Initiation of Alkane Isomerization on Sulfated Zirconia Catalysts Studied by In Situ X-ray Absorption, UV-vis and IR Spectroscopy

MAX-PLANCK-GESELLSCHAFT

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Introduction

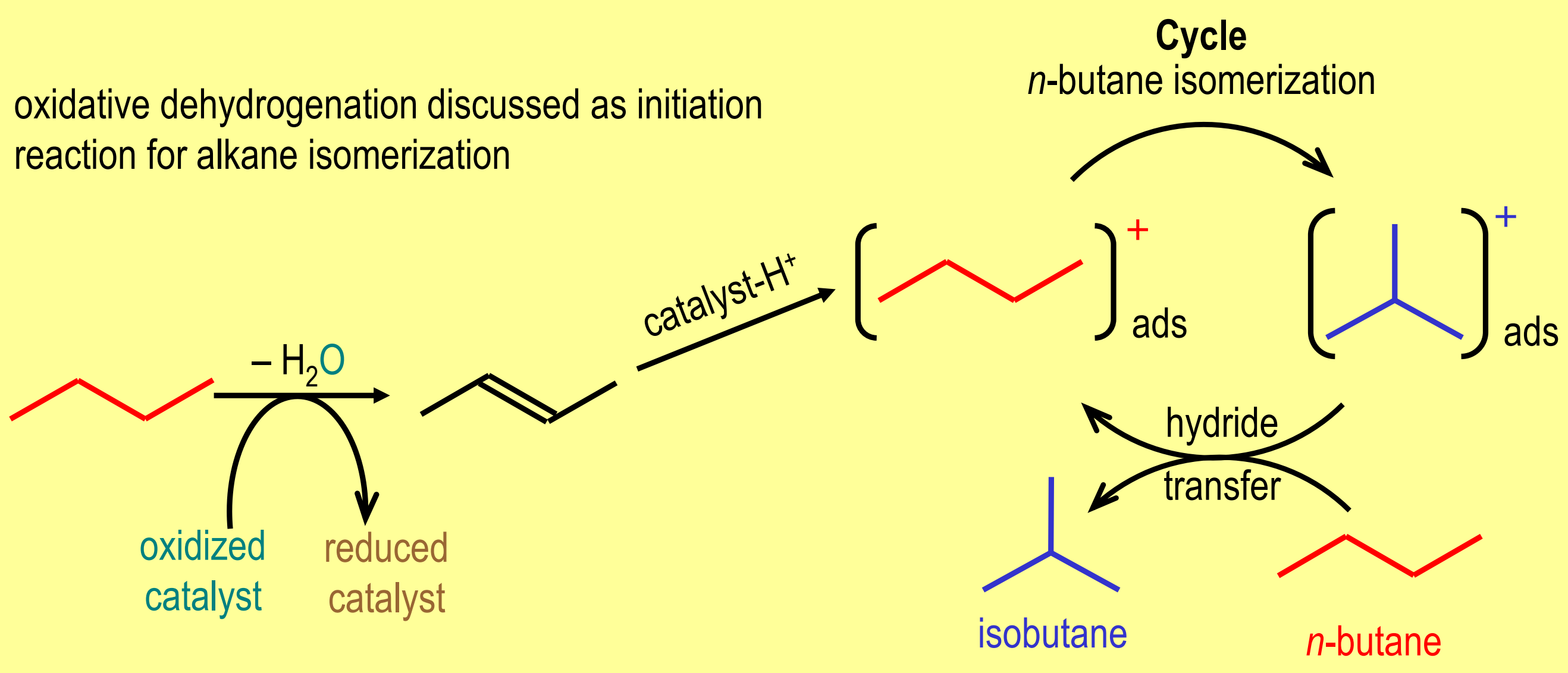
Sulfated zirconia (SZ) can activate short-chain alkanes for skeletal isomerization at room temperature [1]; addition of promoters such as Fe or Mn cations improves this ability [2,3]. First it was believed that superacidic sites are responsible for the extraordinary activity of SZ materials [1,2], but only strongly acidic sites were detected by probe molecule adsorption [4]. It was suggested that the promoters initiate the isomerization by redox processes [5,6] such as oxidative dehydrogenation (ODH, see scheme). However, butane conversion is initiated also on unpromoted material, and alkane activation routes must exist for SZ.

We investigate the role of redox processes for reaction initiation in two ways:

- test influence of activation atmosphere (inert, oxidizing) on SZ or Mn-promoted SZ
- check in situ for products of *n*-butane ODH, i.e. for water, reduced catalyst components (Mn, Zr, S) and butenes or intermediates formed from it

Possible initiation step: Oxidative dehydrogenation (ODH)

oxidative dehydrogenation discussed as initiation reaction for alkane isomerization

