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Sulfated Zirconia Catalysts for Alkane Isomerization: Recent Progress

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Machelen, December 4, 2003

Outline

Introduction

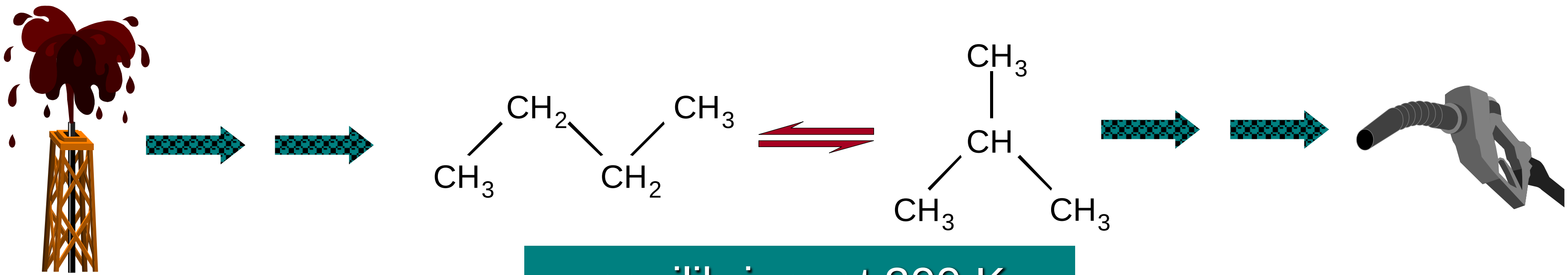
Results

1. Role of sulfate
2. Preparation of sulfated zirconia catalysts
3. Handling of sulfated zirconia catalysts
4. Effect of promoters Mn, Fe
5. Deactivation

Conclusions

Outlook

Introduction

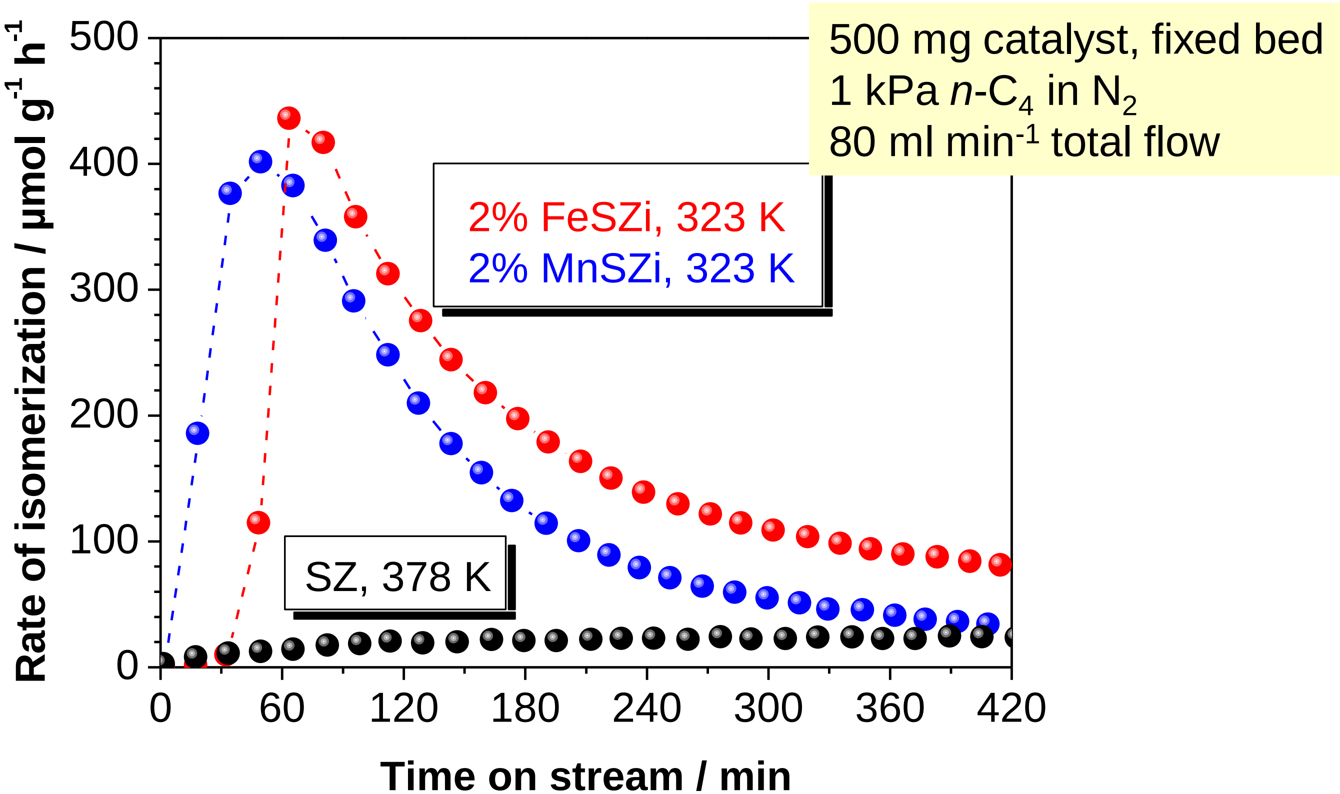


equilibrium at 300 K
71 % isobutane

(solid) acid catalysis

- **"sulfated zirconia"** isomerizes *n*-butane to isobutane at 373 K
  Hino, Arata, JACS 1979 & Chem. Comm. 1980
- "sulfate-treated zirconia-gel catalyst"
  Holm, Bailey 1962, US Patent 3,032,599

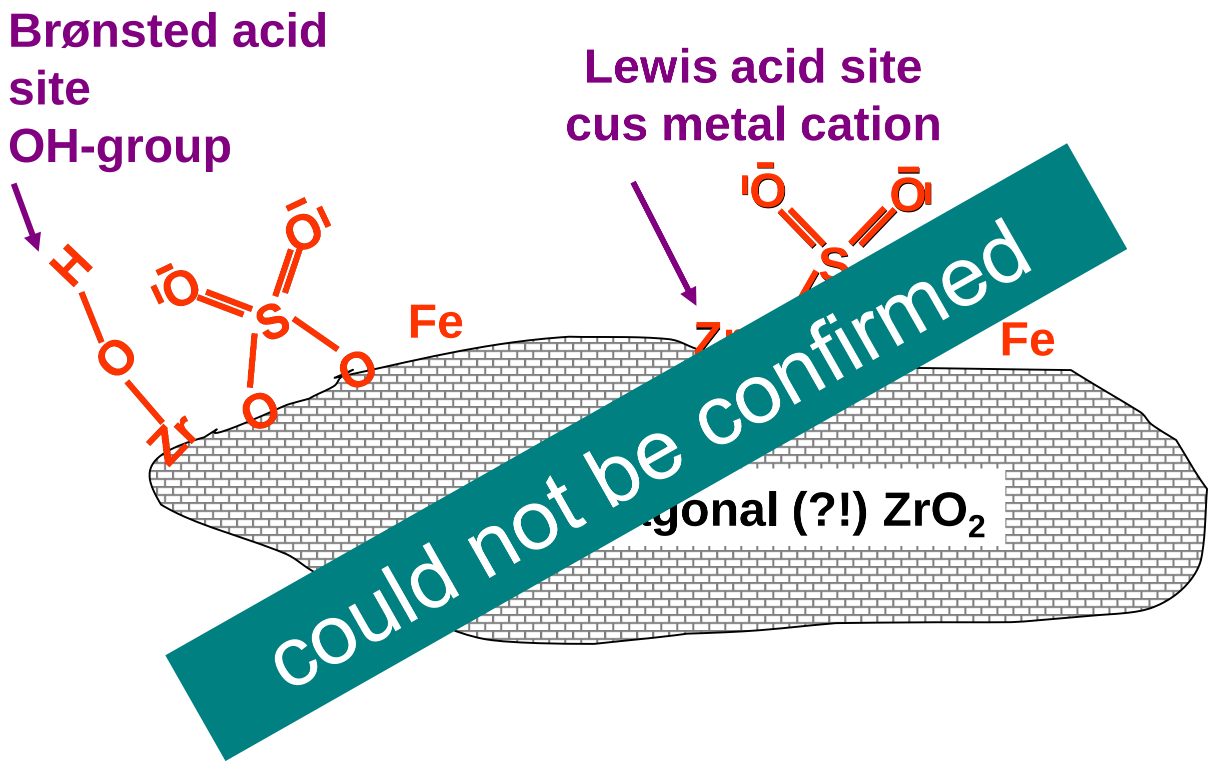
Promotion of Sulfated Zirconia



Low temperature isomerization of *n*-butane

❖ Fe and Mn exert strong promoting effect
Hollstein et al., 1990 US Patent 4,918,041; Hsu et al., Chem. Comm. 1992; Lange et al., Catal. Lett. 1996

