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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 Mn or Fe catalyzes the skeletal isomerization of *n*-alkanes at 323 K [1,2]. Initially, it was believed that the high activity of SZ catalysts arises from superacidic sites [3]. Such sites could not be identified by probe molecule methods [4], and it was suggested that the first reaction step is an oxidative dehydrogenation to give butenes [5], which are easily protonated to carbenium ions, which serve as reaction chain carriers. Here, we seek indications for this mechanism such as a reduction of Mn, Zr, or sulfate [6]; or the formation of water during reaction. If stoichiometric, these reactions will lead to deactivation. Another explanation for the often severe deactivation is the formation of carbonaceous deposits. In situ DRIFT and UV-vis-NIR spectroscopy are suitable to examine all these possibilities. Experiments to optimize activation and regeneration conditions are also performed.

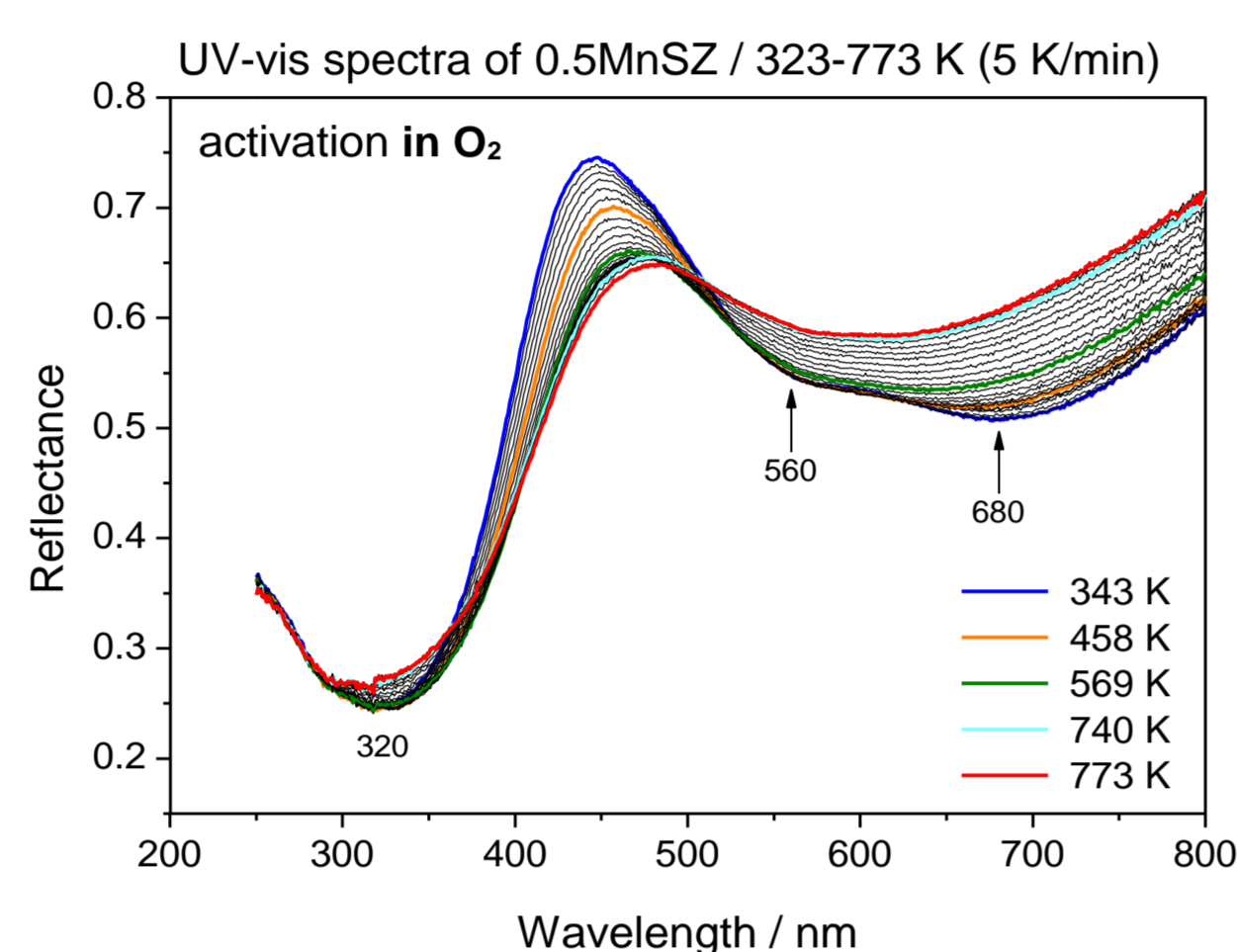
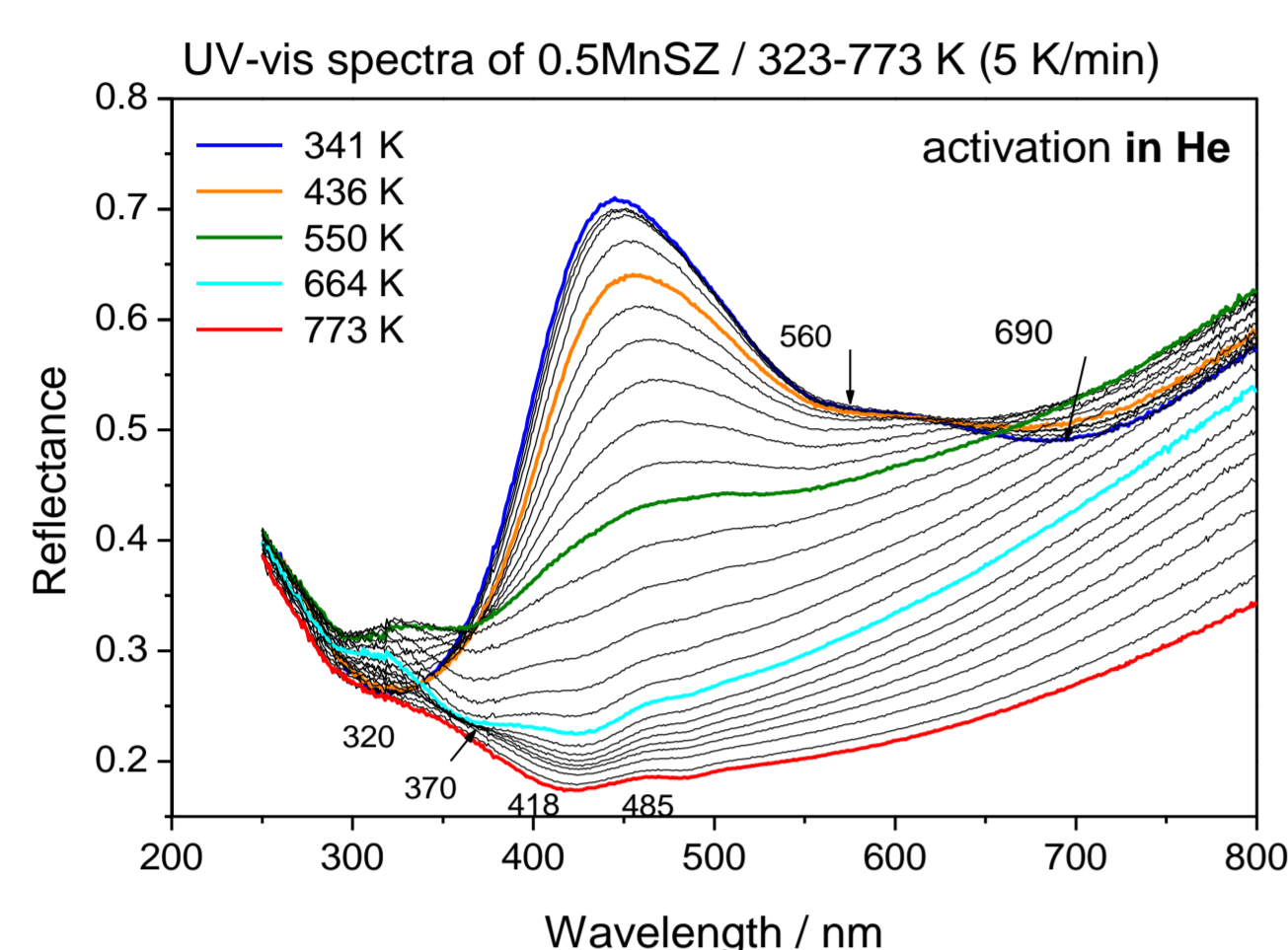
Conclusions