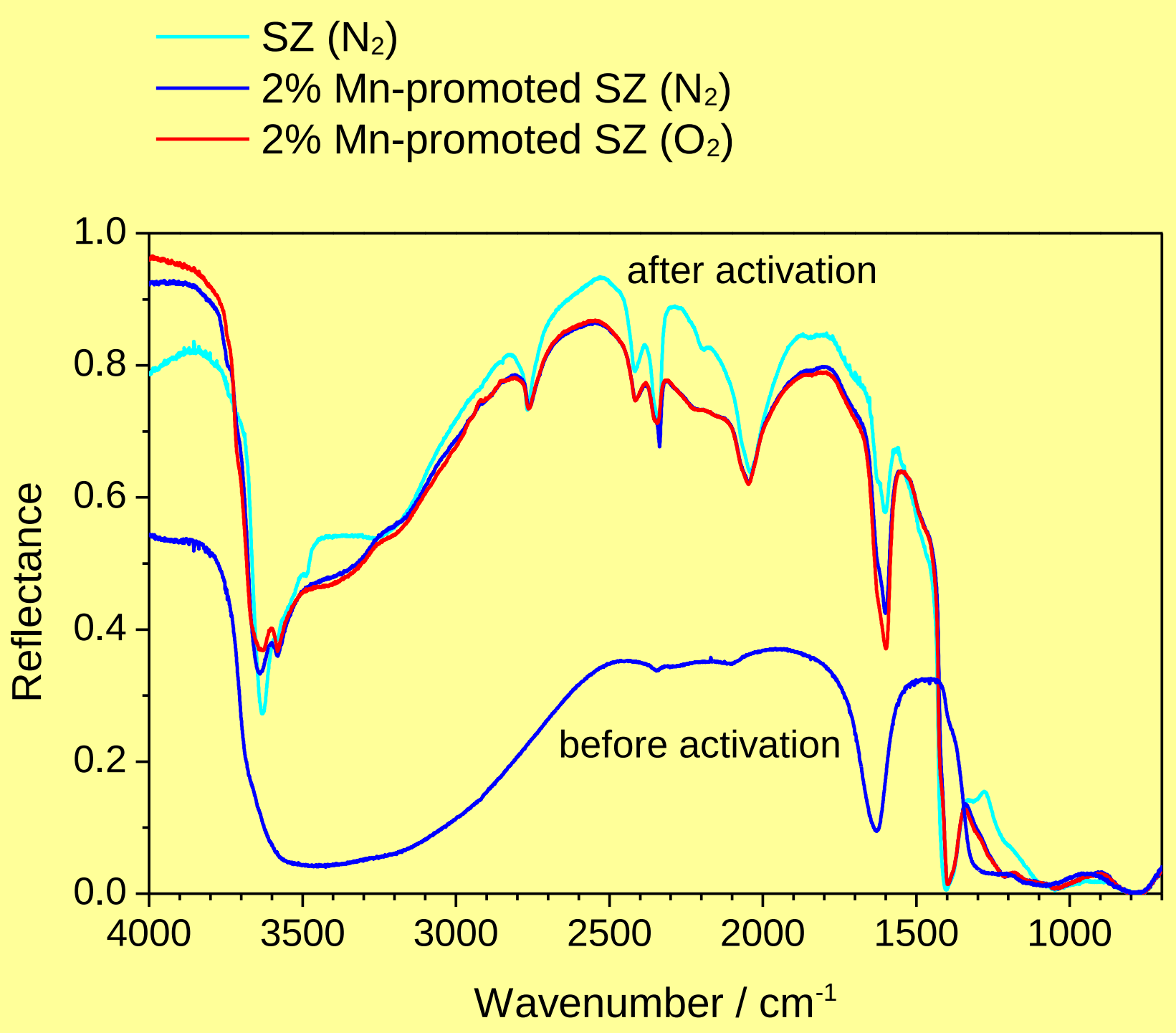


Experimental

Precursor	$(NH_4)_2SO_4$ doped hydrous zirconia (XZO 682/01, MEL Chemicals)
Preparation	drying (21 h, 383 K) – [incipient wetness (Mn(II)nitrate aq.)] – calcination
Calcination	flowing air for 3 hours at 823 (SZ) or 923 K (MnSZ) [7]
In situ XAS	Mn K edge, fluorescence mode, Hamburg Synchrotron Radiation Laboratory beamline E4, fixed-bed reactor, on-line MS
In situ UV-vis	PerkinElmer lambda 9, Harrick Praying Mantis™ diffuse reflectance attachment DRA-4-PE7, HVC-DR3 reaction chamber, on-line GC.
In situ DRIFTS	Bruker IFS 66, Graseby-Specac "Selector" attachment, environmental chamber, on-line GC
Activation	703–773 K, inert (He or N_2) or oxidizing atmosphere
Reaction	323–378 K, 1–5 kPa *n*-butane

