Research Note

Mechanical stress induced activity and phase composition changes in sulfated zirconia catalysts

Barbara S. Klose, Rolf E. Jentoft, Alexander Hahn, Thorsten Ressler, Jutta Kröhnert,
Sabine Wrabetz, Xiaobo Yang, and Friederike C. Jentoft [*]

Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, 14195 Berlin, Germany

Abstract

Sulfated zirconia and Mn-promoted sulfated zirconia (0.5 and 2.0 wt% Mn) catalysts were subjected to mechanical stress. Pressing (10 min 540 MPa), milling (10 min vibrating mill), and grinding (manually, 10 min agate mortar) effected a partial phase transformation from the tetragonal to the monoclinic phase of ZrO_2. The mechanical stress also reduced the n-butane isomerization rate (1 kPa n-butane, 323–378 K, atmospheric pressure) to 30% and less of that measured for untreated catalyst. Standard sample preparation techniques for analytical methods thus alter the structural and catalytic properties of sulfated zirconia. Attempts to correlate data from different methods are futile unless the integrity of the sulfated zirconia is ensured.

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1. Introduction

Sulfated zirconia exhibits extraordinary activity for the industrially important skeletal isomerization of alkanes; it is already active at low temperatures where the branched isomers are thermodynamically favored. The isomerization of n-butane is catalyzed at temperatures as low as 373 K [1]. The activity of sulfated zirconia can be further promoted by 1–2 orders of magnitude through the addition of transition metal cations, e.g., Fe or Mn cations [2,3]. Despite more than 20 years of intense research [4], the origin of the activity, i.e., the nature of the catalytically active sites, has not been identified; equally unknown is the function of the promoters. The influence of certain preparation parameters (e.g., the calcination conditions) on catalytic activity, sulfur content, surface area, and phase composition has been established [4] but no convincing structure–activity relationship has been proposed.

One point of debate is the role of the bulk phase of ZrO_2. The room temperature stable phase of ZrO_2 is the monoclinic phase [5], m-ZrO_2. However, in the usual prepara-

tion of ZrO_2 catalysts through calcination of an amorphous hydroxide precursor at 723–923 K, the tetragonal phase, t-ZrO_2, or a mixture of both phases is obtained. The presence of sulfate increases the fraction of t-ZrO_2 [4] and a stabilizing effect for the tetragonal phase has thus been ascribed to the sulfate. Cationic promoters such as Mn are incorporated into the zirconia lattice and stabilize the tetragonal or the cubic phase [6–9]. For many years it has been believed that only t-ZrO_2 is catalytically active [8], but recent work [10] shows m-ZrO_2 to be similarly active. Transformations between the two phases can be triggered through mechanical stress. For pure zirconia, it has been reported that the phase transitions t-$ZrO_2 \rightarrow m$-ZrO_2 and m-$ZrO_2 \rightarrow t$-ZrO_2 can be achieved by ball milling [11], and the transition t-$ZrO_2 \rightarrow m$-ZrO_2 can be achieved by pressing [12]. There are hints that conditions less forceful than those in a ball mill suffice for the t-$ZrO_2 \rightarrow m$-ZrO_2 transition [12,13].

Obviously, the zirconia bulk, whose role for catalysis is still questionable, is a rather dynamic system. Similarly, the large number of sulfate structures published [4] may indicate a very dynamic surface. A reason for the "elusive nature" of sulfated zirconia, which has so far prevented identification of an active site, may thus be its dynamic behavior. The system responds to many kinds of treatment, which prompts

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[*] Corresponding author.
    E-mail address: jentoft@fhi-berlin.mpg.de (F.C. Jentoft).

the question of whether sulfated zirconia is a material so "sensitive" that it becomes difficult to investigate. The aim of this research was to reveal if normal laboratory procedures, as they are used to prepare samples for a certain type of analysis, affect sulfated zirconia catalysts. The focus was on mechanical stress treatments such as milling, grinding, and pressing and on their effect on the bulk phase composition and the catalytic activity.

