



# In Situ DRIFT and UV-vis Spectroscopic Investigation of Mn-Promoted Sulfated Zirconia during Alkane Isomerization



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## **INTRODUCTION**

Sulfated zirconia (SZ) promoted with Fe or Mn has the ability to isomerize *n*-alkanes at 323 K [1]. After a period of rising activity, these catalysts deactivate rapidly, but their behavior has not been studied as extensively in situ as that of unpromoted SZ [2]. Besides the formation of carbonaceous deposits, reduction of sulfate [3] or of promoter species have been proposed as causes of deactivation, specifically in context with alkane activation via oxidative dehydrogenation rather than through acid catalysis. To further investigate changes to the catalyst during induction period, deactivation, and reactivation we studied Mn-promoted SZ in situ during *n*-butane isomerization using DRIFT and UV-vis spectroscopy.

## **EXPERIMENTAL**

Mn-promoted SZ catalysts with up to 2 wt% Mn were produced from sulfated zirconium hydroxide (MEL Chemicals) via incipient wetness impregnation and subsequent calcination at 923 K [4]. In situ DRIFTS was conducted using a Graseby-Specac "Selector" attachment with environmental chamber placed in a Bruker ifs 66 spectrometer. In situ UV-vis spectra were acquired with a diffuse reflectance attachment and a PE lambda 9. Typical reaction conditions were 1-5 kPa *n*-butane and 323 K. Effluent gases were analyzed by on-line GC.

## **RESULTS AND DISCUSSION**

Activation at 723 K in inert gas dried the catalysts and changed the nature of the promoter; bands at 570 and 675 nm arising from the Mn were weakened. Activation in pure O<sub>2</sub>, potentially advantageous for an oxidative dehydrogenation functionality, yielded catalysts with a lower maximum isomerization rate. During catalysis the overall reflectance in the DRIFT spectra decreased and two bands at 1628 and 1602 cm<sup>-1</sup> were observed. The lower frequency band grew faster initially, and was then "overtaken" by the other band. Usually, a single band is observed in this region for oxides, and it is assigned to the bending vibration of coordinated water. The band of the S=O stretching vibration shifted from 1400 to 1375 cm<sup>-1</sup>; and its position was linearly correlated to the integrated intensity of the bands at 1628 and 1602 cm<sup>-1</sup>. The S=O band is known to shift when polar molecules are adsorbed; and a possible interpretation of the spectral changes is the formation of water during the induction period, consistent with oxidative dehydrogenation. Reactivation in pure O<sub>2</sub> at 773 K restored the pre-reaction IR spectrum and the activity completely, excluding irreversible processes such as sulfur loss. During treatment of deactivated Mn-promoted SZ at 773 K in N<sub>2</sub> two new bands appeared at 1532 and 1465 cm<sup>-1</sup>, probably vibrations of conjugated C=C bonds. Hence, hydrocarbon species remaining from the reaction do not desorb upon heating but react to polyunsaturated compounds. The S=O band was restored but the catalyst was inactive. – The sulfate undergoes changes during *n*-butane isomerization, predominantly in the induction period, but restoring of its original structure is insufficient to reactivate the catalyst. O<sub>2</sub> is necessary to remove "coke" but its effect is not exclusively positive.

## **REFERENCES**

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