Activation

In situ DRIFT spectra

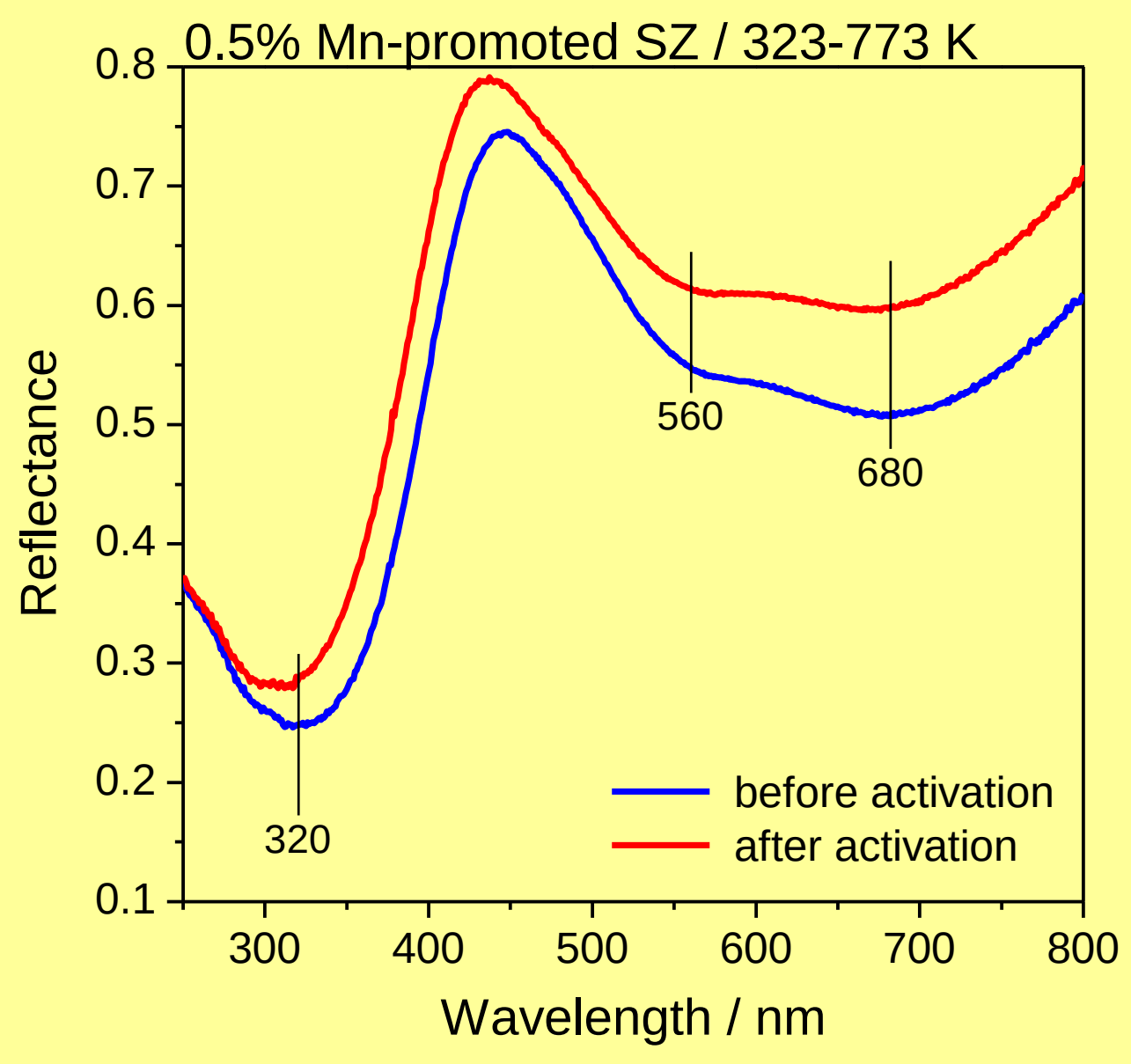


SZ	MnSZ	Assignment
3630	3638	triply bridged ν(OH) next to $S_2O_7^{2-}$
3582	3581	ν(H_2O_{ads}) next to SO_4^{2-}
3489	–	triply bridged ν(OH) on dehydrated ZrO_2
2767	2761	overtone of vibration around 1400 cm^{-1}
2416	2415	combination of vibrations at 1400/1050 cm^{-1}
2341	ca. 2345	overtone of vibration around 1213 cm^{-1}
2336	2336	ν($N_{2,ads}$)
2190	2220	overtone or combination mode of ν(S–O)
2040	2046	overtone of vibration around 1050 cm^{-1}
1625	ca.1625	δ(H_2O_{ads})
1603	1597	δ(H_2O_{ads})
1402 1378 sh	1399 (sh)	ν(S=O) of $S_2O_7^{2-}$, $S_2O_7^{2-}$*H_2O or $SO_{3,ads}$ ν(S=O) of $S_2O_7^{2-}$ or SO_4^{2-}
1308		ν(S=O) of $S_2O_7^{2-}$*yH_2O
(1211)	1213	ν(S–O) of $S_2O_7^{2-}$ or $S_2O_7^{2-}$*yH_2O
	1145	ν(S–O) of $S_2O_7^{2-}$*yH_2O
1050	1050	ν(S–O) of $S_2O_7^{2-}$ or $SO_{3,ads}$

- dehydration of SZ and Mn-promoted SZ during activation (more than 90% of adsorbed water removed)
- slight differences in OH band intensities of Mn-promoted SZ after activation in N_2 or O_2
- $S_2O_7^{2-}$ predominant surface species (comparison of S-O and S=O vibrations in the activated state with results from DFT [8])

