

Influence of storage atmosphere on properties and performance of sulphated zirconia isomerization catalysts

B.S. Klose, F.C. Jentoft, R. Schlögl

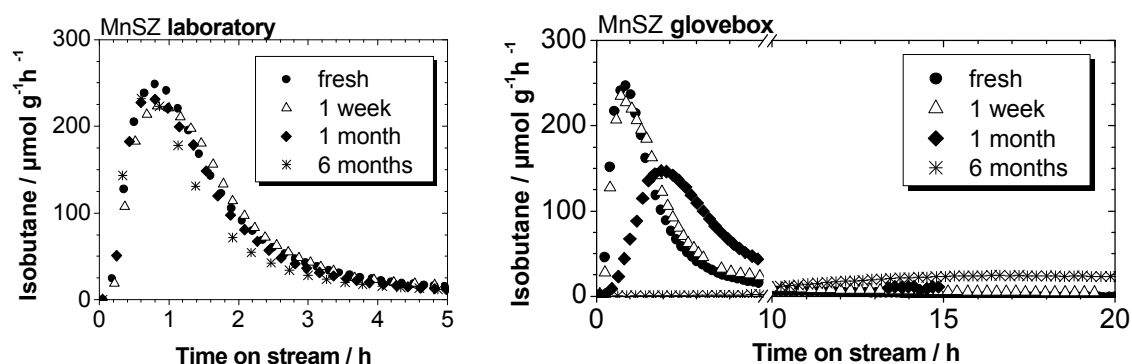
Dept. Inorg. Chemistry, Fritz Haber Institute, MPG, Faradayweg 4-6, 14195 Berlin, Germany

Sulphated zirconia (SZ) is a sensitive material which changes its structure and catalytic activity upon exposure to mechanical stress (grinding, pressing).¹ The bulk phase of pure zirconia can transform at 338–393 K within hours in the presence of water vapour.² Thus a zirconia-based catalyst can be envisioned to age within months at room temperature in ambient atmosphere. It has been shown that even the framework of zeolites changes over months in moist environment.³ Here, SZ and Mn-promoted SZ (MnSZ) were aged in different concentrations of water vapour and the *n*-butane isomerization activity was tested.

SZ was prepared by calcining hydrous sulphated zirconia (SZH, MEL Chemicals) in flowing air at 823 K for 3 h. MnSZ (2 wt% Mn) was obtained through incipient wetness impregnation of SZH with Mn(NO₃)₂ aq. solution and calcination at 923 K for 3 h. Samples were stored in (i) a laboratory cupboard, (ii) air saturated with water vapour at 313 K, or (iii) dry Ar atmosphere (glovebox). Isomerization was carried out after activation in N₂ at 723 K using 25 ml/min 1 vol% *n*-C₄H₁₀ in N₂ at 373 K (SZ) or 323 K (MnSZ). For XRD a STOE-STADI-P diffractometer with Debye-Scherrer geometry was used (Cu K α 0.1541 nm). BET surface areas were measured with a Quantachrome Autosorb-1 after 16 h outgassing at 473 K.

The aged MnSZ samples exhibited an increase in darkness from grey to dark grey in the order laboratory << glovebox < water vapour. SZ remained white. The storage conditions influenced the catalytic performance of MnSZ more strongly than that of SZ. The activity profile of MnSZ kept in the laboratory did not change significantly during half a year, but drastic changes were observed in the isomerization activity of MnSZ stored in the H₂O (<1 ppm) and O₂ (\leq 8 ppm) depleted environment of a glovebox (see figure). The sample exposed to water vapour showed an intermediate behaviour. These differences could result from different oxidation states of Mn, since the maximum rate has been found to increase with the average Mn valence after activation.⁴ The fact that different aging conditions have less influence on the performance of unpromoted SZ supports the role of the Mn oxidation state. Another possible explanation for the difference in activity could be changes to the bulk

structure of the catalyst.¹ The diffractograms of fresh and aged MnSZ indicated only tetragonal zirconia, and no effect of the different conditions was discernable. BET surface areas were constant at $115 \pm 8 \text{ m}^2/\text{g}$ for all promoted samples and about $140 \text{ m}^2/\text{g}$ for SZ. An explicit difference between the aged samples exists in the H_2O content. The ‘right’ amount of H_2O on the catalyst has been inferred to be important and concentrations of $75 \text{ } \mu\text{mol}\cdot\text{g}^{-1}$ or $200 \text{ } \mu\text{mol}\cdot\text{g}^{-1}$ have been proposed to result in best performance.^{5,6} Excess water from humid storage conditions can be removed in the activation procedure before the isomerization reaction,⁷ but lacking water due to dry storage conditions would not be replenished. However, traces of water from the feed system may adsorb on the catalyst while on stream. This scenario could explain why the MnSZ catalyst that had been stored in the glovebox for 6 months started producing isobutane after $\approx 10 \text{ h}$ on stream. The maximum rate though was only 1/10 of that of the fresh sample (figure).



The storage conditions (temperature, O_2 and H_2O partial pressure) can influence the performance of sulphated zirconia catalysts. Through variation of the conditions different materials can be generated from the same parent compound. Such samples provide a unique opportunity to identify properties that are relevant for activity.

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