Sulfate changes during *n*-butane isomerization, predominantly in the induction period. An S=O band shift is related to the changing band intensity at 1600-1630 cm^{-1} , suggesting adsorption of water (additional species possible) on the sulfate.

Water formation in the induction period would be consistent with oxidative dehydrogenation. The initial isomerization rate is proportional to the amount of water formed, but different proportionality factors result for different catalysts. No evidence was found for a correlation between performance and reduction of Mn or sulfate.

Restoring the original sulfate structure is insufficient to reactivate the catalyst. Oxidizing agents remove hydrocarbon deposits, and the activity is completely recovered. However, oxidizing treatments do not exclusively exert positive effects; these results do not support the idea of oxidative dehydrogenation.

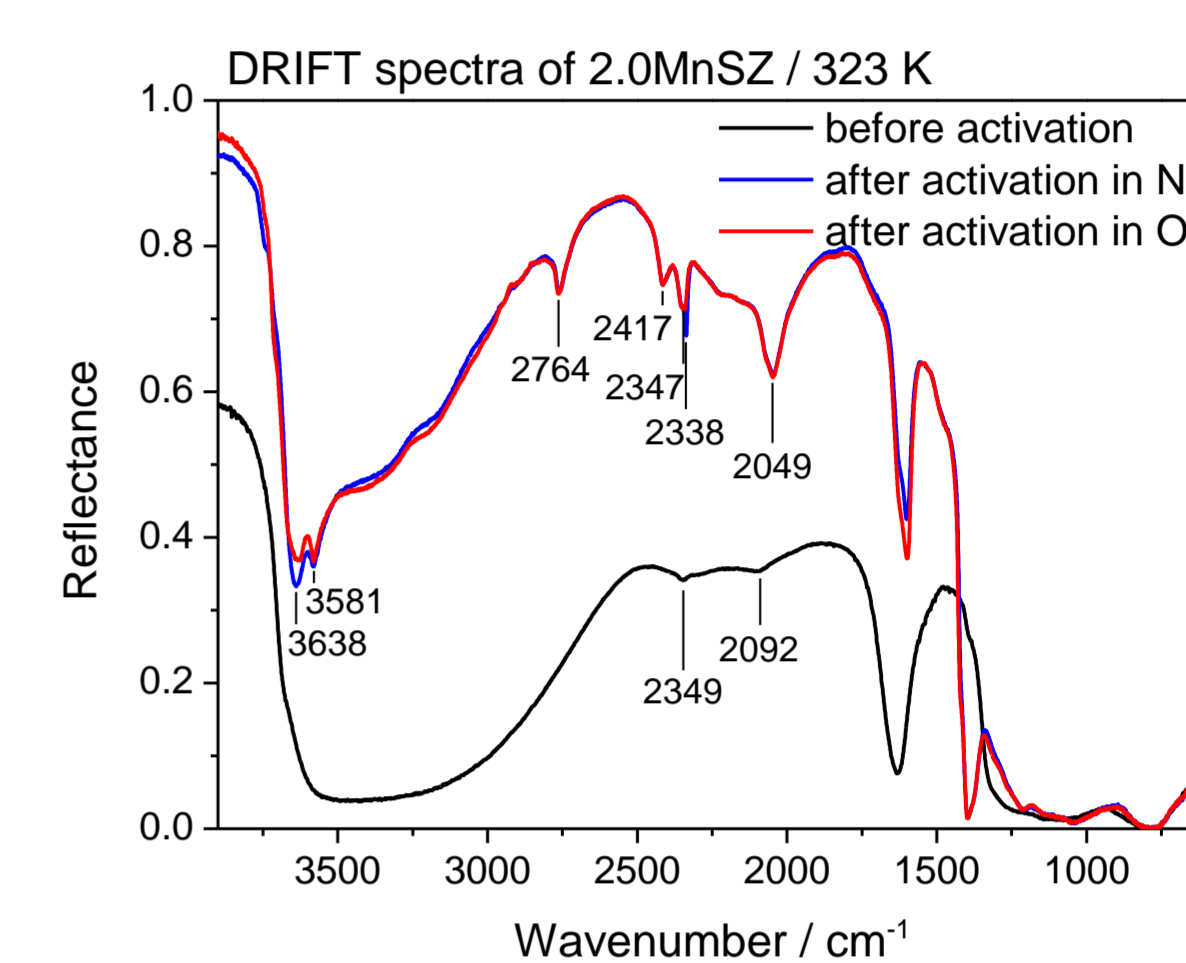
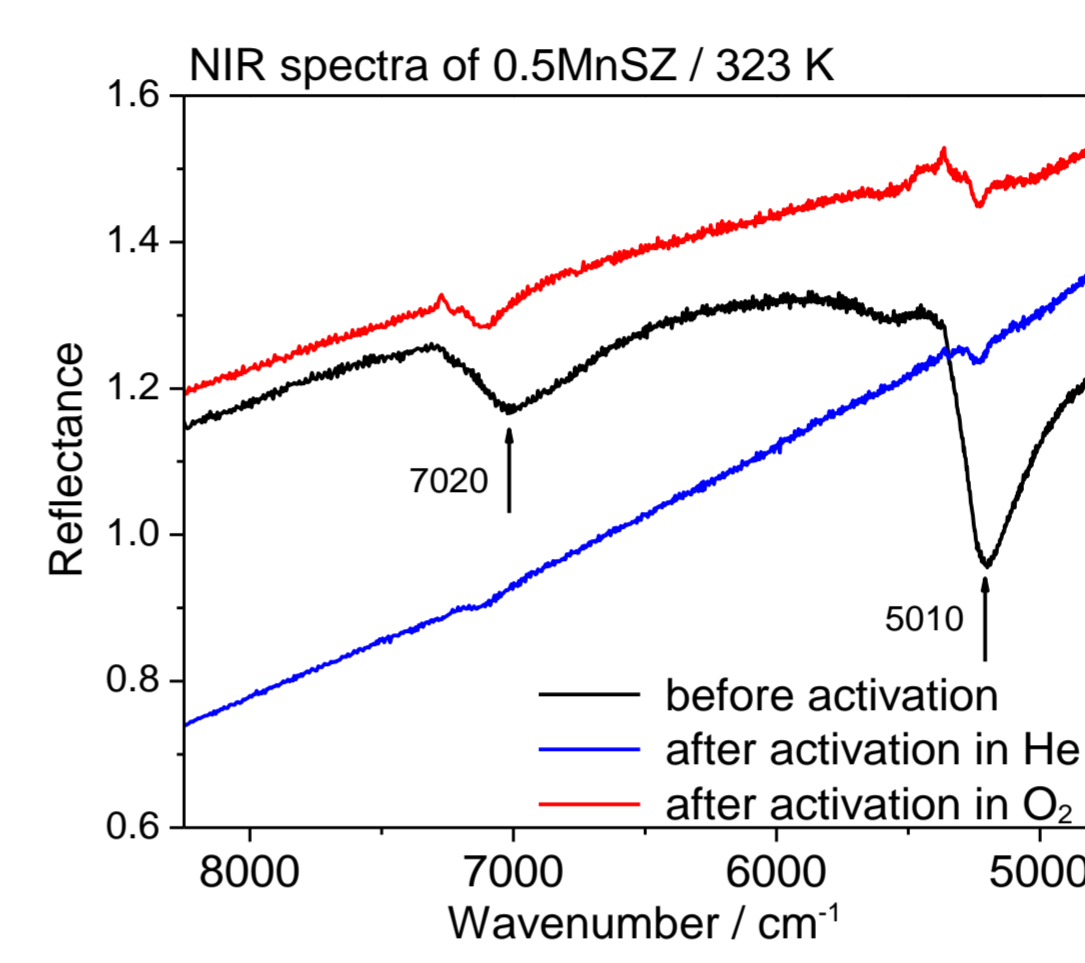
Activation