2. Methods

An X-ray amorphous undoped or ammonium sulfate (5–6 wt% SO_3) doped hydrous zirconia (XZO 632/03 or XZO 682/01, MEL Chemicals) was used as precursor material. The Mn promoter was introduced by the incipient wetness method; i.e., a solution of $Mn(NO_3)_2 \cdot 4H_2O$ (Merck, p.a.) was added dropwise to the dried XZO 682 under vigorous stirring. The amount of Mn was calculated to give a Mn content of 0.5 or 2.0 wt% in the final catalysts. The raw materials were calcined in compactly packed batches [14] of 20–25 g in a 200 ml min^{-1} flow of synthetic air; the heating rate was 3 K min^{-1} and the sample was held 3 h at 823 K (sulfated zirconia) or 923 K (Mn-promoted sulfated zirconia).

The pressing experiments were conducted using flat-surfaced stainless steel tools and a manually operated hydraulic press (Perkin–Elmer). Milling was performed in a vibrating mill (Perkin–Elmer) using 1.5 ml stainless steel capsules, a single ball, and 300 mg of sample. The maximum interval was 30 s; longer milling times were achieved by consecutive intervals. Grinding was performed manually in an agate mortar.

For X-ray diffraction, the loose powders were mixed 1 : 1 by weight with sieved α-Al_2O_3 (through gentle shaking) in order to determine amorphous fractions; the pressed samples were mounted as wafers. Diffractograms were recorded between $2\theta = 5°$ and $100°$ in steps of $0.03°$ using a STOE STADI-P-diffractometer, Debye–Scherrer geometry, and Cu-K$_\alpha$ radiation. The diffractograms were fitted using PowderCell v2.4 [15]. The fits did not always reproduce the composition of the internal standard mixture correctly; i.e., in some cases crystallization of amorphous ZrO_2 and/or amorphization of crystalline ZrO_2 through the treatment cannot be excluded.

Catalytic tests were run in a fixed bed tubular plug flow reactor employing 500 mg of catalyst. The samples were activated at 723 K and then cooled to the reaction temperature of 378 K (sulfated zirconia), 338 K (0.5 wt% Mn-promoted sulfated zirconia), or 323 K (2.0 wt% Mn), all in a 50 ml min^{-1} flow of N_2. The feed was an 80 ml min^{-1} flow of a mixture of 1 vol% n-butane in N_2 at atmospheric pressure. The effluent stream was analyzed by on-line gas chromatography with flame ionization detection.

3. Results and discussion

Some of the calcined samples were mixtures of m-ZrO_2 and t-ZrO_2; the fraction of m-ZrO_2 for pure zirconia was 75 wt%, for sulfated zirconia < 5 wt% (= not detected), and for Mn-promoted sulfated zirconia 8 wt% (0.5 wt% Mn) and < 5 wt% (2.0 wt% Mn).

Figure 1 (top) shows diffractograms of sulfated zirconia before and after 10 min *pressing* at 540 MPa; these diffractograms are normalized to the most intense peak because the wafer could not be mixed with the standard. The reflexes of m-ZrO_2 (e.g., at 28.2° and 31.5°) were present in the diffractogram of the wafer and indicate 33 wt% of m-ZrO_2. A pressure of 540 MPa equals approximately the pressure necessary in the making of self-supporting wafers for transmission IR spectroscopy, and it has already been reported [12] that wafers of pure zirconia may contain an increased
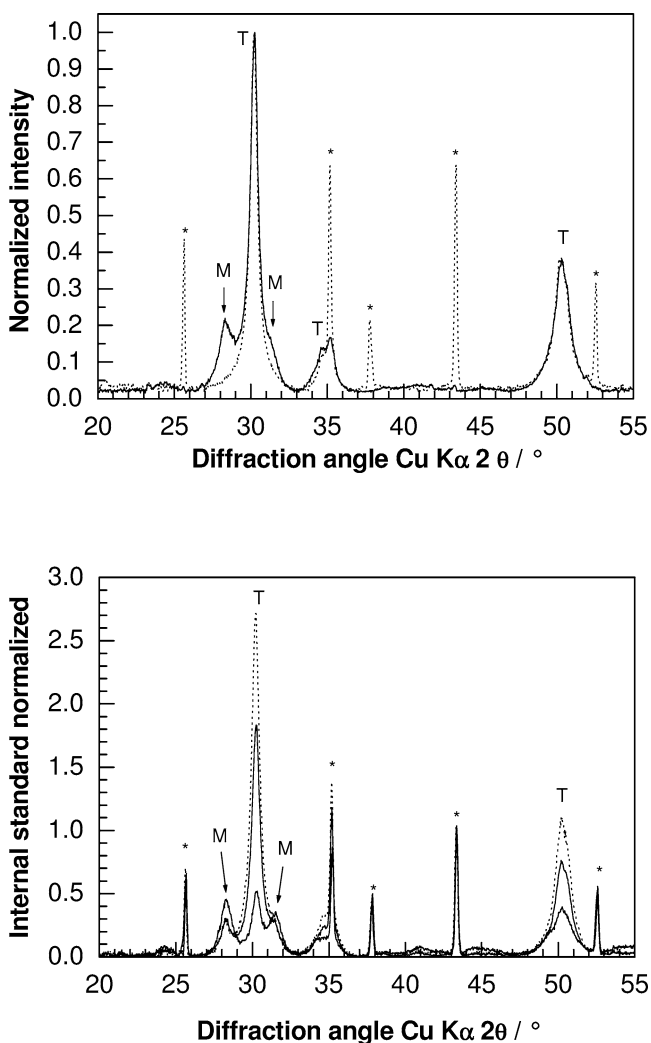

