWZ and GWZ catalysts also showed better catalytic activity and selectivity in n-pentane isomerization. No catalyst deactivation was observed during the 1000 hours test period both in n-pentane isomerization over AWZ and GWZ and in n-hexane isomerization over Pt/AWZ. This suggests that WZ systems are more suitable for industrial application. According to the characterization of acid sites, the improved activity and stability of the Al- and Ga-promoted catalysts are due to a balanced distribution of acid sites strength with a moderate amount of strong Brønsted acid sites.

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