

# Exclusion of Bulk Participation of Sulfated Zirconia in Alkane Isomerization by Using Ordered Mesoporous Catalyst

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## Introduction

Sulfated zirconia (SZ) is a catalyst for isomerization of short chain alkanes, which is active at temperatures as low as RT. A typical profile of the *n*-butane isomerization activity with time on stream is observed as follows: after an induction period the catalyst exhibits a short-term high activity which goes through a maximum, then the activity reaches a steady state at a lower level (Fig. 1). This may be attributed to the presence of at least 2 different types of active sites. On the other hand, an involvement of the crystalline bulk of the catalyst in the reaction is known, for the composition of the different crystalline ZrO<sub>2</sub> modifications in the catalyst, in particular the quantity of the tetragonal zirconia phase which is usually superior to that of the monoclinic modification in an active catalyst, plays an important role for the activity. Furthermore, the activity can be improved by 1 to 2 orders of magnitude through addition of Fe or Mn cations as promoters to the catalyst. It is believed, that the promoting effect of Fe and Mn is achieved mainly by modification of the geometric structure of the zirconia bulk, especially in the case of Mn promotion, Mn atoms are embedded in the zirconia lattice, stabilizing the tetragonal ZrO<sub>2</sub> and modifying the unit cell parameters [1].

MCM-41-like ordered mesoporous zirconia with sulfate components has been available since 1996 [2] and demonstrated to be active for *n*-butane isomerization recently [3]. The mesoporous material possesses no crystalline bulk, and the majority of the Zr atoms is exposed on the internal surfaces within the mesopore system. The participation of crystalline zirconia bulk in alkane isomerization can thus be considered excluded when using this material as catalyst. Should these ideas be true, addition of Fe or Mn cations should not have a promoting effect on the activity of mesoporous sulfated zirconia. The present work is to confirm this hypothesis.

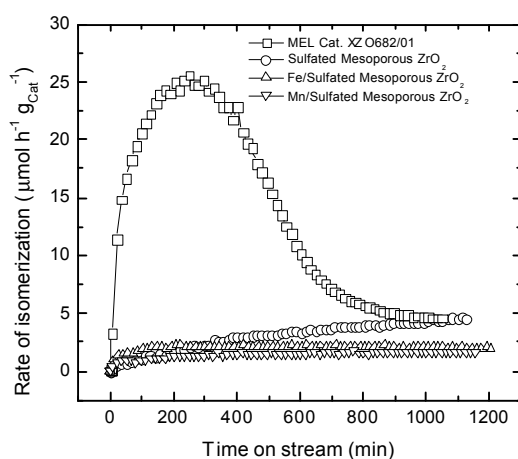
## Experimental Section

Sulfate containing mesoporous zirconia (mesoporous SZ) was synthesized following the recipe of Schüth et al. [2]. A hydrogel was prepared by mixing solution A containing 2.5 g of hexadecyl-*tri*-methyl-ammonium bromide (CTAB), 5.99 g of 70 wt.% Zr(OPr)<sub>4</sub> in propanol, 24.4 g of 37 wt.% hydrochloric acid in 115 g of water and solution B with 1.69 g of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> in 23 g of water. The formation of the

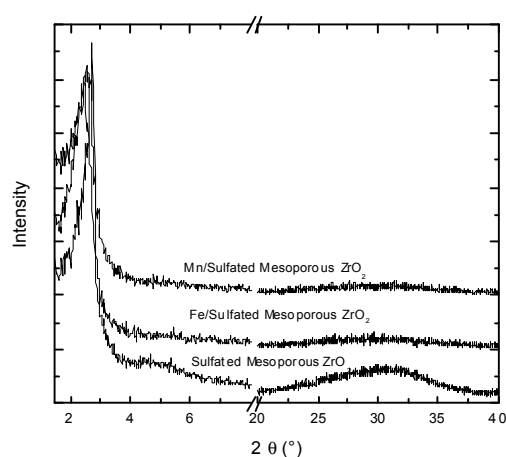
mesostructured  $\text{ZrO}_2/\text{CTAB}$  composite occurred then under autogeneous pressure at  $100^\circ\text{C}$  within 3 days. The recovered solid was calcined at  $540^\circ\text{C}$  for 16 h. Fe or Mn containing samples were synthesized with similar recipes with additional  $\text{Fe}(\text{NO}_3)_3$  or  $\text{Mn}(\text{NO}_3)_2$  in the starting mixture, with ca. 5 wt% of the metal respective to  $\text{ZrO}_2$ . Characterization has been done by XRD, TG/DTA, SEM/EDX,  $\text{N}_2$  adsorption, and EXAFS. The catalytic test was carried out in a flow type fixed bed reactor at  $105^\circ\text{C}$  with a feed of 1 vol.% *n*-butane in  $\text{N}_2$  at a total flow rate of  $30\text{ cm}^3/\text{min}$  over 200.0 mg catalyst.

## Results and Discussion

Fig. 2 shows the XRD patterns of the calcined mesoporous zirconia samples, unpromoted and promoted with Fe and Mn, respectively. Together with characterization results with other physicochemical methods, it is allowed to conclude, that these samples are structural analogues of MCM-41, possessing mesopores and without crystalline zirconia bulk. Nitrogen adsorption on the unpromoted sample revealed a BET specific surface area of ca.  $200\text{ m}^2/\text{g}$ , and a BJH mean pore diameter of 2.2 nm. The catalytic test results of these samples are depicted in Fig. 1, together with the test result of a commercial SZ catalyst MEL Cat. XZO682/01, composed mainly of tetragonal zirconia. It can be seen, that the mesoporous SZ exhibits no short-term high activity like MEL Cat., but reaches the same activity as the latter in the long term. This evidences, that the short-term high activity of SZ is likely related to the crystalline bulk, while the long-term steady activity is provided by the surface. Addition of Fe and Mn has no obvious promoting effects on the mesoporous SZ catalyst.



**Fig.1:** Catalytic test results of mesoporous zirconia samples in comparison with a commercial sulfated zirconia catalyst.



**Fig.2:** XRD of the calcined mesoporous zirconia samples: without promoter and with Fe or Mn promoters.

## References

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