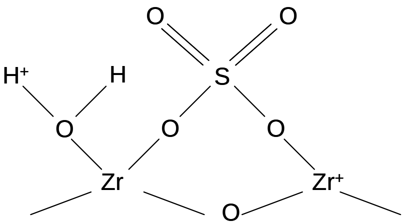
Initial Ideas on Sulfated ZrO_2



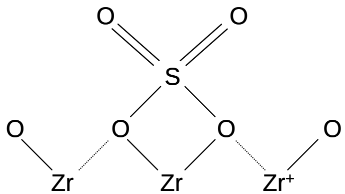
- sulfate introduces acidity
- Mn and Fe increase the acidity of the "solid superacid" sulfated zirconia, evidence: catalytic activity, benzene TPD
  Hsu et al. Chem. Comm. 1992, Lin et al. Chem. Comm. 1992
- …no sites consistent with extreme acidity could be identified….
  Adeeva et al. J. Catal. 1995, Wan et al. J. Catal. 1996

1. Role of Sulfate

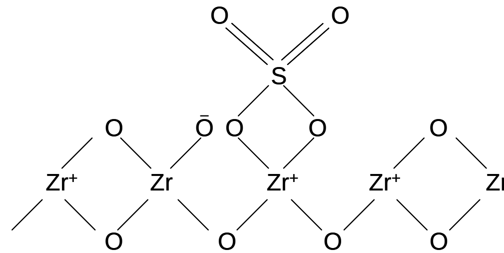
Sulfate Structures I



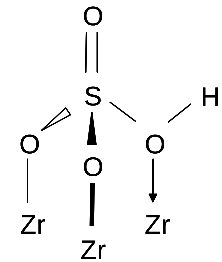
Arata et. al., Adv. Catal. 1990



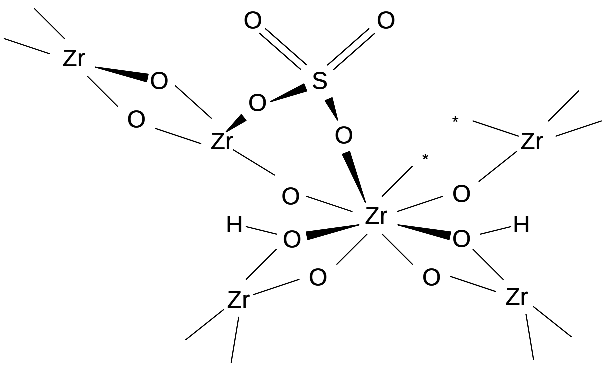
Yamaguchi et. al., Appl. Catal. 1990



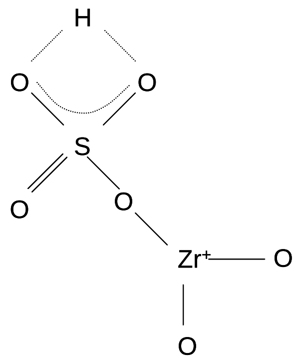
Parera et. al., Catal. Today 1992



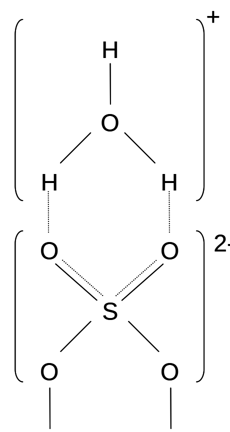
Riemer et. al., Chem. Comm. 1994



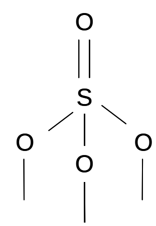
Clearfield, Catal. Today 1994



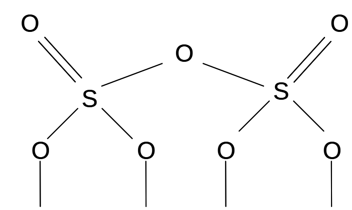
Kustov et al., J. Catal. 1994



hydrated

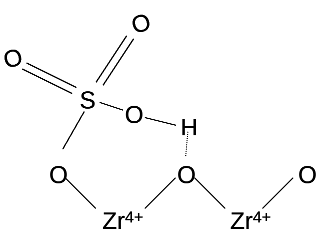


dehydrated

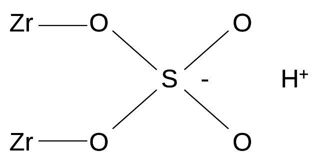


dehydrated

Morterra et al., J. Phys. Chem. 1994



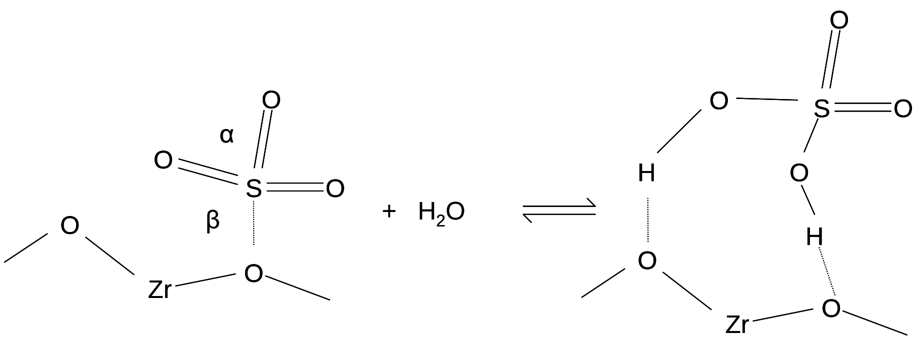
Adeeva et al., J. Catal. 1995



ionic structure in hydrated state

Platero and Mentruit, Catal. Lett. 1995

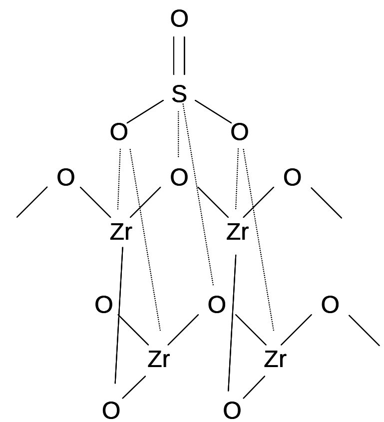
Sulfate Structures II