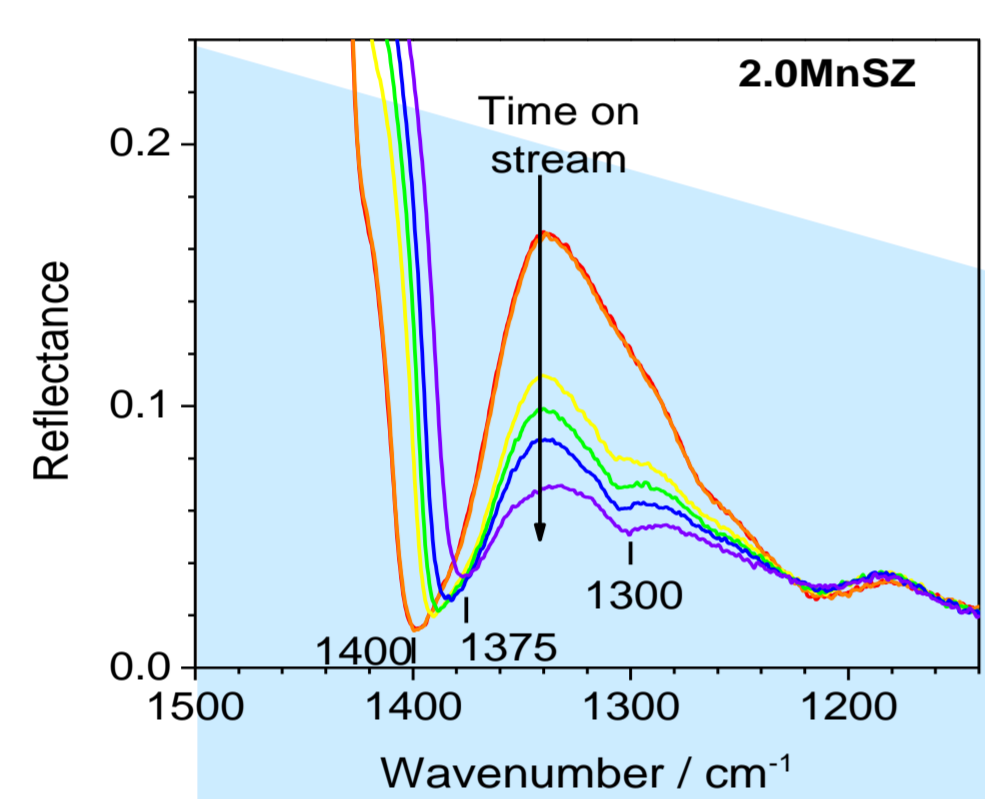
Activation at 723 K dries the catalysts; the gas atmosphere does not influence the final state of OH and sulfate groups

Activation in inert gas changes the nature of Mn (reduction, [7]).