In situ UV/vis spectra

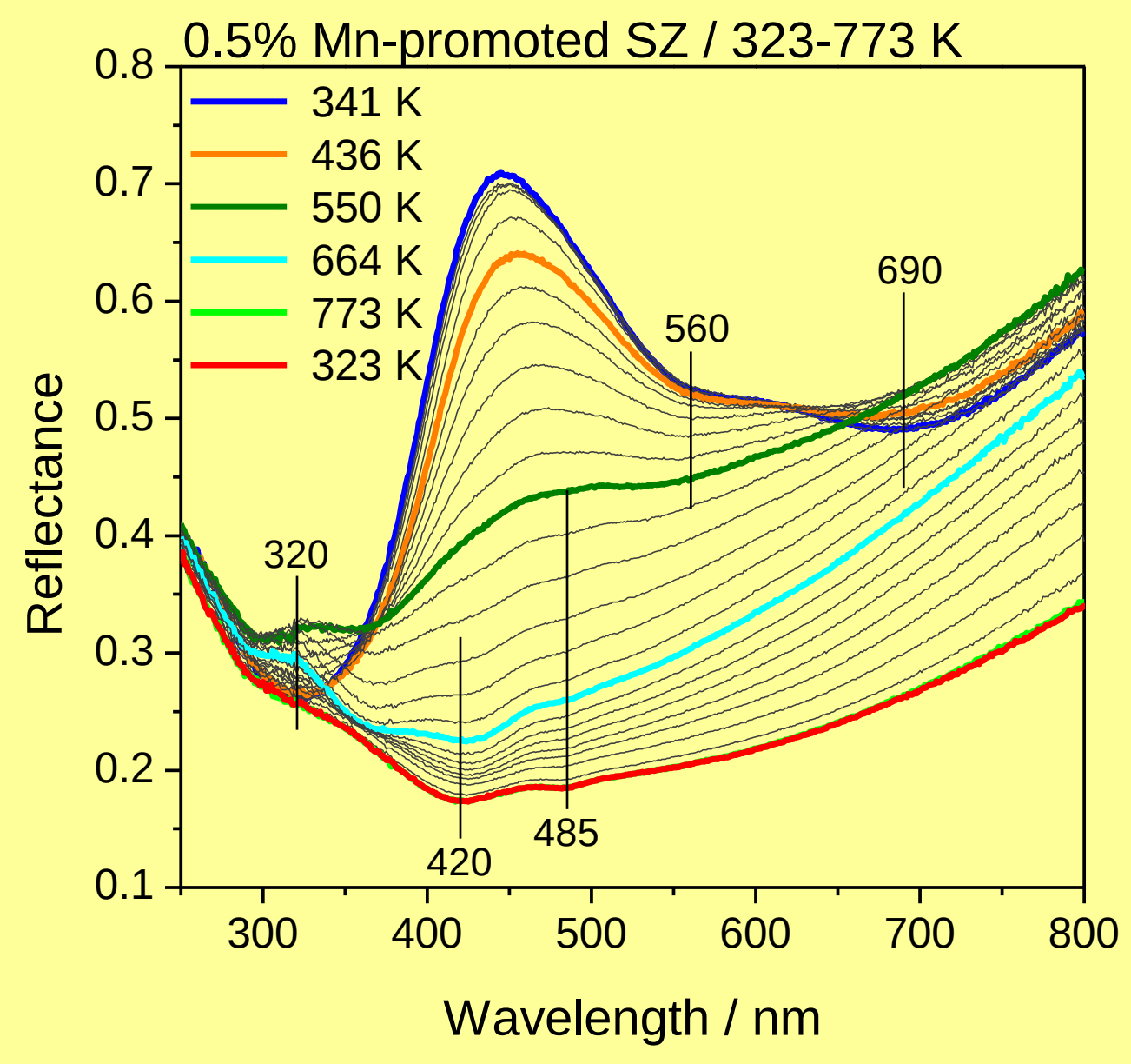
Activation in O_2 (100%)



- only slight decrease of relative intensity at 680 nm
- no other changes in the spectrum

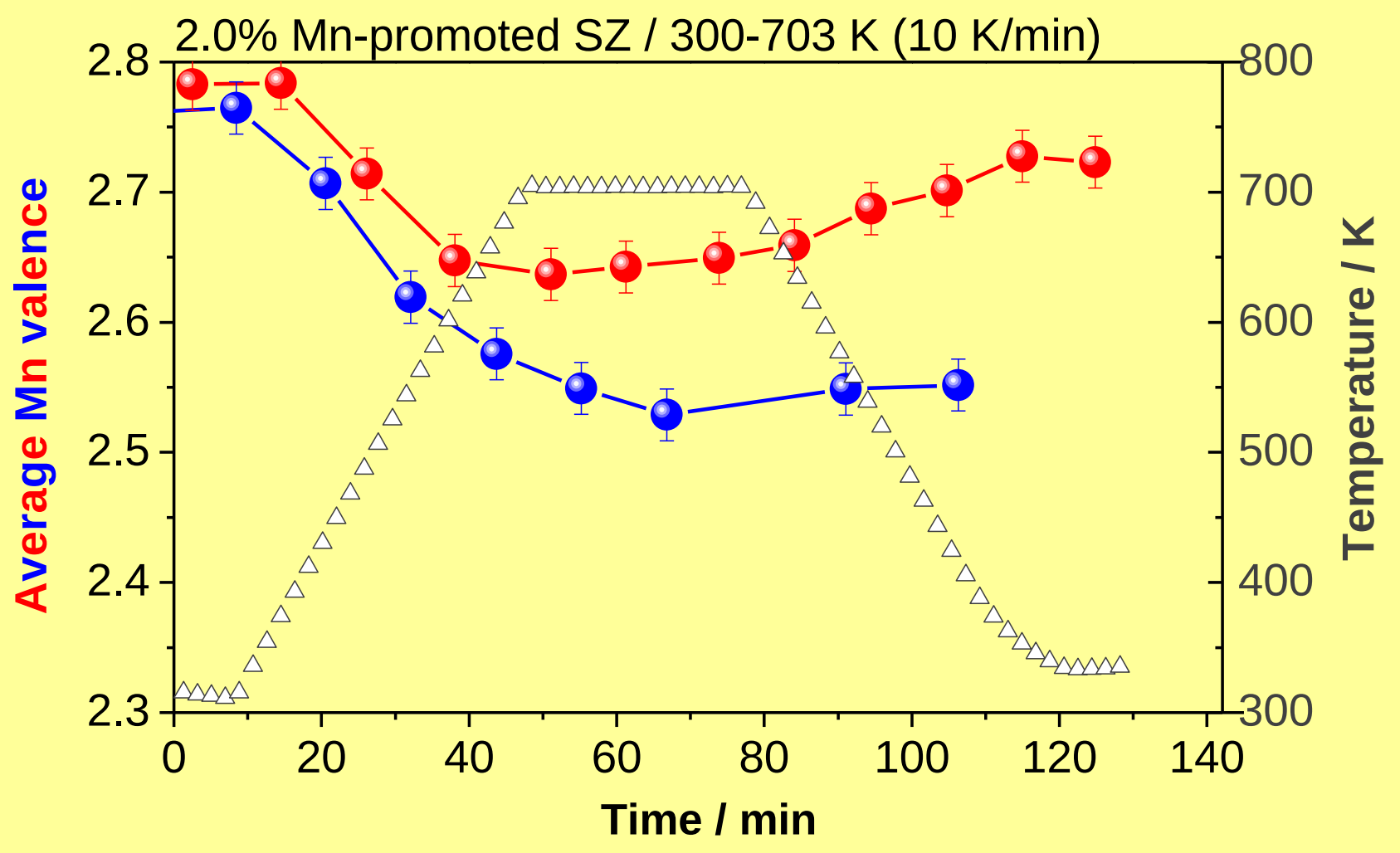
320 nm: charge transfer from O^{2-} to Zr^{3+}
charge transfer from O^{2-} to Mn^{3+} [9]
555 nm: d-d transition of Mn^{2+} or Mn^{3+} [10]
680 nm: d-d transition of Mn^{3+} [11]