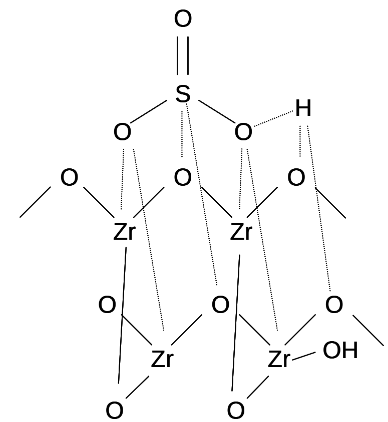
S=O = 140 pm
S-O = 164 pm
α=117°
β=95°

S=O = 140 pm
S-O = 154 pm

Babou et. al., J. Catal. 1995

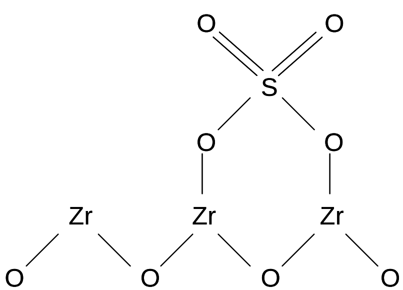


Lewis

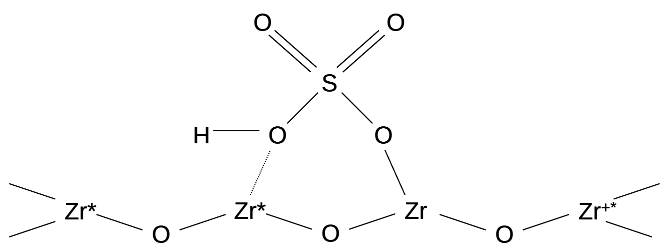


Brønsted

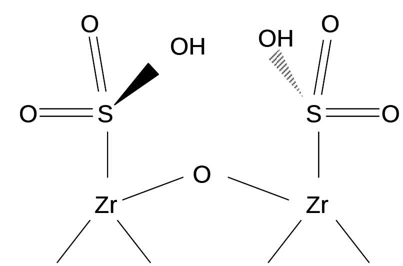
White et al., J. Catal. 1995



Signoretto et al., J. Catal. 1997



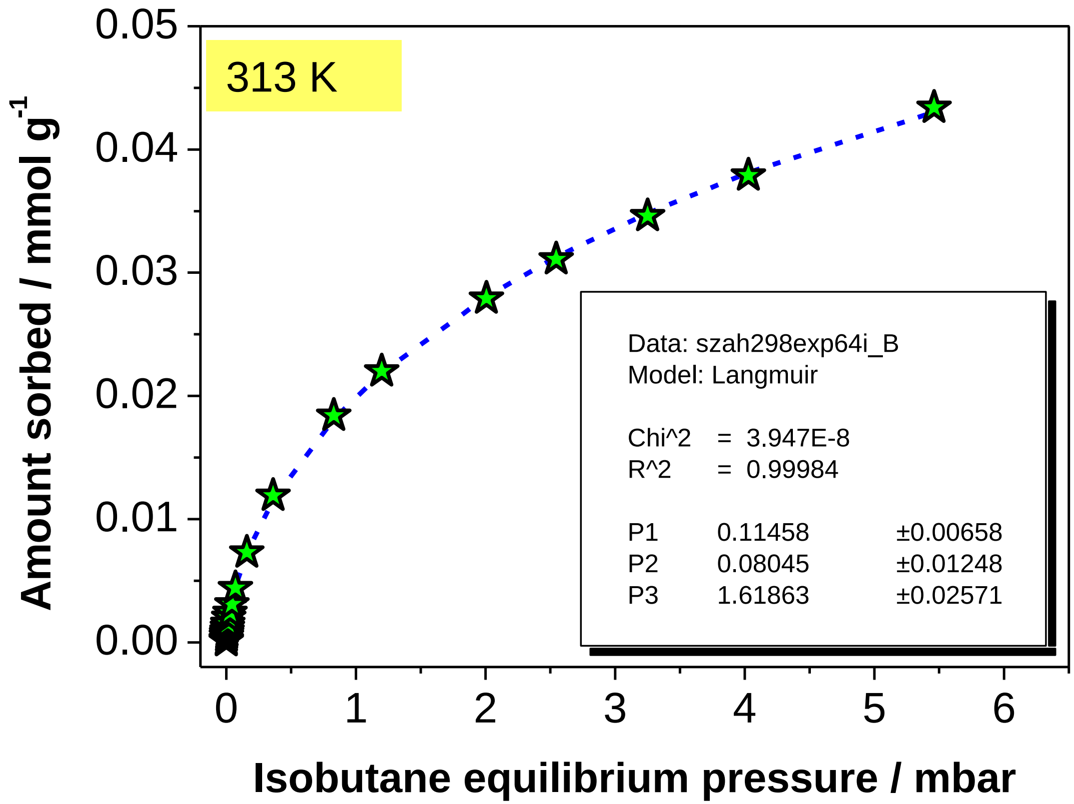
Bolis et. al., Langmuir 1997



Rosenberg and Anderson, Catal. Lett. 2002

- state depends on concentration (typically 5-10 wt% sulfate) / hydration
- sulfate is extremely flexible
- several structures may coexist

Number of Sites on Sulfated Zirconia

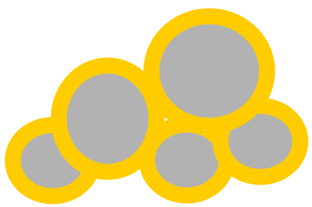


- isobutane adsorption isotherm fit (modified Langmuir model)
- monolayer is ≈80 µmol/g; sulfate content is ≈560 µmol/g

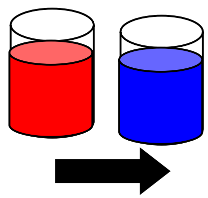
➡ only minority (15%) of sulfate involved in adsorption / reaction
identification of "active" sulfate species will be extremely difficult

2. Preparation of Sulfated Zirconia Catalysts

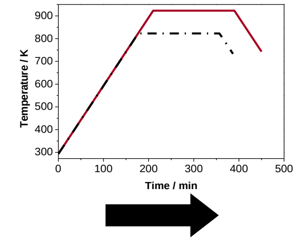
Fe- and Mn- promoted sulfated zirconia



MEL Chemicals XZO 682/01
"ZrO_2*2.5 H_2O", $(NH_4)_2SO_4$
X-ray amorphous



incipient wetness
Fe(III), Mn(II) nitrates

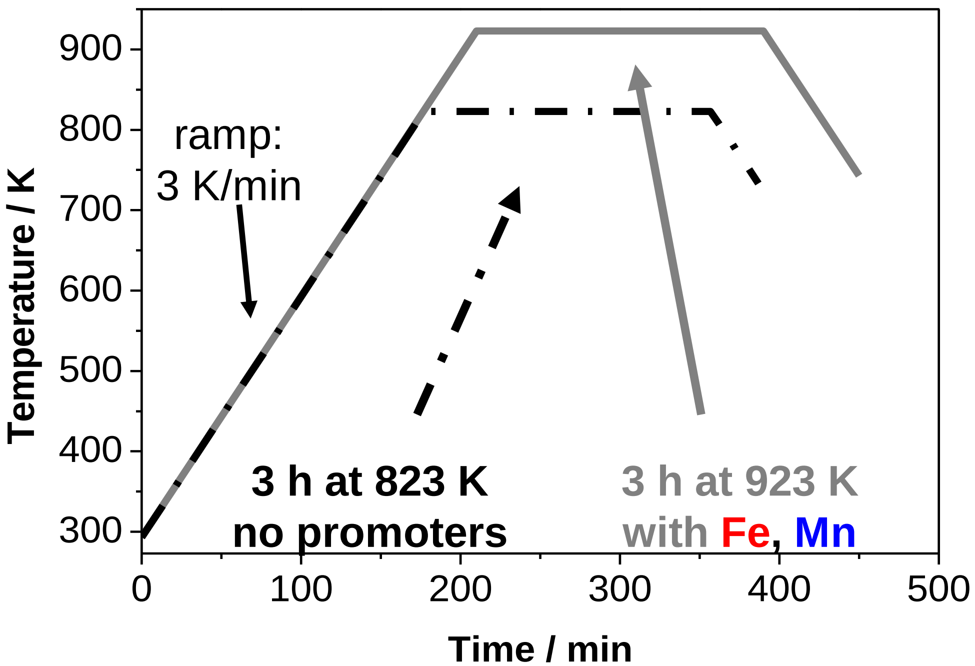


calcination 923 K
(SZ 823 K)

„FeSZi, MnSZi“
nominal promoter content in wt% metal

Reproducibility?

