

Promotion effect of alumina on sulfated zirconia for isomerization of *n*-butane under supercritical conditions

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Introduction

iso-Butane is one of the major constituents of both clean and high-octane gasoline, and can be produced through the isomerization of *n*-butane using heterogeneous solid acid catalysts. However, solid acid catalysts for the isomerization of light paraffins are subject to a rapid deactivation due to coke formation on the catalyst surface. Under supercritical conditions of reactant *n*-butane and product *iso*-butane, the rapid deactivation of isomerization was well suppressed over sulfated zirconia [1]. In this study, we will demonstrate a newly developed alumina-promoted sulfated zirconia (SZA) showing a higher catalytic activity than that of sulfated zirconia (SZ), without serious deactivation under super critical conditions of reactant molecules.

Materials and Methods

Catalyst Preparation: Zirconium hydroxide [Zr(OH)₄] was impregnated with aqueous solution of aluminum nitrate [Al(NO₃)₃·9H₂O] and ammonium sulfate [(NH₄)₂SO₄], and stirred overnight at 333 K. The solid catalyst (SZA) obtained was dried at 373 K for 12 h. The sulfur content ratio of SZA was adjusted to 4.0 wt%. The number in SZA5 is the nominal Al₂O₃ loading (5 mol%) over ZrO₂-Al₂O₃ mixed oxide. Dried SZA catalysts were calcined *in-situ* prior to the reaction in the reactor system.

Isomerization of *n*-butane: Isomerization was carried out in a high pressure fixed bed continuous flow reactor [2]. The critical point of *n*-butane is at 425 K and 3.8 MPa [4]. The reaction conditions were as follows: reaction temperature, 388-588 K; reaction pressure, 0.1-6.0 MPa. The products were analyzed by GC and all SZA catalysts were characterized by XPS, XRD, XRF, and FT-IR.

Results and Discussion

It is known that supercritical fluids facilitate mass transfer very well due to their low viscosities, high diffusivities, and high densities. Therefore, supercritical fluids have the potential to be suitable reaction media and/or new extraction media for this and other reactions [3]. The catalytic activities for isomerization of *n*-butane under the supercritical conditions (4.0 MPa, 488 K) and gas phase conditions (0.1 MPa, 488 K) over SZA1 and SZA5, are shown in **Figure 1**. Under the gas phase reaction, although initial catalytic activity was relatively high, rapid deactivation occurred and no activity was observed after 4 h time on stream. In contrast, above the supercritical conditions of *n*-butane (critical temperature: 425 K, critical pressure: 3.8 MPa), deactivation was extremely retarded. The catalytic activity over SZA5 was much higher than that over SZA1 and SZ, due to the enhanced acidity caused by addition of alumina.

Addition of alumina to sulfated zirconia suppressed the phase transition from the amorphous to the monoclinic and tetragonal zirconia phases, which causes higher catalytic activity and improved thermal stability of sulfate groups. Zr 3d XPS spectra of ZrO₂, SZ, SZA, and SZ+SA (sulfated alumina) are shown in **Figure 2**. All samples were calcined at 873 K prior to XPS measurements. When sulfate ion was introduced to zirconia, the binding energy of Zr 3d was shifted toward higher energy level. This result suggests that sulfate groups exhibit electron withdrawing effects to give a positive charge on the Zr atoms. In addition, SZA showed higher binding energy than that of SZ and SZ+SA (mechanical mixture of SZ and SA), suggesting that Al atoms are incorporated into the zirconia lattice. Due to the higher electronegativity of Al, the enhancement of positive charge on Zr atoms strengthen those acidic sites.

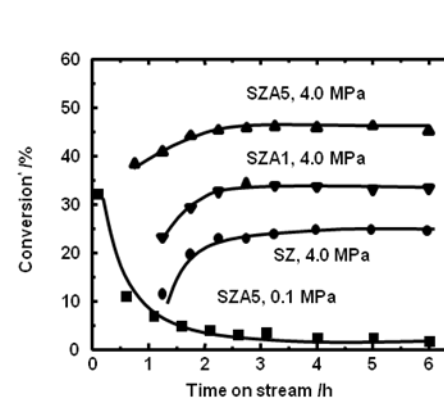


Figure 1. Catalytic activity of isomerization of *n*-butane over SZA1, SZA5, and SZ at 0.1-4.0 MPa, 488 K, W/F=6.0 g h mol⁻¹.

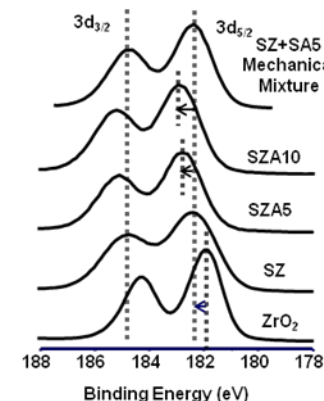


Figure 2. Zr 3d xps spectra of ZrO₂, SZ, SZA, and SZ + SA.

Significance

It was found that a newly developed Al-promoted sulfated zirconia catalyst (SZA: SO₄²⁻/ZrO₂-Al₂O₃) had both higher thermal stability of sulfate groups and higher catalytic activity for isomerization of *n*-butane than conventional sulfated zirconia (SZ). Under supercritical conditions, no significant deactivation of the SZA solid acid catalyst was observed, and a higher activity was obtained as a function of time on stream.

References

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