Fig. 1. X-ray powder diffractograms of zirconia materials before (dotted lines) and after (solid lines) mechanical stress treatment. Top: sulfated zirconia before and after 10 min pressing at 540 MPa. Bottom: Mn-promoted sulfated zirconia (0.5 wt% Mn) before and after manual grinding (two different operators). Asterisks indicate internal standard α-Al_2O_3.

fraction of m-ZrO_2. We found that the phase composition of sulfated zirconia materials also changed during pressure treatments, even under more moderate pressing conditions (130 MPa, 1 min) and despite the presence of sulfate, which stabilizes the tetragonal phase, at least with respect to thermal treatments [16].

Formation of m-ZrO_2 also occurred when the mechanical stress was induced by *milling.* For treatment of pure zirconia in the vibrating mill, the fraction of m-ZrO_2 increased with increasing milling time, from about 75 wt% in the original sample to 87 wt% after 10 min of milling. These results are in principle consistent with reports of such an effect on pure zirconia in the literature [11–13]. The fraction of m-ZrO_2 in sulfated and in Mn-promoted sulfated zirconia (2.0 wt% Mn) was ca. 30 wt% after 10 min of milling. Because Mn ions can be incorporated into the t-ZrO_2 lattice [6–8] and a number of different (incorporated) cations are known to stabilize the tetragonal phase [6], Mn-promoted sulfated zirconia might be expected to remain unaffected by milling; however, this is not the case. A comparison of the extent of phase transformation for sulfated zirconia materials with that for pure zirconia is difficult because of the different initial m-ZrO_2 content.

Figure 1 (bottom) shows diffractograms of the Mn-promoted sulfated zirconia (0.5 wt% Mn) before and after *grinding in a mortar* for 10 min; these diffractograms are internal-standard normalized. The grinding effected a partial transition from t-ZrO_2 to m-ZrO_2 in this material, from about 8 wt% m-ZrO_2 to 19 or 57 wt%. The extent of transformation was poorly reproducible in this type of experiment, and an operator influence is likely.

Surface areas were checked because the pore system of mesoporous materials can collapse or become inaccessible after mechanical stress in the form of pressing [17]. There were no significant changes to the BET surface area of sulfated zirconia after 10 min milling and of Mn-promoted sulfated zirconia (0.5 wt% Mn) after pressing at 750 MPa for 10 min. The sulfate content was estimated by means of thermogravimetry coupled with mass spectrometry; the weight loss at about 968 K was attributed to the decomposition of sulfate (evolution of SO_2). The weight loss was 4.6% for the unmilled sulfated zirconia and 4.2% for the 10 min milled sulfated zirconia. As there are results indicating that only a fraction of the sulfate actually contributes to the catalytic activity [18,19], the significance of this difference remains to be clarified.