Activation in inert gas (He)



- broad band with two weak peaks after activation

420 nm: Mn^{2+} in octahedral environment [12]
485 nm: Mn^{2+} (MnO [12]), Mn^{3+} (Mn_2O_3 [9])
⟶ reduction of promoter cation

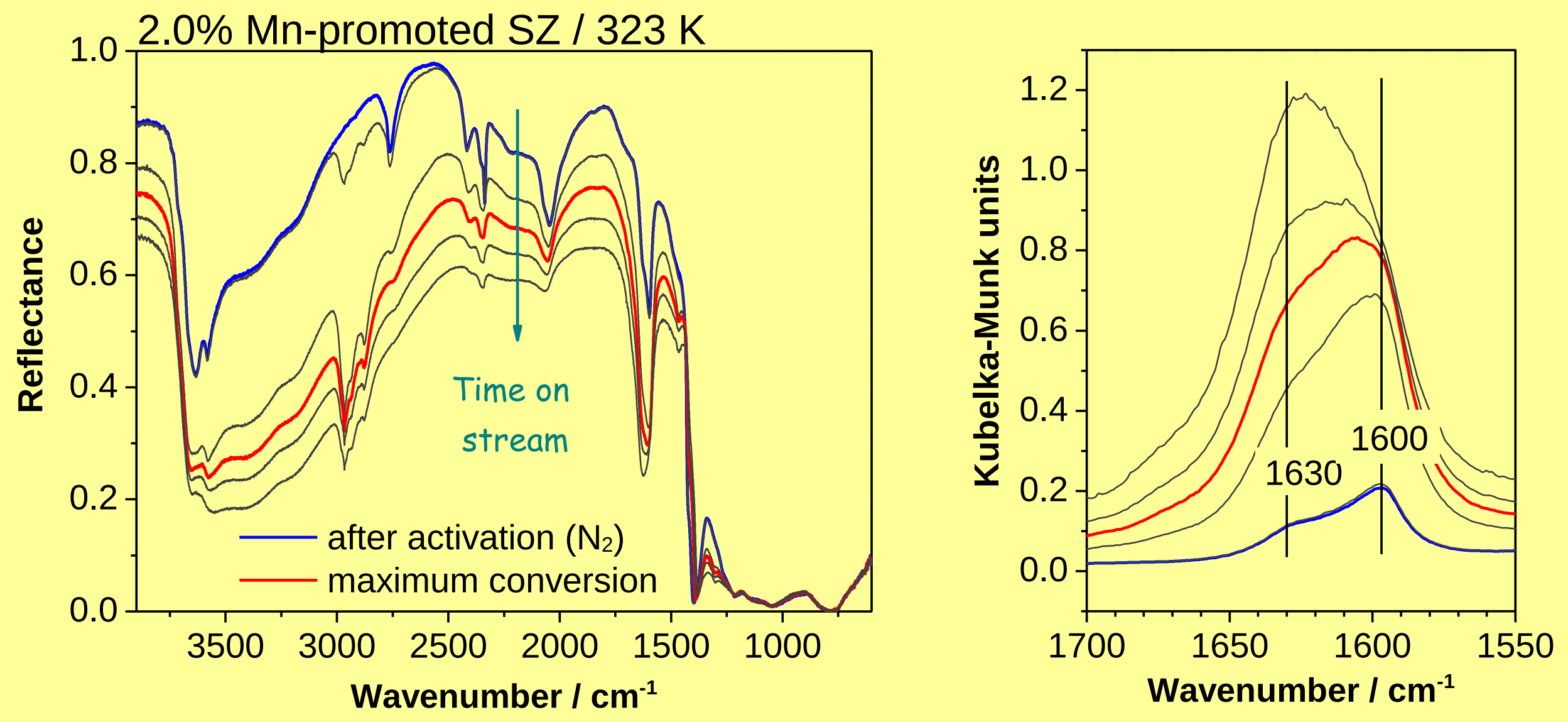


In situ XAS spectra during activation [13, 14]

