



In Situ Diffuse Reflectance IR Spectroscopic Investigation of *n*-Butane Isomerization on Promoted Sulfated Zirconia Catalysts



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Introduction

Sulfated zirconia (SZ) is an attractive catalyst for low temperature butane isomerization [1]. Its activity can be improved by 1–2 orders of magnitude through addition of promoters such as iron or manganese in cationic form [2,3]. The state of these promoters has been characterized, and depending on the method of preparation, a major fraction is found to form a solid solution with zirconia [4]. It has been proposed that promoters facilitate reaction initiation via oxidative dehydrogenation to butenes, which may be converted into the reaction carriers, viz. carbenium ions. Only indirect evidence such as better activity after activation in oxidizing than in inert atmosphere has been presented [5]. Reaction profiles recorded under moderate reaction conditions (e.g. 323 K, 1 kPa *n*-butane) show an induction period and zero conversion in the extrapolation to zero time on stream. Either the catalyst becomes active only in the feed, or intermediates accumulate on the surface. We have focused on manganese as a promoter and have used in situ diffuse reflectance IR spectroscopy (DRIFTS) to reveal the effects of activation or regeneration in inert gas or O₂, and to monitor the events during the induction period.

Experimental

Sulfated zirconium hydroxide XZO 682/01 (MEL Chemicals) served as a precursor. Promoters (2 wt.%) were introduced via the incipient wetness method, using aqueous solutions of either Fe(III) or Mn(II) nitrates. Samples were calcined in portions of 20–25 g at either 823 K (SZ) or 923 K (“MnSZ”, “FeSZ”) for 3 h [6]. A Bruker IFS 66 FTIR spectrometer with diffuse reflectance attachment “The Selector” and “Environmental Chamber” from Graseby Specac was used. Catalysts were activated or regenerated at 773 K in flowing N₂ or O₂. Reaction conditions were 323–358 K, 1–5 kPa *n*-butane in balance

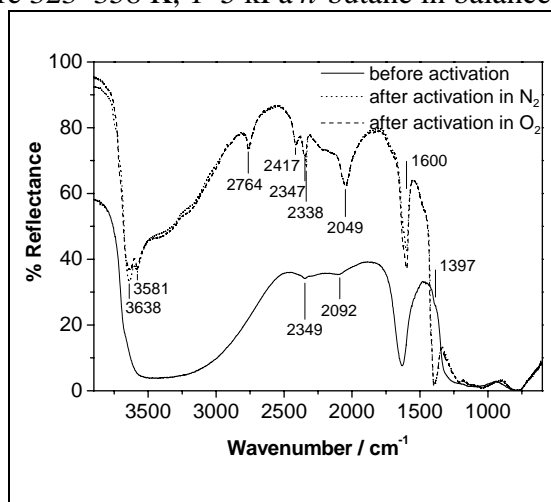


Fig. 1: DRIFT spectra of MnSZ recorded at 323

of N₂, with a total flow of 30 ml/min. Effluent gases were analyzed by on-line GC.

K before and after activation at 773 in O₂ or N₂.

Results and Discussion

DRIFT spectra of SZ, MnSZ, and FeSZ after activation in N₂ were very similar; bands typical of OH and SO vibrations were detected. With the help of DFT calculations [7] it was possible to identify S₂O₇²⁻ as a predominant surface species, characterized by a band at $\approx 1400\text{ cm}^{-1}$. Strong Lewis acid sites capable of adsorbing N₂ at temperatures up to 358 K were present. The surface was still hydrated with 60–125 $\mu\text{mol H}_2\text{O/g}$.

Change of the activation atmosphere from inert to O₂ did not alter the IR spectra of MnSZ significantly (Fig. 1). The activity increased and decreased more rapidly than after activation in N₂. Measured maximum rate data ranged within $\pm 15\text{--}20\%$ relative to those obtained after activation in N₂, and further experiments are required. Variations of the water content in the range 2.5–5%, clearly visible in the spectra, did not affect the catalytic performance of MnSZ. The spectrum and the catalytic properties of deactivated MnSZ could be completely reestablished in O₂ at 773 K. In N₂, the spectral signature of the hydroxyl and sulfate groups was recovered but the material was rendered inactive. All of these observations indicate that solely from the state of the hydroxyl and sulfate groups it is impossible to predict catalytic activity.

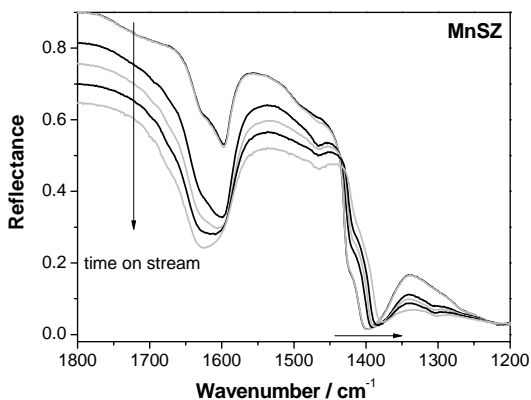


Fig. 2: Evolution of DRIFT spectra of MnSZ with time on stream at 323 K and 1 kPa *n*-butane.

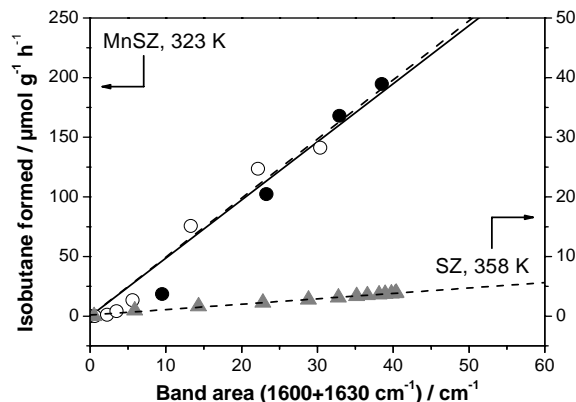


Fig. 3: Rate of isomerization during induction period vs. area of bands around 1600–1630 cm^{-1} .

Spectra recorded during *n*-butane isomerization show several bands growing between 1720–1550 and at 5200 cm^{-1} , and a shift of the S=O vibration at 1400 cm^{-1} to lower wavenumbers (Fig. 2). The new bands may arise from adsorbed water, potentially a product of oxidative dehydrogenation, but other species can not be excluded. At early times on stream, before maximum conversion is reached, the rate of isomerization is proportional to the area of the feature including the bands at 1630 and 1600 cm^{-1} (Fig. 3). Hence, the absorbing species must be active intermediates or side products of the reaction producing the intermediates. It follows that the rate during the induction period depends on two factors: the number of active surface species formed and the intrinsic turnover per such species. The presence of Mn enhances this intrinsic turnover frequency (Fig. 3). So far it has been believed that promoters such as Fe or Mn facilitate the reaction initiation; here, for the first time, an effect of a promoter on the isomerization itself is demonstrated.

References

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