

Evolution of an Active Catalyst Material during Thermal Treatment

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Introduction

Many catalysts are prepared by precipitation of a precursor from solution followed by calcination [1]. The precipitation is typically thoroughly optimized, whereas for the calcination merely holding temperature and time may be considered. When producing highly reactive nanoscale materials, a careful balance between generating the active site – e.g. through crystallization of an oxide – and avoiding unwanted effects – surface area loss or conversion into a thermodynamically stable but inactive phase – is essential, and may be difficult to maintain during scale-up.

As an example for the above synthesis route, we have selected sulfated zirconia catalysts, which are of commercial interest because of their high activity in the skeletal isomerization of small alkanes. Moreover, the calcination is critical in the preparation of these materials [2,3]. We varied parameters such as oven geometry and air flow and investigated a variety of properties during the course of calcination to understand the evolution of an active material.

Materials and Methods

Sulfated hydrous zirconia (MEL Chemicals XZ0 1249) was used as raw material. Calcination was performed in a crucible (fixed bed) suspended in a vertical reactor or in a horizontal rocking reactor (agitated bed) (UTP, Xerion Adv. Heating). Typical conditions were 20 g of precursor, 773–973 K maximum temperature, 0.5–12 h holding time, 3 K min⁻¹ heating rate, and air flow 80–700 ml min⁻¹. Performance in *n*-butane isomerization (5 % *n*-butane in He at 1 atm) at 373 K was monitored by on-line gas chromatography. Further characterization included XRD, N₂-adsorption, TG-MS, and UV–vis spectroscopy.

Results and Discussion

Temperature measurements in the *fixed bed* evidence deviations from the program; specifically, during the heat-up stage, a short overheating (glow exotherm) is observed (Fig. 1) [2,3]. On-line mass spectrometry indicates that during calcination, not only water but also traces of sulfur oxides evolve. Samples obtained through quenching in liquid N₂ at the points indicated in Fig. 1 varied considerably in their properties. During the ramp, the surface area decreases, the material crystallizes, and catalytic activity develops. Around the temperature overshoot crystallization proceeds very fast. Within seconds the amount of tetragonal phase (t-ZrO₂) increases from 33% to 74% (Fig. 2). Shortly after the glow maximum, the material is completely crystalline and consists of 97% tetragonal and 3% monoclinic phase. Lattice parameters (t-ZrO₂) reach stable values at the glow maximum with *a* = 3.601 Å and *c* = 5.191 Å. At this point, the band gap reaches a value of 5.3 eV and then does not change further.

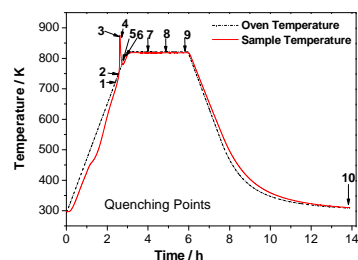


Figure 1. Temperature program, actual sample temperature, and sampling points.

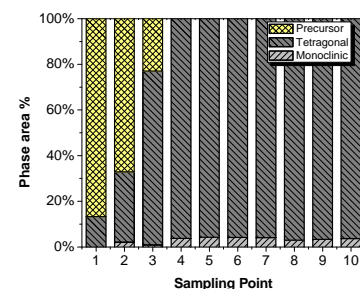


Figure 2. Evolution of phase composition of sulfated zirconia during calcination, including amorphous, tetragonal, and monoclinic fractions.

Decrease in surface area and crystal growth however are completed only at the beginning of the temperature plateau at 823 K. The crystals have an average size of 5–10 nm with a surface area of 185 m² g⁻¹. Analysis of the sulfate decomposition by TG showed that samples that had undergone the entire calcination program contained slightly less sulfate in comparison to samples quenched right after the glow; the typical content was around 6.7 wt% (SO₃).

Samples calcined in the *fixed bed* were more active catalysts than samples calcined in the *agitated bed*. The results of both types of calcination were strongly affected by the air flow through the calcination tubes. Surprisingly, the catalytic activity increased with increasing air flow; e.g. the steady state isobutane formation rates after calcination at 873 K for 12 h in the *agitated bed* were 375, 745, and 830 μmol g⁻¹ h⁻¹ for flows of 500, 700, and 1000 ml min⁻¹.

The results demonstrate that many material characteristics are determined in a short section of the heat-up phase. The sensitivity of the product properties to heat transfer and gas exchange conditions during calcination is striking. To obtain an active catalyst, a metastable oxide (t-ZrO₂) needs to form, while extensive crystal growth and conversion into the thermodynamically stable but inactive modification (m-ZrO₂) through thermal activation are to be avoided. Conversion of a hydroxide into an oxide produces water, and sulfate is easily decomposed into volatile oxides, and these reaction equilibria are governed by local partial pressures.

Significance

Using sulfated zirconia as an example, observations generic to the formation of oxides through calcination of a precursor have been made. The effects of bed geometry and flow conditions outweigh those of temperature and holding time.

References

- Schüth, F., Hesse, M., and Unger, K. in “Handbook of Heterogeneous Catalysis” (G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp, Eds.), Vol. 1, p. 100. WILEY-VCH, Weinheim. 2008.
- Hahn, A., Ressler, T., Jentoft, R.E., and Jentoft, F.C. *Chem. Commun.* 537 (2001).
- Hahn, A.H.P., Jentoft, R.E., Ressler, T., Weinberg, G., Schlögl, R., and Jentoft, F.C. *J. Catal.* 236, 324 (2005).