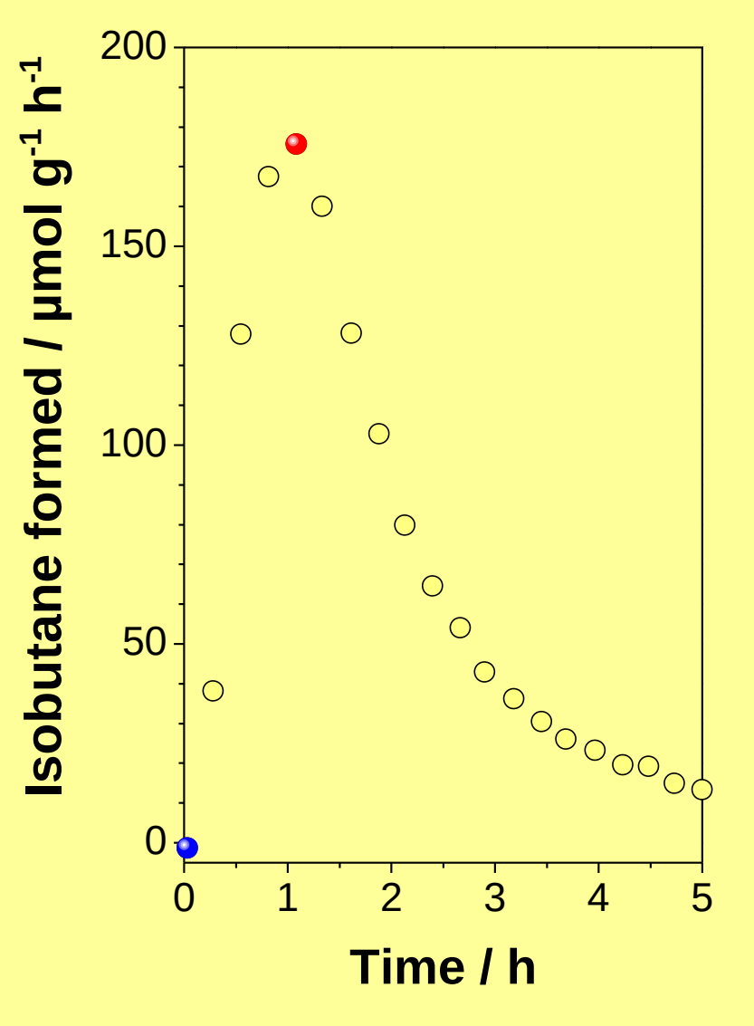
activation in He
decrease of average Mn valence to **2.55**

activation in 50% O_2
also reduction but only to **2.70**

Reaction

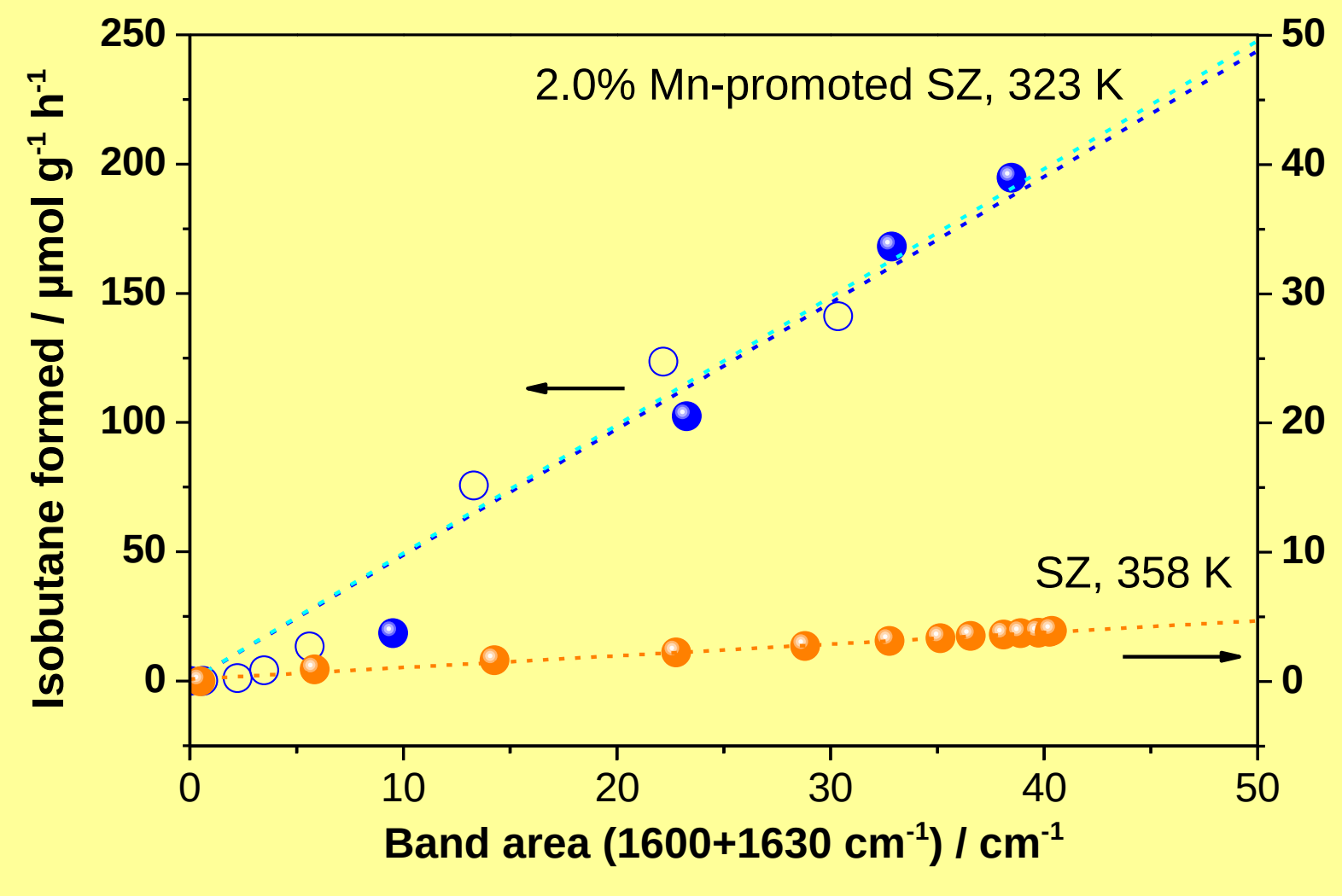


in situ DRIFT spectra of 2% Mn-promoted SZ during isomerization at 323 K and 1 kPa *n*-butane