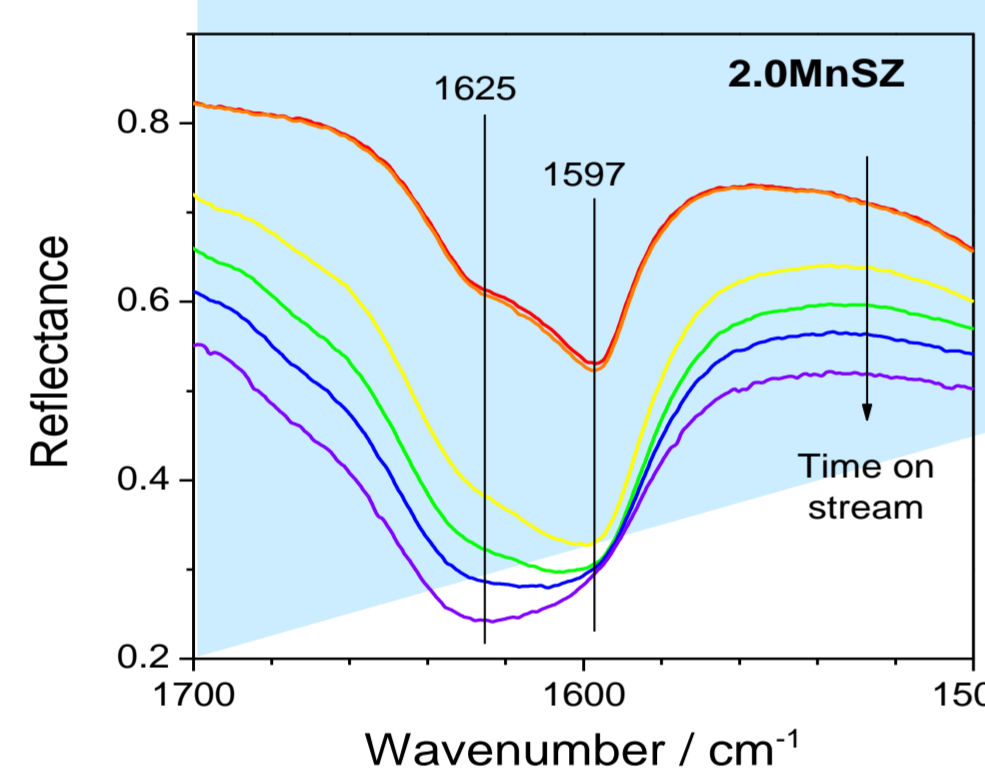
Activation in 100% O_2 yields catalysts with a lower maximum isomerization rate (see section "Reactivation").



Reaction

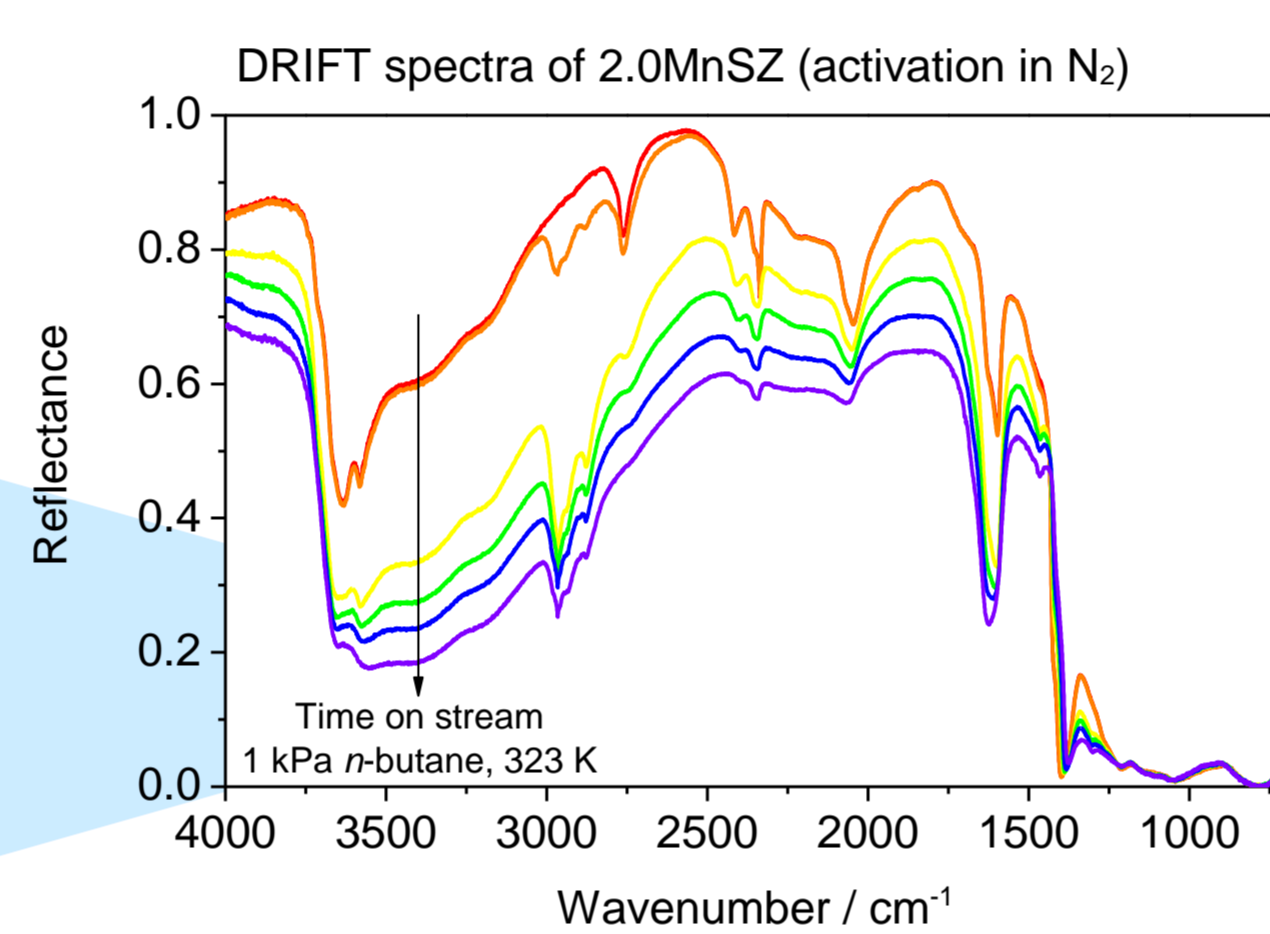


The band of the S=O stretching vibration shifts from 1400 to 1375 cm^{-1} .



Two bands in the region for bending vibration of coordinated water or C=C stretching vibrations:

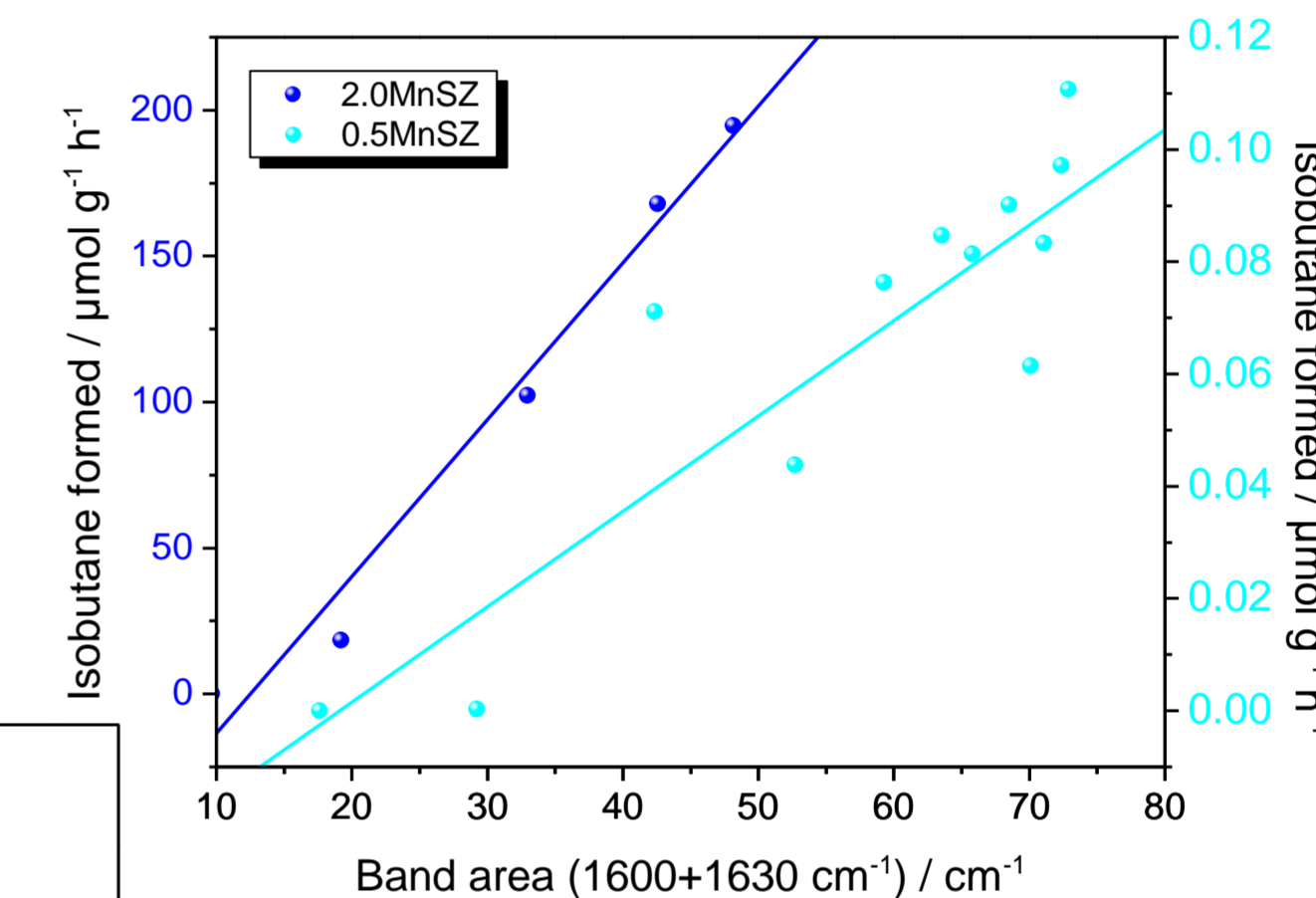
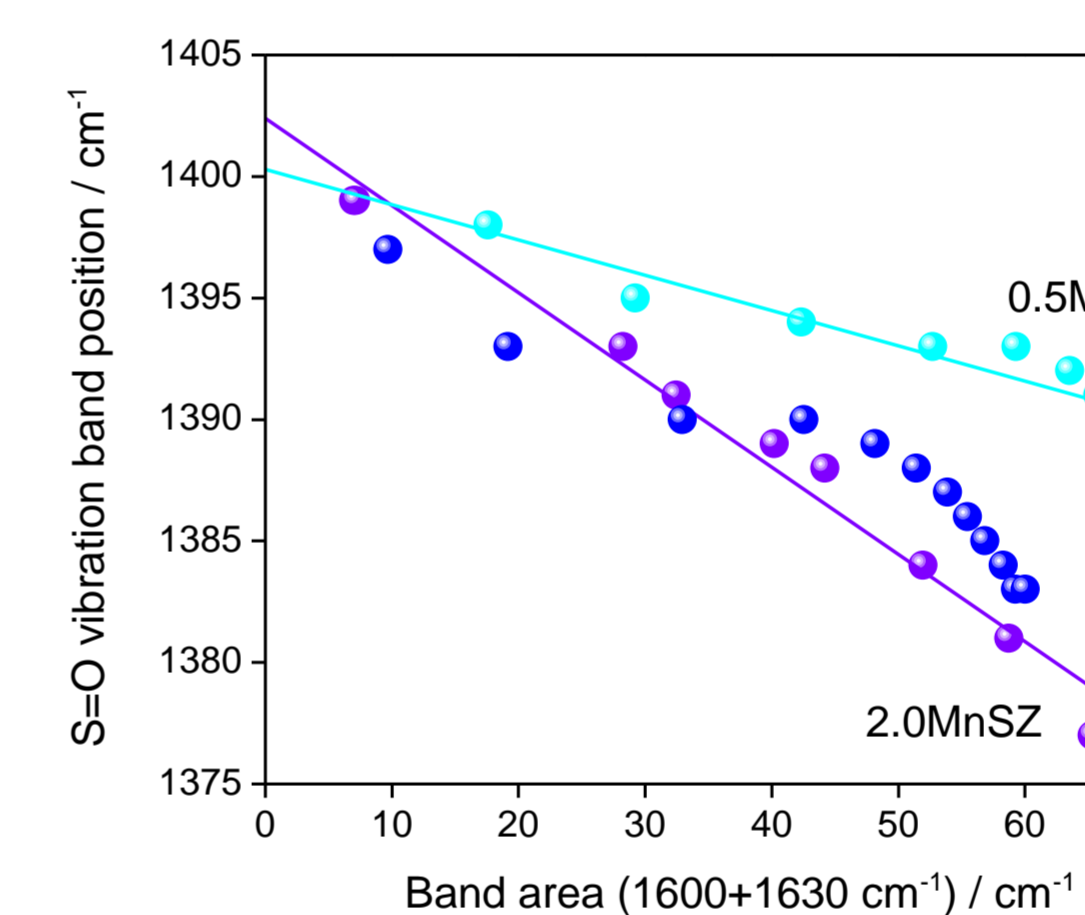
The band at 1597 cm^{-1} grows faster initially, but is "overtaken" by the other band.



During catalysis the overall reflectance in the DRIFT spectra decreases.