Calcination Procedure



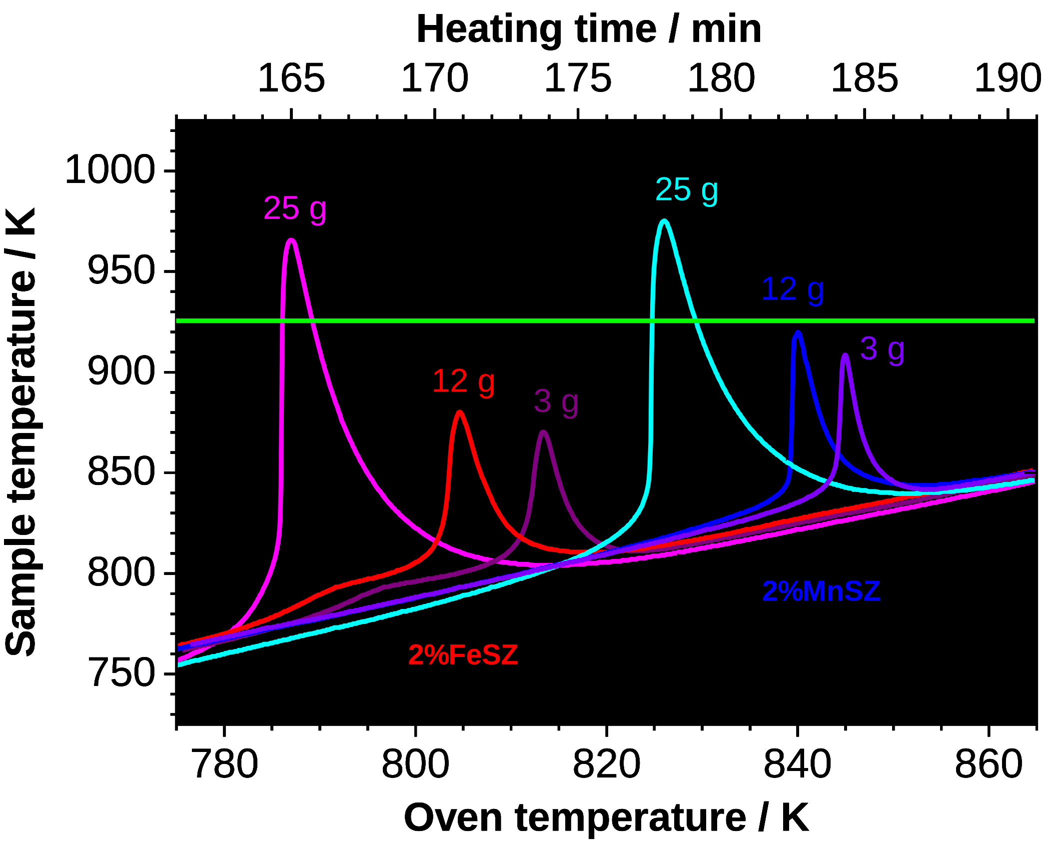
events during calcination

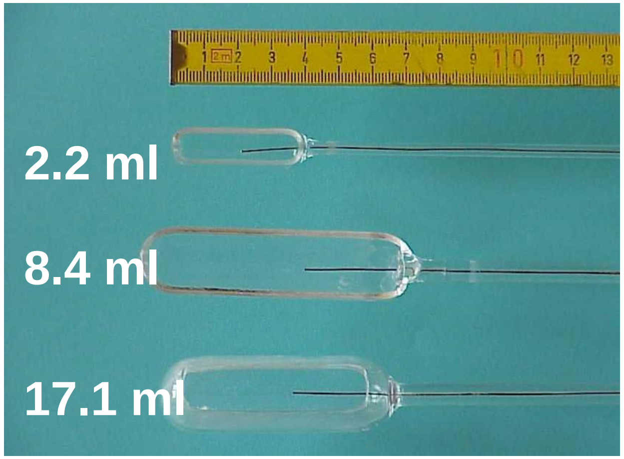
- loss of water
- decomposition of NO_3^- and NH_4^+
- crystallization / sintering of ZrO_2

endo- / exothermic events

→ temperature deviations from program? (preparative scale)

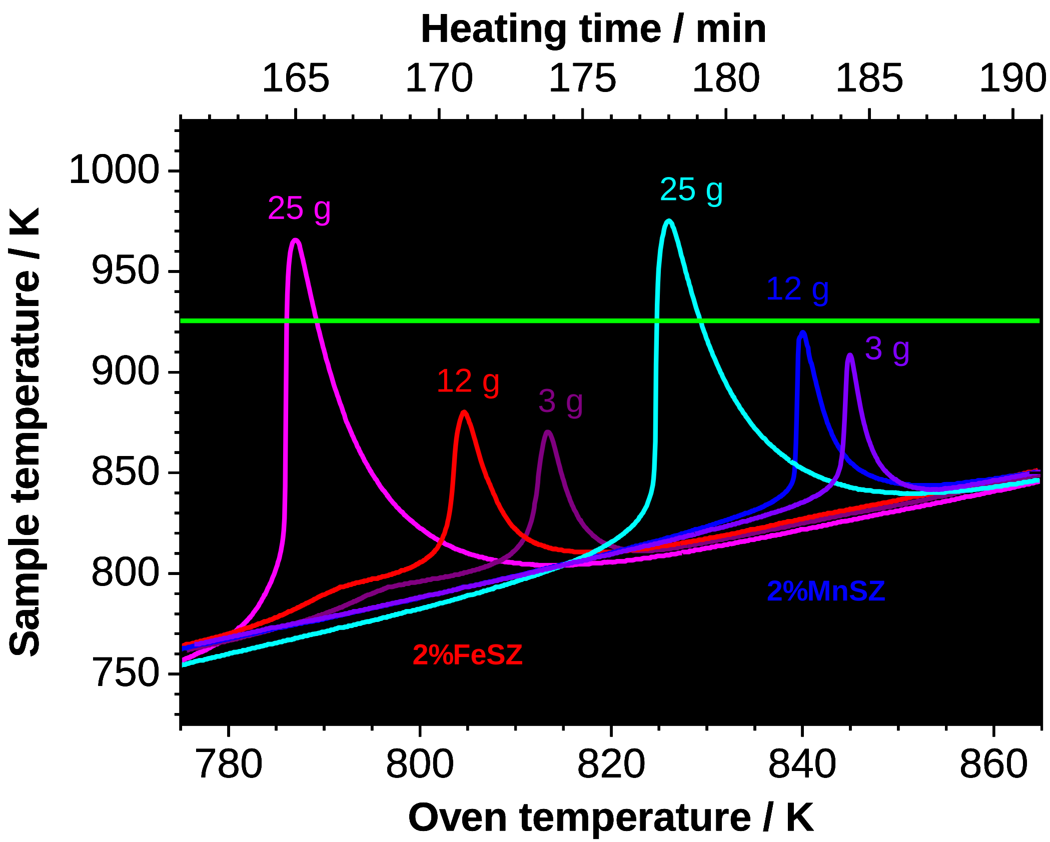
"Glow Phenomenon": MnSZ and FeSZ

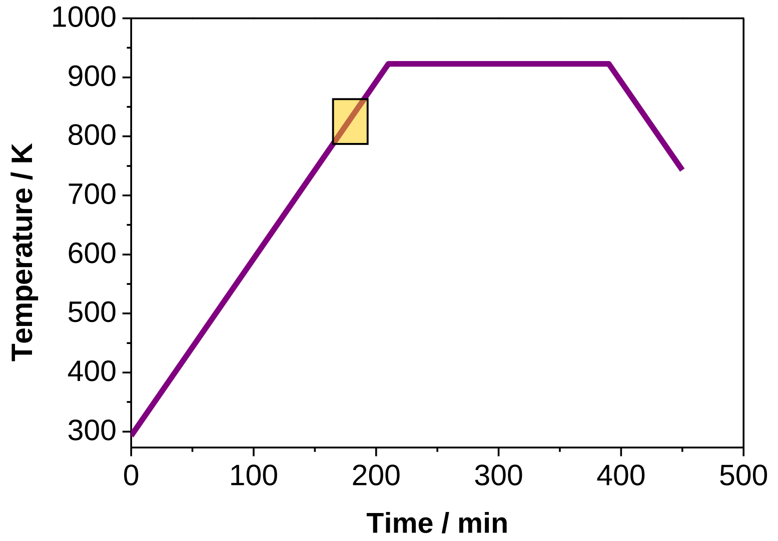




- temperature overshoot, max. calcination T may be exceeded
  "glow phenomenon", Berzelius 1812
- promoters influence calcination chemistry (systemic), Fe and Mn different
- strong batch size dependence