rate of isomerization

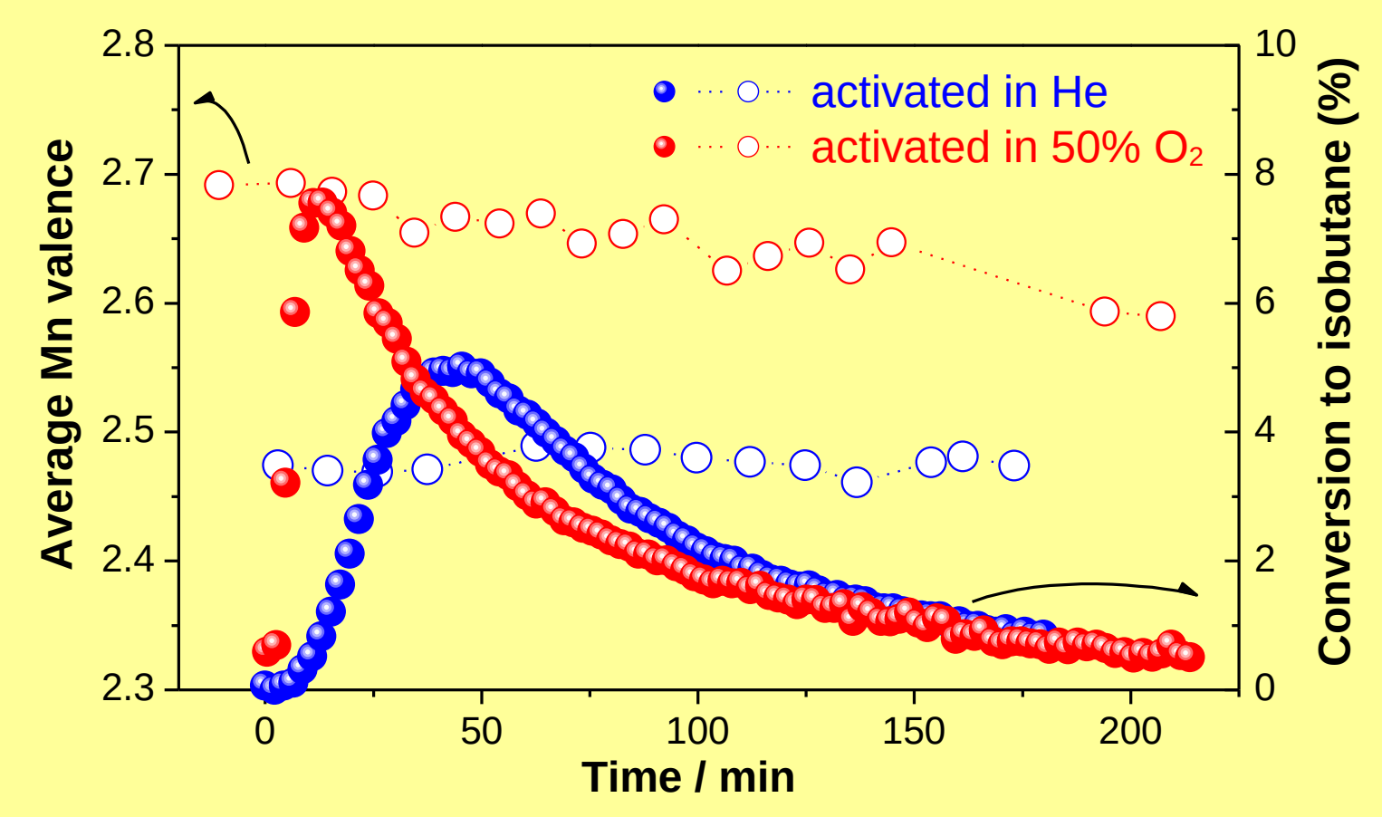
- increasing intensity in the range 1600–1675 cm^{-1} in the DRIFT spectra consistent with water formation during the initial phase of increasing activity (“induction period”)
- especially a band at 1600 cm^{-1} grows during this period



