

Investigating Zirconia Catalysts = Handling Sensitive Materials

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Introduction

Sulfated zirconia (SZ) based catalysts are active for *n*-butane isomerization at 373 K [1]. Despite intense research, no convincing structure-activity relationship for these materials has evolved. Still in question is the role of the bulk phase of ZrO₂ which in its room temperature stable form is monoclinic [2], *m*-ZrO₂. The presence of sulfate [3] and the incorporation of cationic promoters such as Mn [4] increase the fraction of the tetragonal phase, *t*-ZrO₂. Transformations between the two phases are achieved for pure zirconia through ball milling [5] and pressing [6]. Our research focused on the influence of mechanical stress treatments on the catalytic activity. For SZ and manganese promoted SZ (MnSZ) the effect of milling, grinding, and pressing, on the bulk phase composition and the catalytic activity was investigated [7].

Experimental

The precursor was (NH₄)₂SO₄ doped hydrous zirconia (XZO 682/01, MEL Chemicals). The promoter was introduced by the incipient wetness method to give a Mn content of 0.5 or 2.0 wt%. The raw materials were calcined in 17 ml batches [8] in flowing air for 3 hours at 823 (SZ) or 923 K (MnSZ). For pressing, flat-surfaced stainless steel tools and a manually operated hydraulic press were used; milling was performed in a vibrating mill using 1.5 ml stainless steel capsules and 300 mg of sample (all Perkin-Elmer). Grinding was performed manually in an agate mortar. X-ray diffractograms were recorded using a STOE STADI-P-diffractometer, Debye-Scherrer geometry, and Cu K α radiation. Catalytic tests were run in a fixed bed flow reactor. Samples (500 mg) were activated at 723 K in N₂. The feed was 1.0 vol.% *n*-butane in N₂ (80 ml min⁻¹) at atmospheric pressure; reaction temperatures were 378 K (SZ), 323 K (2 wt% MnSZ), or 338 K (0.5 wt% MnSZ). The effluent stream was analyzed by on-line GC with flame ionization detection. Further characterization included surface area and thermal analysis.

Results and discussion

During 10 min *pressing* at 540 MPa the phase composition of SZ changed from *t*-ZrO₂ to 33 wt% of *m*-ZrO₂. Also at more moderate pressing conditions (130 MPa, 1

min) an increase in the monoclinic fraction was detectable. For treatment of SZ and MnSZ (2.0 wt% Mn) *in a vibrating mill* the fraction of m-ZrO₂ increased with increasing milling time from <5 wt% in the original sample to ca. 30 wt% after 10 min of milling. *Grinding* 0.5 wt % MnSZ *in a mortar* for 10 min resulted in a partial transition of t-ZrO₂ to m-ZrO₂; the fraction of m-ZrO₂ was increased from about 8 wt% to either 19 or 57 wt%, depending on the operator.

Catalytic tests focused on untreated, *ground*, or *milled* samples because these materials need no further sample manipulation. In all cases the catalytic performance was severely reduced by treatment. For *milled* SZ the maximum isobutane formation rate was only about 25% of its value for untreated SZ (Fig. 1). The initial maximum isobutane conversion for 2 wt% MnSZ was similarly reduced by *milling*; the long term activity (>2 h) remained unaffected. *Ground* 0.5 wt% MnSZ showed a prolonged induction period. The isomerization rate was never more than 30% of values measured for the untreated catalyst.

For many experiments (e.g. IR spectroscopic), powders need to be pressed or ground. All of these "standard laboratory practice" treatments alter not only the structural, but also the catalytic properties of sulfated zirconia catalysts. This can lead to problems in data correlation because data obtained in experiments that involve different sample handling procedures can reflect the properties of different materials.

References

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