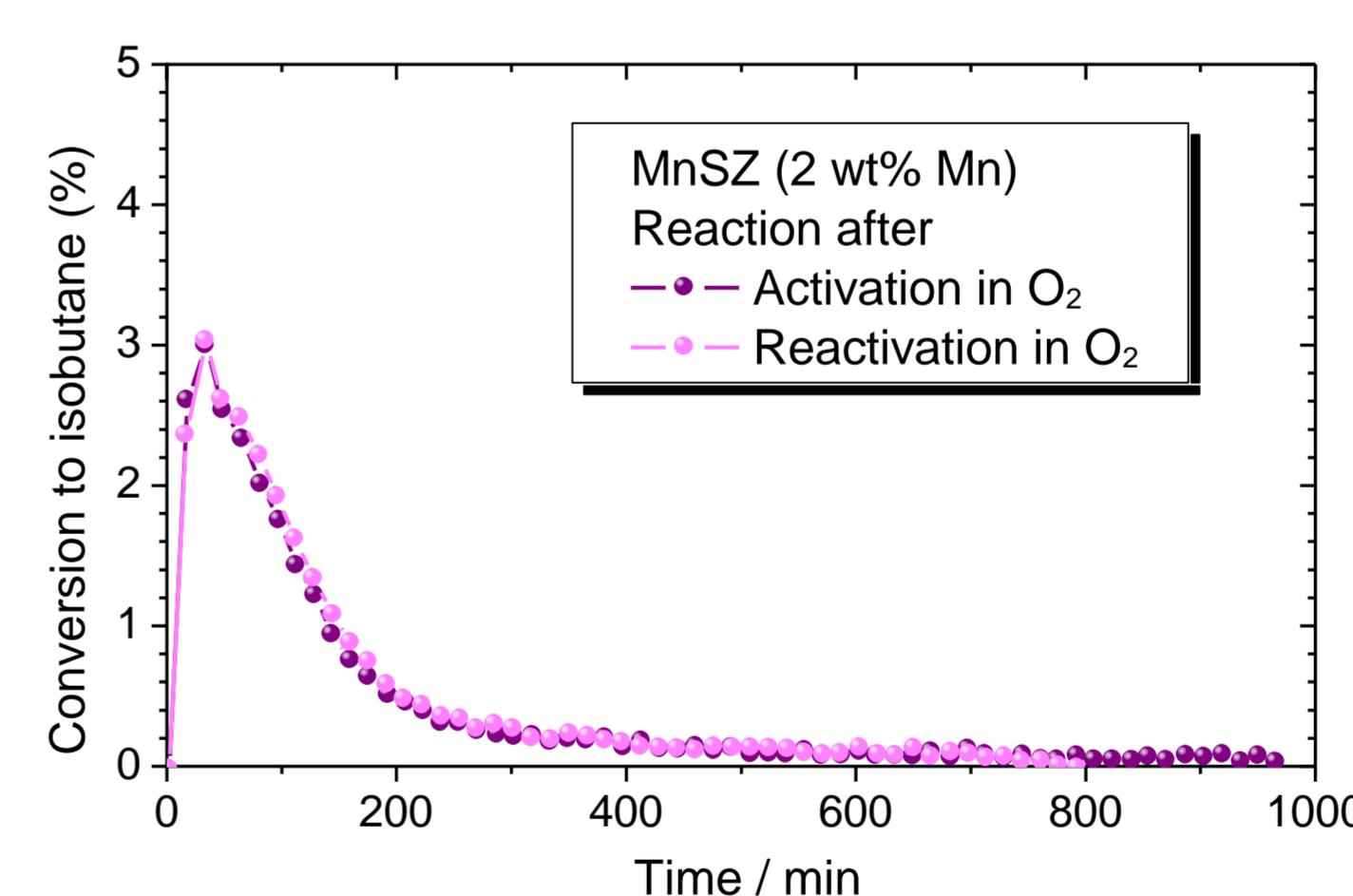
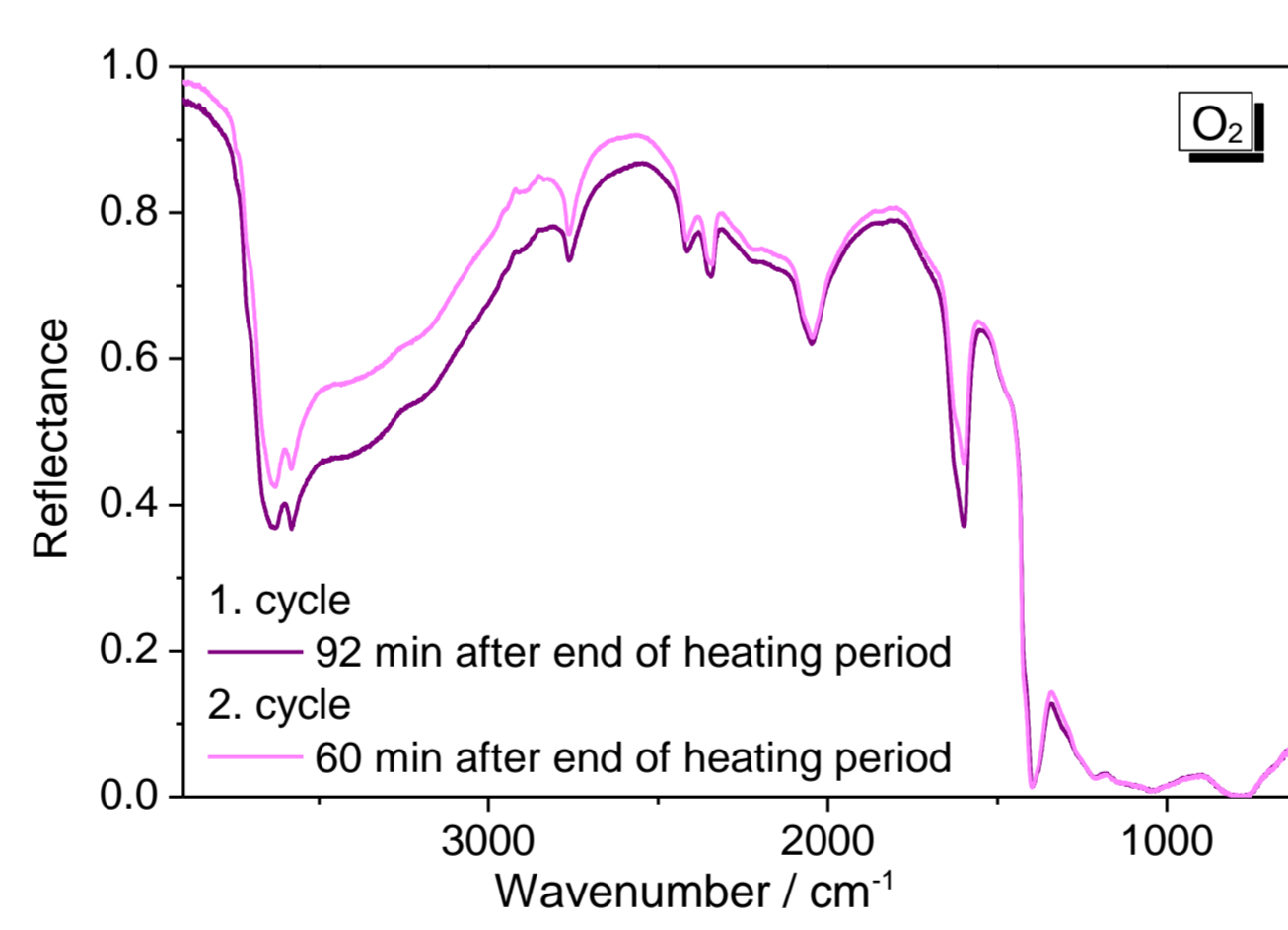
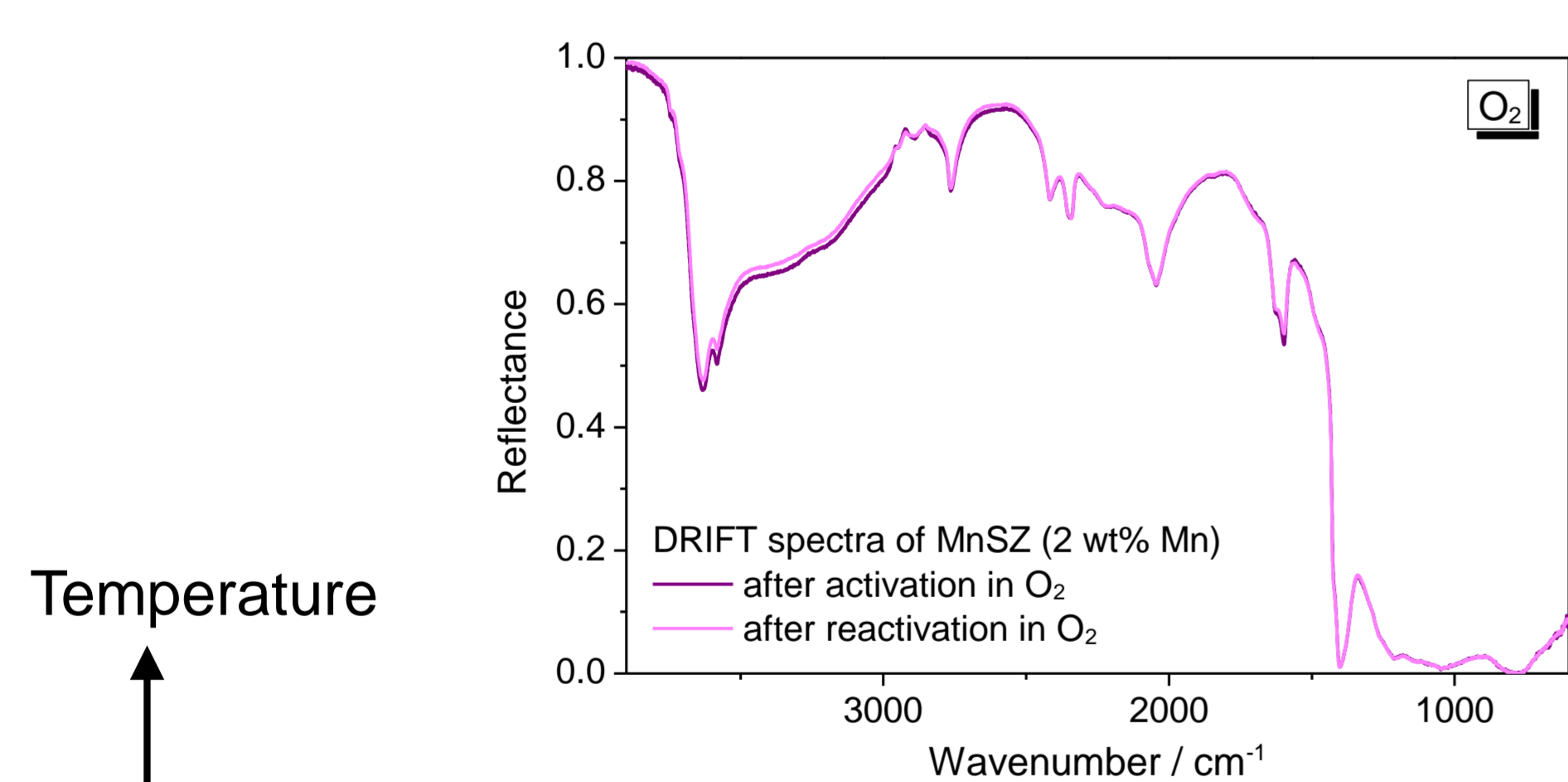
For a catalyst activated in inert gas, the Mn valence remains constant during reaction [7], inconsistent with a role of Mn as a redox initiator.