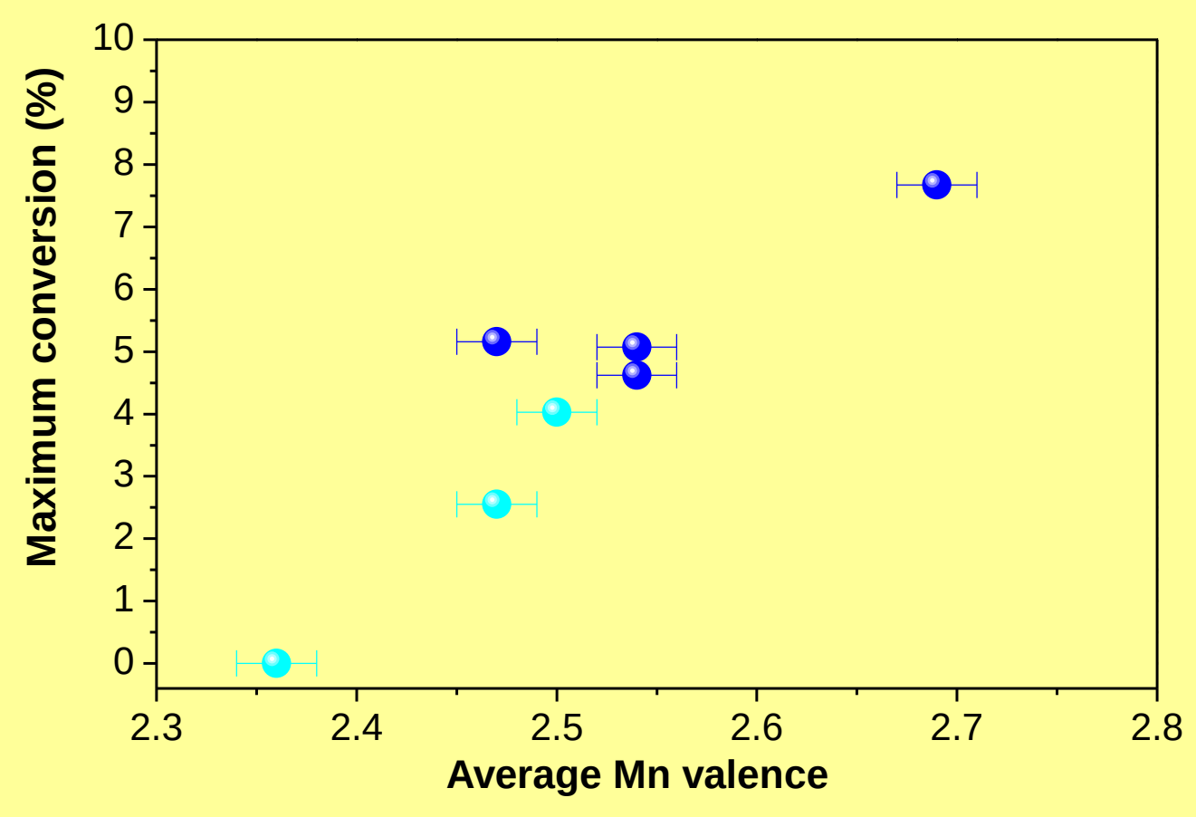
(cumulative water produced)

rate of isomerization vs. intensity of bands in the range 1600–1630 cm^{-1}. Reaction conditions: 323 or 358 K,1 kPa *n*-butane

- isomerization rate proportional to intensity of water bands during induction period
  → formation of chain carriers through ODH
- much higher turnover per water molecule, i.e. per number of chain carriers formed by ODH, for Mn-promoted catalyst than for SZ
  → faster isomerization after reaction initiation



in situ XAS of 2% Mn-promoted SZ during isomerization at 333 K and 1 kPa *n*-butane [14]



correlation: initial Mn oxidation state - catalytic activity
- higher maximum rate when higher Mn valence in activated state [14]

- mostly higher maximum rate after activation in the presence of O_2 (50 or 100%) than after activation in inert gas
- sometimes negative effect of long activation times or high O_2 partial pressures for both SZ and Mn-promoted SZ (not shown)
- no evidence for reaction initiation by *stoichiometric* ODH via reduction of Mn, neither in the XAS nor in the UV-vis data

Conclusions

- Main process during activation (703-773 K) is dehydration (IR)
- Heating causes reduction; activation atmosphere (oxidizing/inert) determines average Mn valence (UV-vis, XAS)
- Structure of sulfate and accessibility of hydroxyl groups do not fully determine the activity of the catalyst; surface functionalities and Mn are independent (different atmospheres)
- Main effect of promoter is faster isomerization / higher turnover rate (comparison with unpromoted SZ)
- Higher average Mn valence before reaction leads to higher maximum rate; higher activity is observed after pretreatment in oxidizing atmosphere (supporting ODH)
- Average Mn valence during reaction does not correlate with catalytic performance → Mn is not a stoichiometric oxidant (S or Zr)
- Formation of water proportional to initial rate (supporting ODH)

References and Acknowledgements

1. M. Hino, S. Kobayashi, K. Arata, *J. Am. Chem. Soc.* 101 (1979) 6439.
2. C.-Y. Hsu et al., *Chem. Commun.* (1992) 1645.
3. F.C. Lange, T.-K. Cheung, B.C. Gates, *Catal. Lett.* 41 (1996) 95.
4. V. Adeeva et al., *J. Catal.* 151 (1995) 364.
5. K.T. Wan, C.B. Khouw, M.E. Davis, *J. Catal.* 158 (1996) 311.
6. X. Li, K. Nagaoka, L.J. Simon, J.A. Lercher, A. Hofmann, J. Sauer, *J. Phys. Chem. B*, submitted.
7. A. Hahn et al., *Chem. Commun.* (2001) 537.
8. A. Hofmann, J. Sauer, *J. Phys. Chem. B* 108 (2004) 14652.
9. F. Milella et al., *J. Mater. Chem*. 8 (1998) 2525.
10. W. Sjoerd Kijlstra et al., *J. Phys. Chem. B* 101 (1997) 309.
11. E. Fernández López et al., *Appl. Catal. B: Environmental* 29 (2001) 251.
12. G.W. Pratt Jr., *Phys. Rev*. 2 (1959) 281.
13. R.E. Jentoft et al., *Physica Scripta*, T115 (2005) 794.
14. R.E. Jentoft, A.H.P. Hahn, F.C. Jentoft, T. Ressler, *PCCP*, to be published.

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