Catalytic tests focused on untreated, *ground,* or *milled* samples because these materials could be tested as fixed powder beds without further sample manipulation. Figure 2 shows the isobutane production rate as a function of time on stream for untreated and mechanical-stress-treated sulfated zirconia (top, milling) and 0.5 wt% Mn-promoted sulfated zirconia (bottom, grinding). In both cases the catalytic performance was severely reduced after the treatment. *Milled* sulfated zirconia passed through an induction period similar to the one observed for its unmilled state, but the maximum
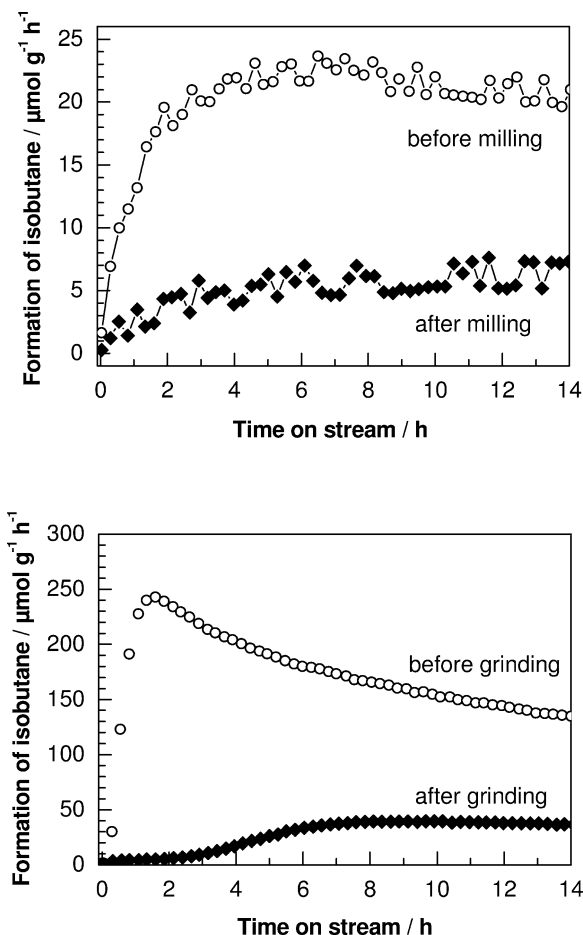

Fig. 2. *n*-Butane isomerization activity before (open symbols) and after (solid symbols) mechanical stress treatment, depicted as isobutane production rate vs time on stream. Top: sulfated zirconia, 10 min vibrating mill, reaction at 378 K. Bottom: Mn-promoted sulfated zirconia (0.5 wt% Mn), 10 min manual grinding, reaction at 338 K. Catalyst mass 500 mg, total pressure atmospheric, *n*-butane partial pressure 1 kPa (balance of N_2), total feed flow 80 ml min^{-1}.

isobutane formation rate was only about 25% of its value for untreated sulfated zirconia. *Ground* Mn-promoted sulfated zirconia (0.5 wt% Mn, 19 wt% m-ZrO_2) was characterized by a prolonged induction period and lack of a pronounced maximum in the conversion; the isomerization rate was never more than 30% of values measured for the untreated catalyst. The initial maximum isobutane conversion of 2 wt% Mn-promoted sulfated zirconia was similarly reduced by *milling;* the long-term activity (> 2 h) remained unaffected. Mechanical stress not only converts the metastable tetragonal phase of ZrO_2 into the thermodynamically stable monoclinic phase, but in sulfated zirconia-based catalysts, concomitantly reduces the alkane isomerization activity.

For many experiments it is necessary or common practice to press powders, e.g., in order to produce particles of a certain size for a catalytic test, to produce a wafer or pellet for transmission spectroscopy, or to avoid uncontrolled distribution in a vacuum environment. Equally, grinding is often used to homogenize samples or to mix them with standards

or diluents. Particularly, in situ experiments often require such sample preparation techniques. Our results demonstrate that all these "standard laboratory practice" treatments alter not only the structural, but also the catalytic properties of sulfated zirconia catalysts. The sensitivity towards mechanical stress renders investigation of sulfated zirconia catalysts difficult and explains why the system has so far escaped fundamental understanding. Data correlation is hindered because data obtained in experiments that involve different sample handling procedures can reflect the properties of partially different materials and thus do not represent pieces of the same puzzle.

Acknowledgments

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