

A Highly Active Solid Superacid Catalyst for n-Butane Isomerization: a Sulfated Oxide Containing Iron, Manganese and Zirconium

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A porous sulfated metal oxide containing Fe, Mn and Zr is described; it is the most active nonhalide superacid catalyst yet reported, catalysing the isomerization of n-butane at 301 K and being about three orders of magnitude more active than sulfated ZrO₂.

Liquid superacids,¹ combinations of Brønsted and Lewis acids such as HF + SbF₅, are active catalysts for alkane conversions at low temperatures, but they are not applied industrially because they are corrosive and lack stability. Researchers have long sought to replace the liquid superacids with solids having the same chemical properties while also being stable and noncorrosive.² Examples include sulfonated polymers combined with AlCl₃ or SbF₅⁴ and sulfated ZrO₂, TiO₂ and Fe₂O₃.⁵⁻⁷ The former are highly active but unstable, and the most promising has been noted as sulfated ZrO₂, although there is a lack of quantitative data characterizing its catalytic activity and stability. Here, we report a new solid superacid catalyst⁸⁻¹⁰ that is more active for isomerization of n-butane than any nonhalide yet reported.

The new catalyst was made by impregnation of dried Zr(OH)₄ with aqueous Fe(NO₃)₃, Mn(NO₃)₂ and (NH₄)₂SO₄, containing 1.5 wt% Fe, 0.5 wt% Mn and 4.0 wt% sulfate. It was calcined at 998 K for 1 h. Sulfated ZrO₂ was made for comparison by impregnation of dried Zr(OH)₄ with aqueous (NH₄)₂SO₄. The catalyst containing Fe, Mn and Zr, a grey solid, had a surface area of 97 m² g⁻¹ and a pore volume of 0.28 cm³ g⁻¹ (the volume of pores with diameters > 1 nm). The sulfated ZrO₂, a white solid, had a surface area of 101 m² g⁻¹ and a pore volume as defined above of 0.28 cm³ g⁻¹.

The solid samples were ground and sieved to give particles with diameters in the range of 0.18 to 0.25 mm and tested as catalysts for conversion of n-butane (impurities: 0.097 mol% isobutane and 0.0064 mol% propane). Before testing, each catalyst was pretreated by drying at 773 K for 4 h in dry air flowing at 30 cm³ (NTP) min⁻¹. The conversion was carried out in a standard isothermal once-through, fixed-bed flow reactor. It was operated at 2.1 × 10⁵ Pa and 301–318 K for the catalyst containing Fe, Mn and Zr and at 2.1 bar and 373–413 K for the sulfated ZrO₂. The products were analysed with an on-line gas chromatograph. The space velocity was in the range (1.82–5.01) × 10⁵ g s⁻¹ (mol of n-butane)⁻¹, and the conversions were up to 20% for the former catalyst. The space velocity was 2.80 × 10⁵ g s⁻¹ (mol of n-butane)⁻¹ and the conversion was <2.2% for the latter catalyst.

Both catalysts were found to be active for the conversion of n-butane into isobutane; small amounts of propane and isopentane and traces of n-pentane were also observed in the products. The catalyst containing Fe and Mn was active even at 300 K, whereas a temperature of about 413 K was needed with the sulfated ZrO₂ just to give a rate of reaction about one quarter that observed at 300 K with the Fe- and Mn-containing

catalyst. The former catalyst lost ca. 75% of its highest measured activity in 40 h on stream in the flow reactor, and the latter lost about 45% of its highest measured activity in this time.

Rates of the n-butane isomerization reaction were determined from slopes of linear plots of conversion vs. inverse space velocity. Data were extrapolated to give estimates of the rates at zero on stream time. Temperature was varied during the deactivation, and rates were normalised (by using the measured dependence of rate on time on stream for each catalyst) to estimate the activities of the undeviated catalysts at each temperature. These extrapolated and normalised rates are shown in the Arrhenius plot of Fig. 1. The apparent activation energies and pre-exponential factors are summarised in Table 1. The catalyst containing Fe and Mn is almost three orders of magnitude more active than sulfated ZrO₂. Activities of other catalysts determined in comparable experiments (not including those done with pulse and internal recirculation reactors) (Fig. 1) are also less than that of the new catalyst.

The new catalyst could be regenerated by treatment in air flowing at 30 cm³ (NTP) min⁻¹ at temperatures > 723 K and used repeatedly.

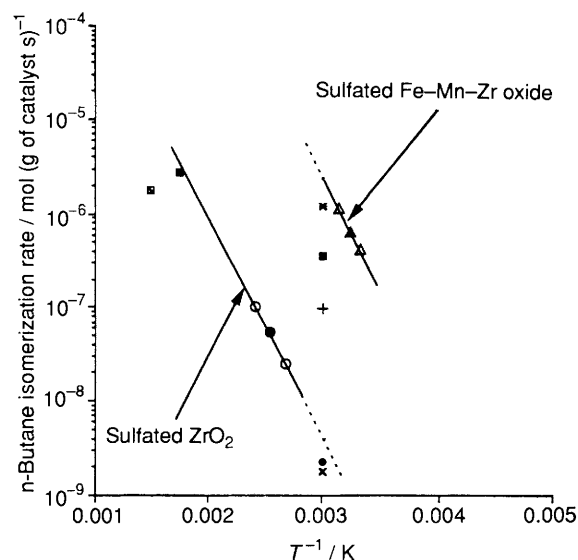


Fig. 1 Activities of solid superacid catalysts for n-butane isomerization. \blacktriangle and \triangle represent the sulfated oxide catalyst containing Fe, Mn and Zr (this work). \bullet and \circ represent sulfated ZrO₂ (this work). \blacktriangle and \bullet represent rates extrapolated to zero on stream time. (The extrapolated rate for the former catalyst is 60% greater than the maximum observed rate. The extrapolated rate for the latter catalyst is 10% greater than the maximum observed rate.) \triangle and \circ represent rates normalised to the undeviated state by using an empirical equation to represent the activity as a function of time on stream. The other catalysts are AlCl₃ supported on sulfonated SiO₂ (\blacklozenge),³ AlCl₃ supported on sulfonated poly(styrene-divinylbenzene) (+),³ SbF₅ supported on sulfonated poly(styrene-divinylbenzene) (\times),⁴ SbF₅ supported on Al₂O₃ treated with SO₂ (\times),¹¹ SbF₅ supported on Al₂O₃-B₂O₃ (\square),¹¹ sulfated zirconia (\blacksquare),¹² and H-mordenite (\square).¹²

Table 1 Solid superacid catalysts for n-butane isomerization: kinetics parameters

Catalyst	Apparent activation energy/kcal mol ⁻¹	Pre-exponential factor mol (g of catalyst s) ⁻¹
Sulfated metal oxide containing Fe, Mn and Zr	11.4	74.4
Sulfated ZrO ₂	10.7	0.048

The acid strength of the catalyst containing Fe and Mn could not be measured by colour changes of Hammett indicators, since the solid is grey. The Hammett acidity function of sulfated ZrO_2 has been found to be < -16 ,¹³ and the comparison of activities suggests that the new catalyst is a superacid with greater acid strength than sulfated ZrO_2 . The near equality of the activation energies for the two catalysts (Table 1) suggests that the improvement represented by the new catalyst is associated with a larger number of catalytic sites than in sulfated ZrO_2 . Further characterizations¹⁴ show that the new catalyst has both greater acid strength and more strong acid sites than sulfated ZrO_2 .

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