Glow Phenomenon: MnSZ and FeSZ





- temperature overshoot, max. calcination T may be exceeded
  "glow phenomenon", Berzelius 1812
- promoters influence calcination chemistry (systemic), Fe and Mn different
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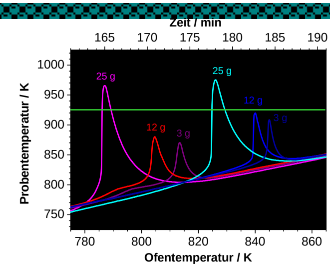
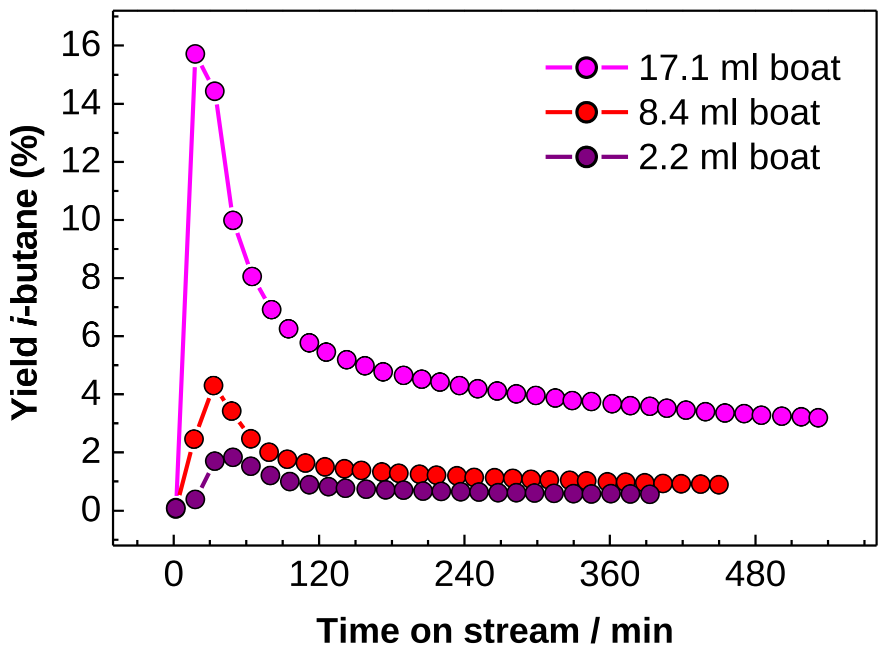
Influence on Catalytic Activity?!

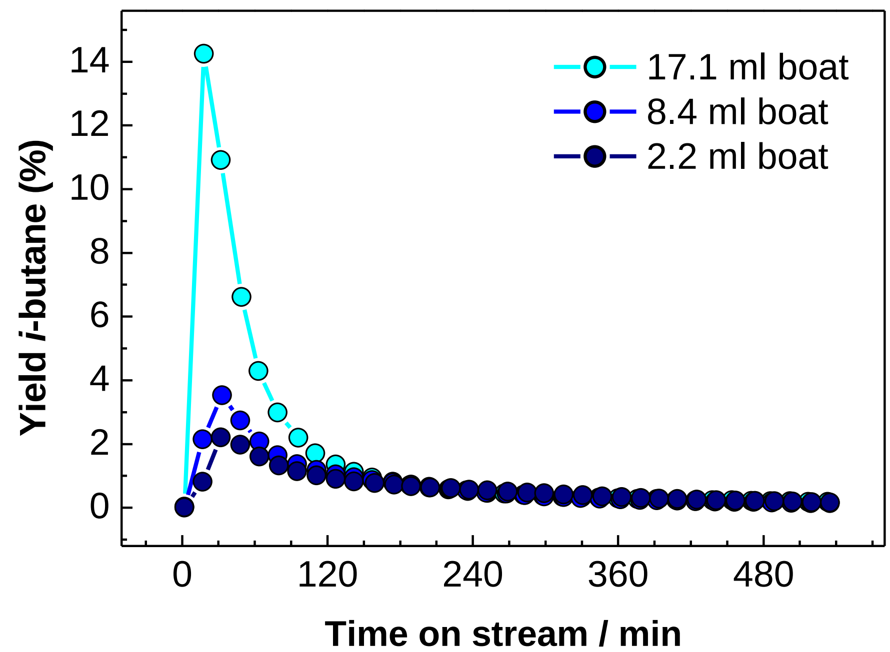
Hahn, Jentoft et al.
Chem. Comm. 2001

2%FeSZ



2%MnSZ





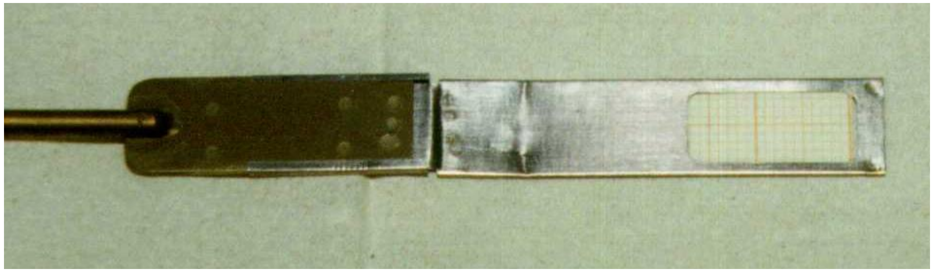
- samples calcined in larger batches are more active (1 vol% *n*-butane at 338 K)

→ an extensive quantity influences the activity

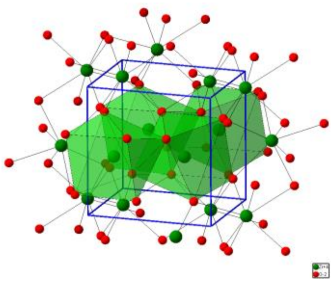
3. Handling of Sulfated Zirconia Catalysts

❖ samples are ground or milled
to homogenize or obtain a fine powder

❖ samples have to be "prepared" for certain analytical techniques;
pressing of wafers for transmission spectroscopy

