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Interaction between Promoters Mn/Fe, Sulfate, and Zirconia in Accordingly Composed Alkane Isomerization Catalysts

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Motivation

The catalytic activity of sulfated zirconia for *n*-butane isomerization can be increased by 1-2 orders of magnitude through addition of Mn or Fe cations [Hsu et al., Chem. Commun. 1992]. Initially, promoters were believed to enhance acidity, but this idea was dismissed and it was proposed that the promoter ions may act as redox initiators. Here, we present a comprehensive investigation on

- the effect of the promoters on the sulfate (TG-DSC) including comparison of Mn to Fe

- the nature of the promoters and their effect on the zirconia bulk (XRD, EPR, ISS) including comparison of Mn to Fe
- the oxidation state of Mn during *n*-butane isomerization (in situ XAS)

Interaction of Promoters and Sulfate

Experimental

Catalyst preparation (thank you, Gisela Lorenz!): Commercial sulfated zirconium hydroxide (MEL Chemicals) promoted with aqueous Mn(II) or Fe(III) nitrates via incipient wetness technique. Calcination: 20 g batches, 200 ml/min air, 3 K/min, 923 K (SZ: 823 K) for 3 hours.

Catalyst nomenclature: 3.5MnSZ means promoted sulfated zirconia with 3.5 wt% Mn.

n-Butane isomerization: 500 mg of sample in a once-through plug-flow fixed bed reactor. Activation for 30 min at 723 K in flowing dry nitrogen. Reaction temperature 323-378 K, atmospheric pressure, 80 ml min⁻¹, 1% *n*-butane/nitrogen. Product analysis by on-line GC with FID detector.

XRD: STOE STADI-P diffractometer, Cu Kα1 radiation, Debye-Scherrer geometry, primary monochromator, linear PSD (res. 0.01° 2Θ).

In situ XAS: In-house design powder bed flow reactor with on-line MS analysis. Data taken in fluorescence mode at HASYLAB beamline E4. Energy calibration with Mn foil via beam bypass; edge shift translates to Mn valence [Ressler et al., J. Phys. Chem. 1999].

TG/DSC: Netzsch STA 499 C with on-line MS (OmniStar®, Pfeiffer QMS 200).

ISS: Leybold LHS 12 MCD instrument with a hemispherical analyzer, using 2 keV He⁺ ions and a flood gun.

EPR: JEOL JES-RE2X system at X-band frequency. Microwave frequency 9.05 GHz; microwave power 5 mW, modulation amplitude 0.4 mT, time constant 0.1 s, modulation frequency 100 kHz, temperature 150 K.

- 2.0% Fe exceed that of SZ

samples in 80 ml/min 1% *n*-butane in N₂

TG - DSC











XRD: Fe stabilizes the tetragonal phase (compare SZ and 2.0FeSZ calcined at equal temperatures); Mn also stabilizes t-ZrO₂

Tetragonal unit cell volume shrinks with increasing Mn content: solid solution formation





Ion scattering spectroscopy does not detect Mn on 2.0MnSZ; Fe is clearly detectable Despite different distribution, Fe and Mn have similar promoting effect





About 42% Fe can be removed from 2.0FeSZ by washing with oxalic acid; remaining species are located in the zirconia lattice

Difference spectra (original-washed) show surface species resemble Fe₂O₃





Interaction of Promoters and Zirconia

Isolated promoter ions