Crystallization of sulfated zirconia nanoparticles

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Sulfated zirconia is an attractive catalyst used in industry for heterogeneous *n*-alkane isomerisation because of its activity at low temperatures (below 373 K) (M. Hino and K. Arata 1979). Nanosized particles of the metastable tetragonal phase (R.C. Garvie 1965) are highly active and selective for this reaction. Sulfated zirconia catalysts are typically obtained through calcination of amorphous precursors at 773–973 K. Crystallisation and sintering (surface area loss) during this process are strongly exothermic, and frequently lead to an overheating of the sample known as the glow phenomenon. This glow exotherm is observed for many catalytically relevant oxides, e.g. zirconia, titania, and chromium oxide (L. Wöhler 1926). Hahn et al. proposed that the active phase of sulfated zirconia is formed rapidly during the glow (A. Hahn 2005). Here, we are seeking to follow the formation of the active phase during calcination with high time resolution by quenching.

An industrial precursor material was calcined in a cylindrical container suspended in a vertical tubular furnace. Calcination was performed in flowing air at 823 K with a 3 h holding time and 3 K/min ramps. Sample and furnace temperature were monitored. The calcination routine was stopped at defined times through quenching the sample in liquid N_2. Isomerization of *n*-butane was used as catalytic test reaction, product analysis was done by on-line GC. Materials characterization included XRD, BET and TEM measurements.

Samples taken with second resolution during the exothermic reaction could be differentiated in their characteristics. Surface area loss, crystallisation and development of catalytic activity are gradual processes. In the time window of the temperature overshoot crystallisation is very fast. Within seconds the amount of tetragonal phase increases from 33% to 74%. Shortly after the glow maximum, the material is completely crystalline and consists of 97% tetragonal and 3% monoclinic phase. Lattice parameters (t-ZrO_2) reach stable values at the glow maximum with a= 3.601 Å and c = 5.191 Å. Decrease in surface area and crystal growth are completed at the beginning of the temperature plateau at 823 K. The crystals have an averaged size of 5–10 nm with a surface area of 185 m^2g^{-1}. At the same point the maximum of catalytic activity can be detected.

The results show the evolution of surface area, crystal size and catalytic activity to be linked for sulfated zirconia.

References

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Abs. No. **582**
Meeting: **DMG 2008**
submitted by: **Hensel, Nicole**
email: **hensel@fhi-berlin.mpg.de**
date: **2008-06-10**
Req. presentation: **Vortrag**
Req. session: **S16**