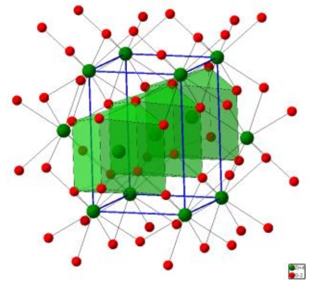


Zirconia Bulk Structures



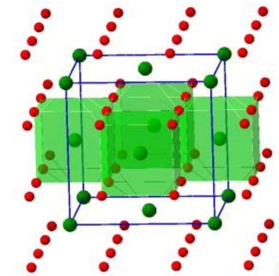
monoclinic

1223 - 1473 K



tetragonal

>2473 K

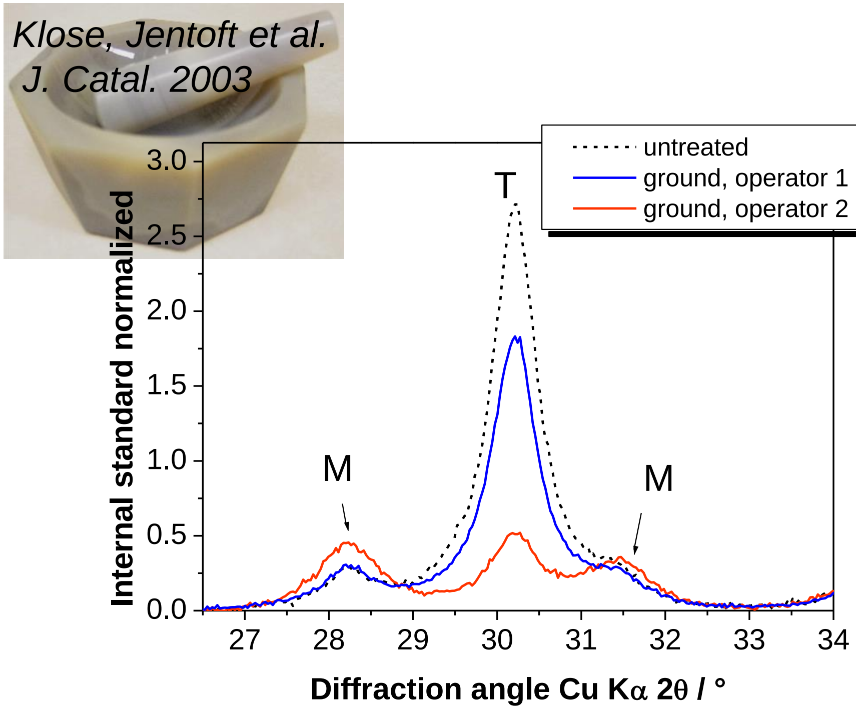


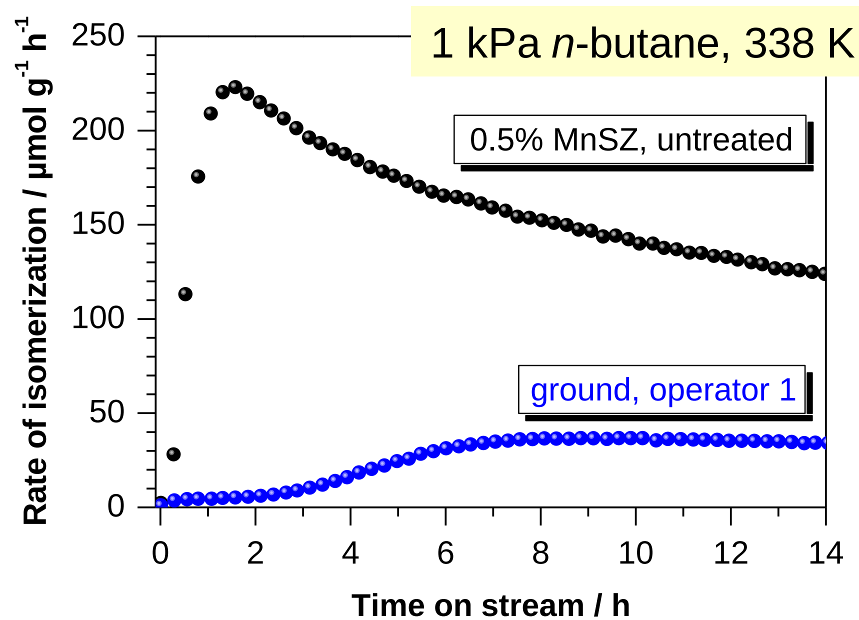
cubic

- „…tetragonal ZrO_2 phase is ... necessary“
  Morterra et al., J. Catal. 1995
- „…activity... of monoclinic samples … just by a factor 5-7 lower“
  Stichert and Schüth, J. Catal. 1998
- tetragonal and cubic can be stabilized through dopants (Y)

Grinding: 0.5% MnSZi

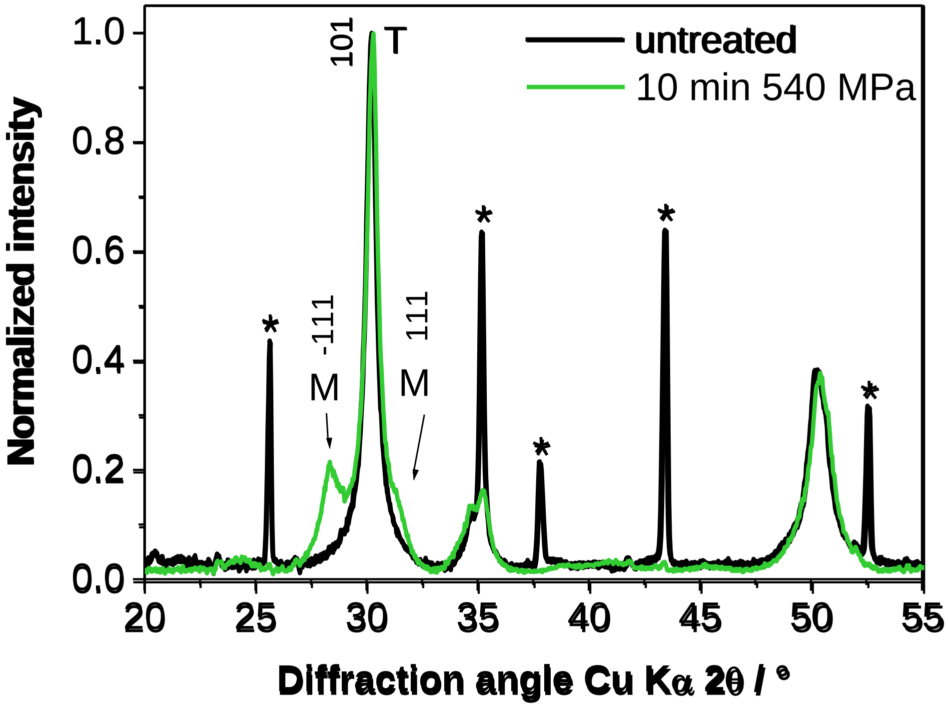
Klose, Jentoft et al.
J. Catal. 2003





- ❖ zirconia sensitive to mechanical stress, tetragonal to monoclinic transition
  Whitney, Trans. Faraday. Soc. 1965 (footnote!)
- ❖ manual grinding: strong operator influence
- ❖ catalytic activity affected

Pressing of Sulfated Zirconia



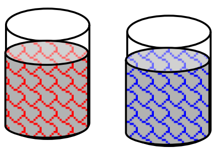
❖ pressing of a self-supporting wafer (as for IR): ca. 33 wt% monoclinic ZrO_2

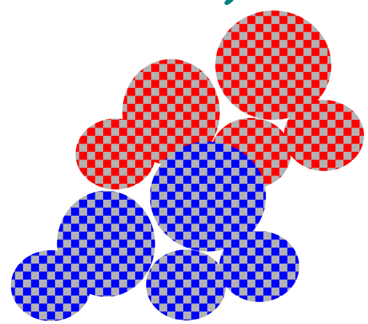
➡ sample preparation for analysis may alter catalyst

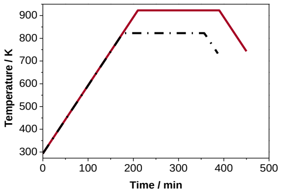
4. Effect of Promoters
Preparation of Reference Compounds

Can Mn, Fe stabilize certain zirconia bulk phases?

