The role of the "glow phenomenon" in the preparation of sulfated zirconia catalysts

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Abstract

During the calcination procedure that is necessary to obtain sulfated zirconia catalysts from hydroxide precursors an exothermic reaction occurs in the heat-up period which can lead to a rapid overheating ("glow") of the sample bed; the batch size is identified as a critical parameter that influences heat transfer and thus the extent of the temperature overshoot and the catalytic activity of the product.

Sulfated zirconia has attracted interest as a solid acid catalyst[1,2] because it is capable of isomerizing alkanes at temperatures below 373 K where the more valuable branched alkanes are thermodynamically favored. The activity of sulfated zirconia for *n*-butane isomerization increases 1-2 orders of magnitude upon addition of transition metal cations (Fe, Mn, typically ~2 wt%) as promoters,[3,4] whose function has not yet been clarified. For preparation of these materials, X-ray amorphous zirconium hydroxide is treated with sulfate solutions (e.g. ammonium sulfate, sulfuric acid) and, optionally, with solutions containing the respective cations (e.g. metal nitrates). The final step of the preparation is a thermal treatment at 773 – 973 K, typically conducted in air (calcination). Important catalyst properties such as sulfur content, surface area, phase composition, and activity are seemingly correlated to the calcination temperature.[2,5-7] A number of reactions occur during calcination - typically already in the heat-up period -, among them water loss, decomposition of species (e.g. ammonium, nitrate), and changes of morphology and structure (crystallization). Using thermal analysis, the heat of these reactions has been monitored, and for pure zirconium hydroxide typically a broad endothermic signal is found between 273-373 K, followed by a sharp exothermic signal around 725 K.[2,8] Not only is the origin of the exothermic signal - crystallization or a surface area

reduction - still under debate,[6,8-11] also the extent of the temperature increase has never been accurately determined for catalyst precursor samples not of analytical (~10 mg) but of preparative scale (~10 g). We measured the temperature in the sample bed when calcining gram amounts of zirconium hydroxide based catalyst precursors and tested the activity of the obtained catalysts.

Zirconium hydroxide (ZH) and sulfated zirconium hydroxide with 5-6% SO_3 (SZH) from MEL Chemicals were used as starting materials. SZH was promoted by adding aqueous solutions of $Mn(NO_3)_2 * 4 H_2O$ or $Fe(NO_3)_3 * 9 H_2O$ (both Merck p.a.) under vigorous stirring, followed by room temperature drying (incipient wetness method[4]) to give xFSZH and xMSZH (x = nominal promoter content after calcination in wt% metal). For calcination, the powders were loaded into differently sized quartz boats (2.2, 8.4, 17.1 ml) providing different surface-to-volume ratios. Single boats were placed in a 29 mm i.d. quartz tube in a tubular furnace with PID control. In order to monitor the bed temperature during calcination, an additional thermocouple was placed in the center of the bed. Sheathed thermocouples with 0.5 mm outer diameter were used for fast response and to minimize heat-sink effects. The quartz tube was continuously purged with 200 ml min^{-1} synthetic air and the oven was heated to 923 K at 3 K min^{-1}, held for 3 h at 923 K – a temperature

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recommended for best activity of promoted sulfated zirconia[7] - and then cooled to room temperature. Isomerization of *n*-butane to isobutane was conducted at atmospheric pressure in a once-through plug-flow fixed bed reactor employing 500 mg of catalyst. After a 30 min activation at 723 K in dry nitrogen, the isomerization was run at 338 K, feeding 80 ml min^{-1} of a 1% *n*-butane in nitrogen mixture. Analysis was performed with on-line gas chromatography.
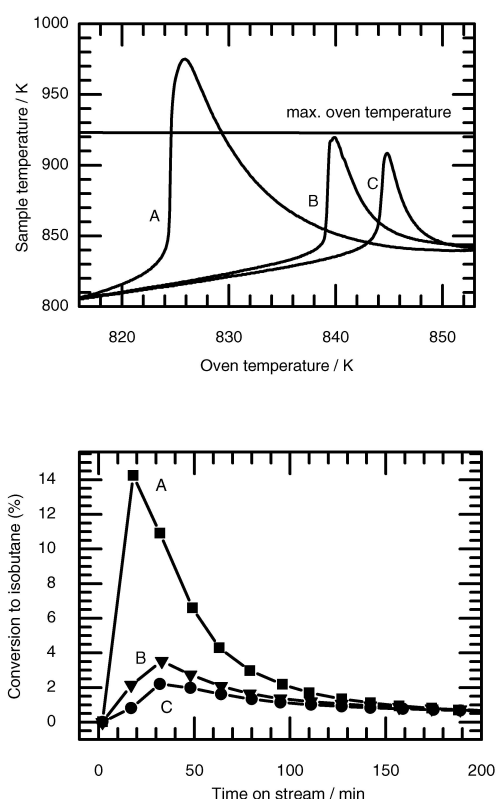
Fig. 1 shows the bed temperature vs. oven temperature during the calcination of ZH, SZH, 2FSZH, and 2MSZH in the largest boat. During the heat-up period, at oven temperatures of 650 to 850 K, a rapid temperature rise inside the bed was observed for all samples with maximum rates of 50 K s^{-1} (ZH). The bed temperature rose by up to 300 K (ZH) and exceeded the desired maximum temperature of 923 K in all cases. Increasing promoter content shifted the start of the temperature rise to higher oven temperatures, with Mn exerting a stronger effect than Fe. According to preliminary results, the heating rate also has an influence.
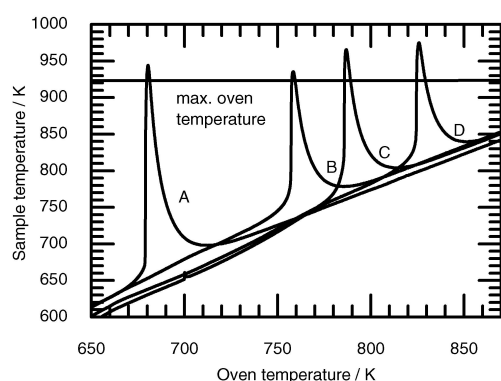
Fig.1: Bed temperature vs. oven temperature during calcination of zirconium hydroxide (A, reproduction A'), sulfated zirconium hydroxide (B), sulfated zirconium hydroxide promoted with 2 wt% Fe (C), and sulfated zirconium hydroxide promoted with 2 wt% Mn (D). Conditions: 17.1 ml boat (20 to 25 g sample), flowing air, nominal heating rate: 3 K min^{-1}