During the period of increasing activity, the amount of adsorbed species (water) increases linearly, but without general correlation to the rate.



The position of the S=O band is linearly correlated to the integrated intensity of the bands at ca. 1630 and 1600 cm^{-1} .

Reactivation



Reactivation in pure O_2 at 773 K restores the pre-reaction IR spectrum and the activity completely, excluding that major amounts of sulfate are reduced and volatilized in the form of SO_2 during reaction.

Temperature

500°C

end of heating period

0 min

35 min

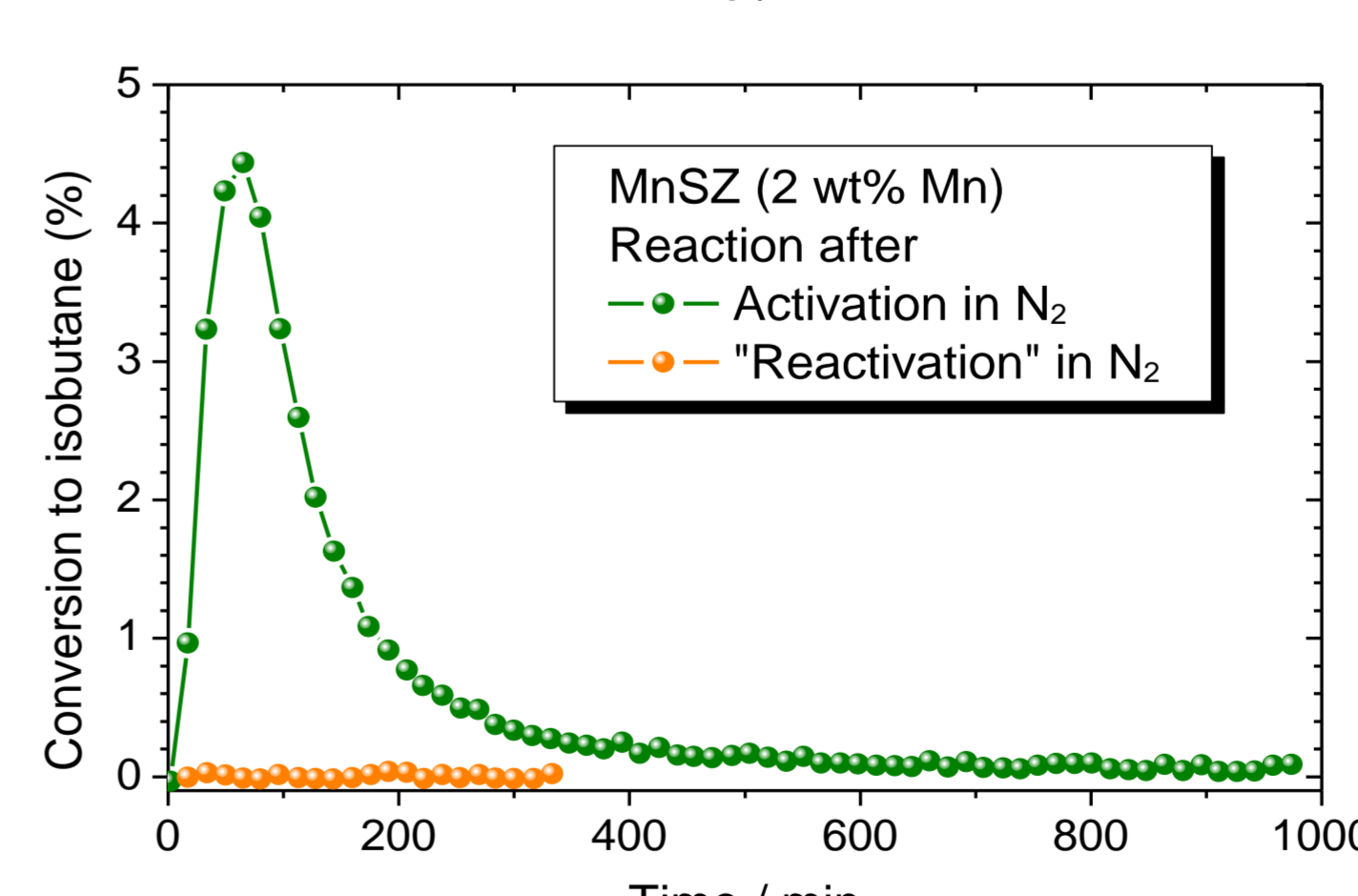
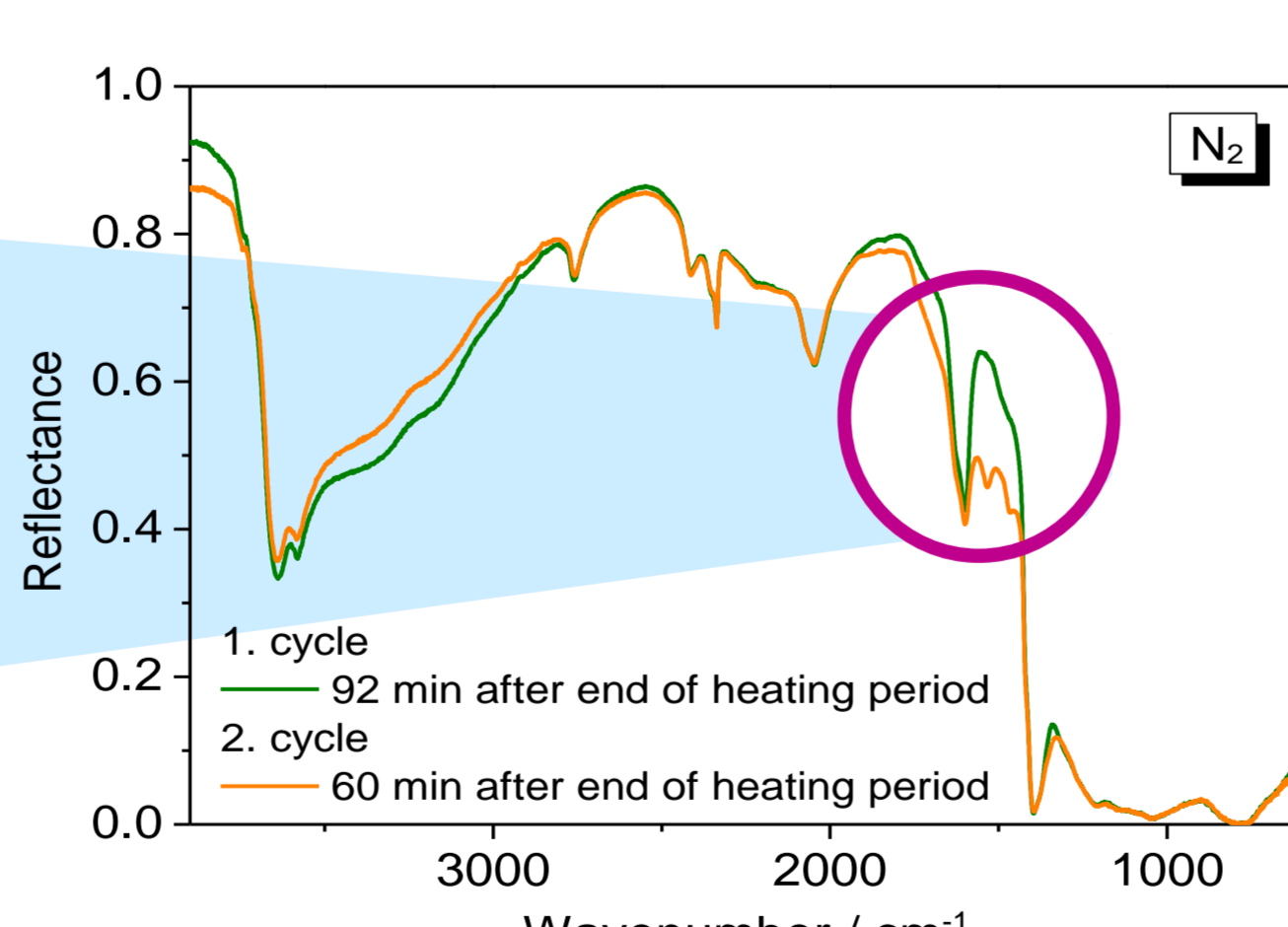
60 min

92 min

Activation / Regeneration

Reaction

Time



During treatment of deactivated Mn-promoted SZ at 773 K in N_2 two new bands appear at 1532 and 1465 cm^{-1} , probably vibrations of conjugated C=C bonds due to conversion of adsorbed species into polyunsaturated compounds.

The S=O band is restored but the catalyst is inactive.

Experimental

Catalyst preparation [8]: Incipient wetness impregnation using $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and sulfated zirconium hydroxide (MEL Chemicals XZO 6862/01). Calcination at 923 K in 20 g batches. Mn content 0.5 or 2 wt%.

DRIFTS: Bruker IFS 66 spectrometer, Graseby-Specac "Selector" attachment with "Environmental Chamber". Reflectance reference material KBr. Catalyst (150-185 mg) loaded into gold cup.

UV-vis-NIR spectroscopy: PerkinElmer Lambda 9, Harrick Praying Mantis diffuse reflectance attachment type DRA-4-PE7 with a HVC-DR3 reaction chamber. Reflectance standard Spectralon®. Catalyst (160-200 mg) supported on stainless steel grid.

Reaction conditions: Typical reaction conditions were 1 kPa *n*-butane and 323 K. Flow during reaction 30 ml/min. Effluent gases were analyzed by on-line GC (Varian 3800, flame ionization detection).

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