Reference compounds (sulfate-free)







„FeZc, MnZc“

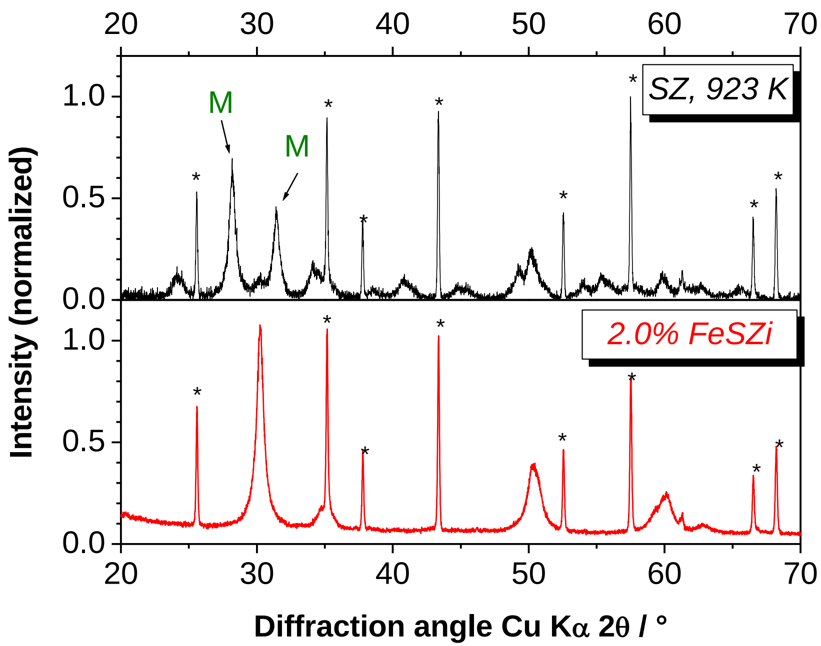
solutions, $ZrO(NO_3)_2$
Fe(III), Mn(II) nitrates

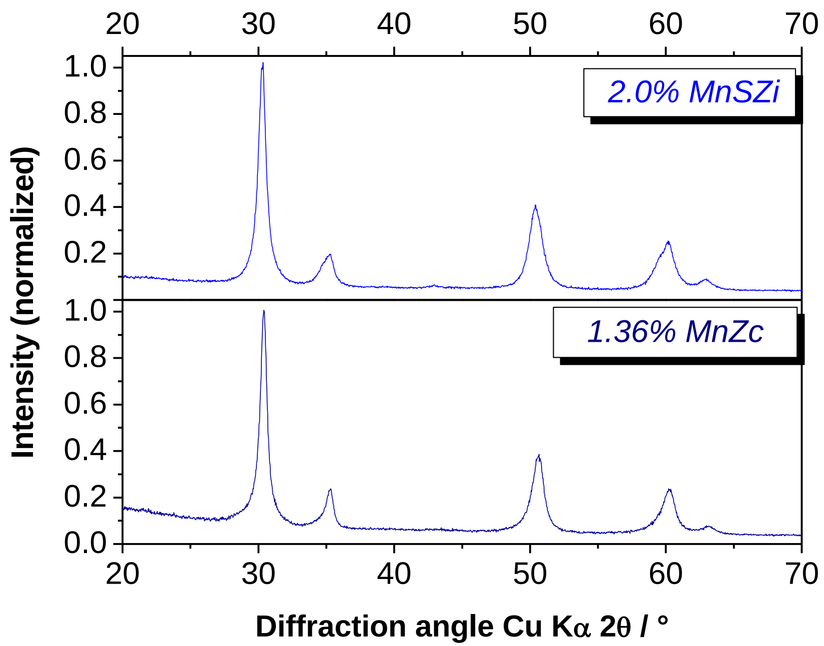
coprecipitation
NH_4OH

calcination 923 K

❖ promoters and zirconia are interspersed in the primary solid

X-ray Diffraction

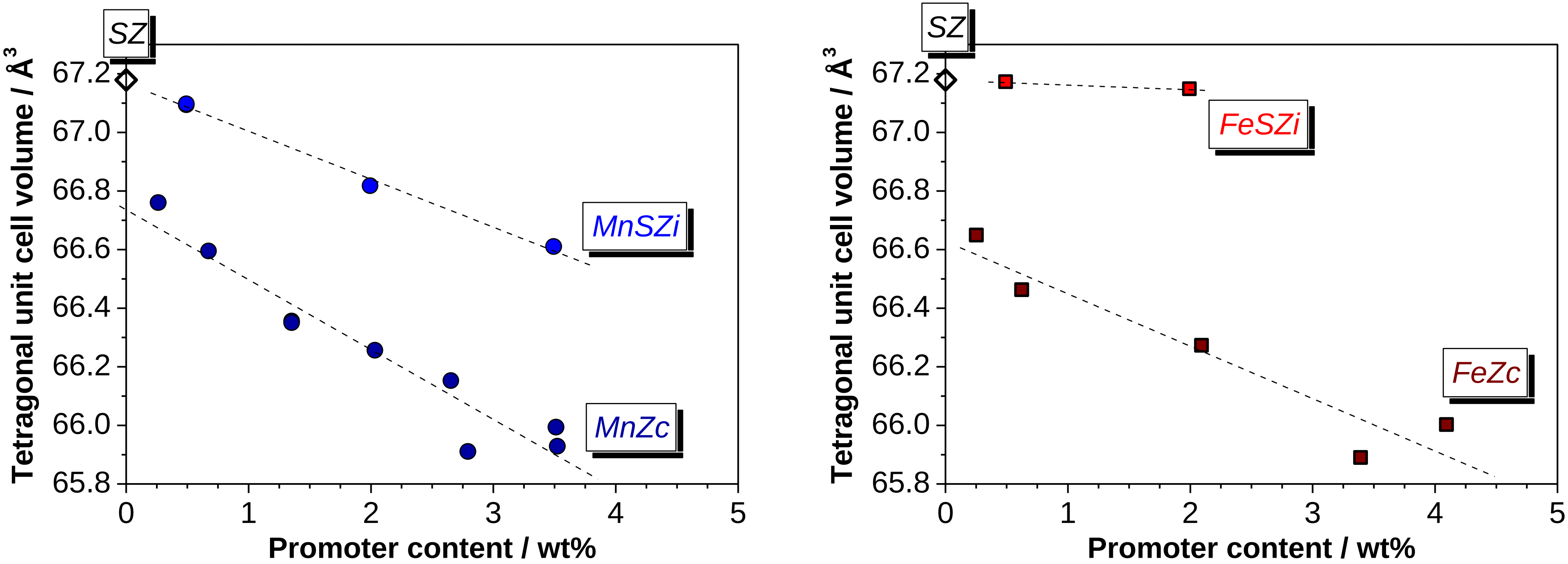




Analysis of bulk phase by X-ray diffraction

- SZ (calc. 823 K): t-ZrO_2, sometimes traces of m-ZrO_2
- SZ (calc. 923 K): predominantly m-ZrO_2
- MnSZi, FeSZi (calc. 923 K): t-ZrO_2
- MnZc, FeZc (calc. 923 K): t-ZrO_2, towards c-ZrO_2

Analysis of Lattice Parameters



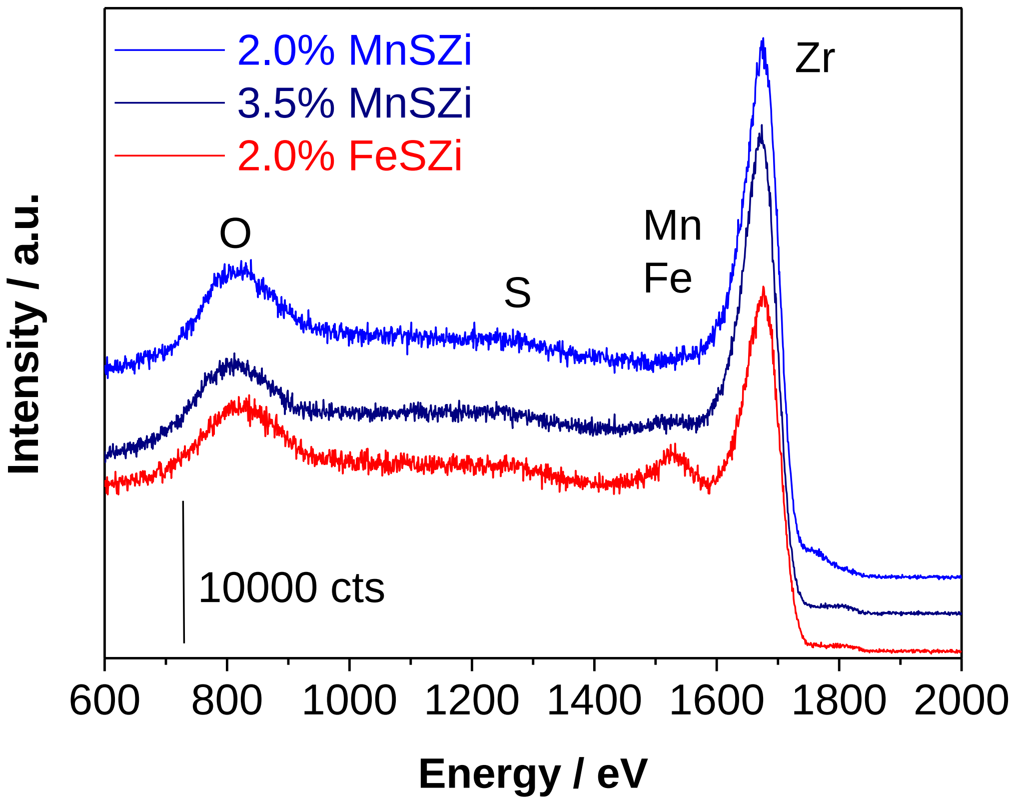
Unit cell shrinkage with increasing promoter content