Fig. 2a shows the bed vs. oven temperature for three differently sized batches taken from a single preparation of 2MSZH. The temperature rise in the large batch started first during the ramp, followed by the medium and the small batch. The largest batch produced the highest temperature rise and only this sample reached more than 923 K. These three batches underwent the entire calcination program as described above, the only difference being the batch size, and were then tested for *n*-butane isomerization. The sample taken from the large batch exhibited a significantly higher maximum conversion than the samples taken from the smaller batches (Fig. 2b). This result was qualitatively the same for a number of samples with different promoter contents (Mn and/or Fe in the range from 0.5 % to 3.5 %). The BET-surface area of Fe- or Mn-promoted samples increased with increasing calcination batch size, covering a

range of 85 - 115 m^2 g^{-1}. Fe- or Mn-promoted samples consisted predominantly of tetragonal zirconia, and the size of crystalline domains decreased with increasing calcination batch size, covering a range of 80 to 120 nm.

Fig. 2:
(a) Bed temperature vs. oven temperature with the sample amount as parameter. Sample: sulfated zirconium hydroxide promoted with 2 wt% Mn. Conditions: flowing air, nominal heating rate: 3 K min^{-1}, holding time: 3 h at 923 K. Large boat – 25 g (A), medium boat – 12 g (B), and small boat – 3 g (C).
(b) Butane isomerization reaction performance of the samples from Fig. 2a. Reaction conditions: 500 mg sample, 1 % *n*-butane in nitrogen, 80 ml/min total flow, p = 1 atm, T = 338 K.

The spontaneous temperature rise in the sample bed during the heat-up phase corresponds to the reported thermal analysis data[2,6] in that an exothermic reaction occurs. Older literature gives some indication that the temperature rise may be considerable, depending on the amount and packing, e.g. Wöhler[11] heated as much as 0.25 g zirconium hydroxide and measured a ~60 K temperature rise. The effect has been observed for a number of different hydroxides and is also referred to as "glow phenomenon"[9,11,12] because it can lead to a visible light emission. In the presence of sulfate[6] or other hydroxides, the "glow"[9] or the thermal signal[6,8] were found to be subdued and/or shifted to higher temperature.[6,8,9] Our results are consistent with previous findings but additionally demonstrate how an extensive and typically

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not reported quantity, i.e. the mass to be calcined, influences heat transfer and thus the temperatures reached, and the catalytic properties of the final product. In sufficiently large and compact batches, the peak temperature may exceed the desired maximum calcination temperature; if this is the case, then for equally sized batches of differently promoted zirconium hydroxides, the nature and amount of additive (sulfate, Fe, Mn) may determine the true maximum temperature. Thus, the promoters have a systemic influence in that they alter the calcination chemistry. The start temperature correlates with the batch size, as does the catalytic activity. The series of events - rapid temperature increase, high peak temperature, rapid temperature decrease – allows for a chemistry that is reflected in the final product although the sample is subsequently treated for 3 h at 923 K.

Similar effects are potentially possible in the processing of other hydroxides that exhibit the "glow", namely hydroxides of iron, chromium, and titanium.[9,11] Certainly

for the preparation and characterization of zirconia catalysts all details of the thermal treatment must be reported, i.e. the heating rate and any parameter influencing heat transfer such as sample size and shape. This applies particularly to experiments involving very small or large amounts (thermal analysis, scale-up) and in situ calcinations with the sample pressed into a pellet or wafer. Our results suggest that any two experiments involving thermal treatment of a zirconium hydroxide under non-identical conditions may not yield the same material and may not deliver related analytical data.

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