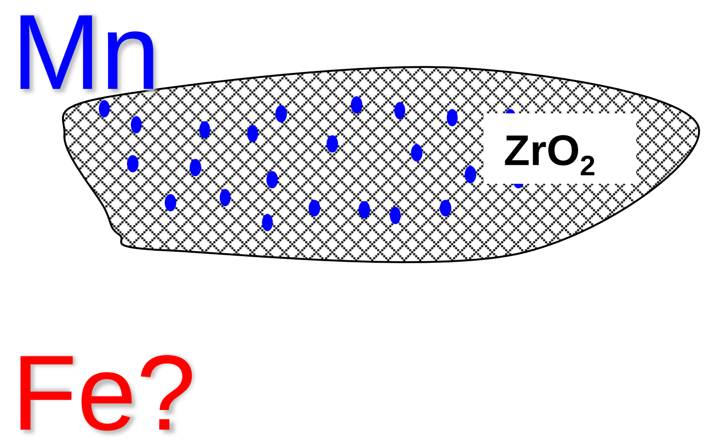
❖ incorporation of Mn, Fe into zirconia lattice *J. Stöcker Ann. Chim. 1960*

❖ determination of incorporated amount difficult, 2 additional factors

❖ Mn more easily incorporated than Fe? More surface Fe in presence of Mn?

Surface Analysis of MnSZi, FeSZi

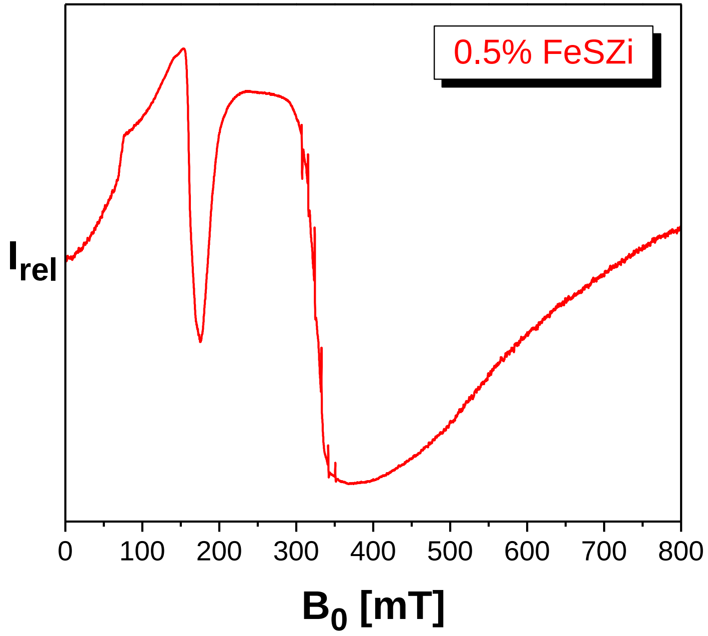


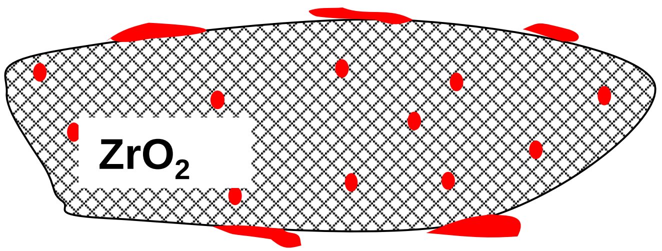


Analysis of top-most layer by ion scattering spectroscopy (ISS)

- Fe detectable at content of 2 wt%, Mn not detectable
- Fe: surface and bulk species?

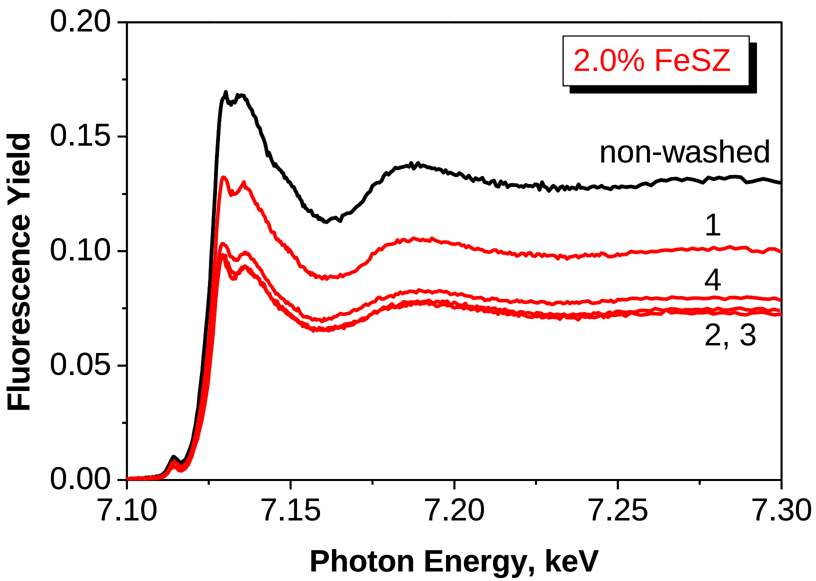
Fe as Promoter: EPR

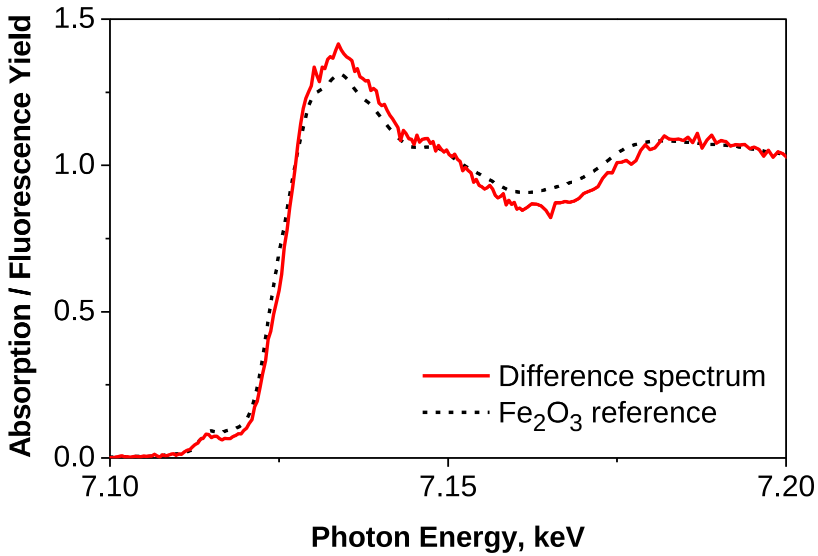




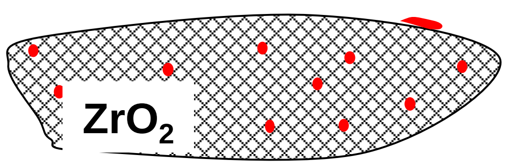
- isolated Fe^{3+} (incorporated)
  small Fe_2O_3 particles
  Fe^{3+} in oxygen environment of lower symmetry
- supported by Mössbauer spectra, only Fe^{3+}

Removal of Surface Species from FeSZi



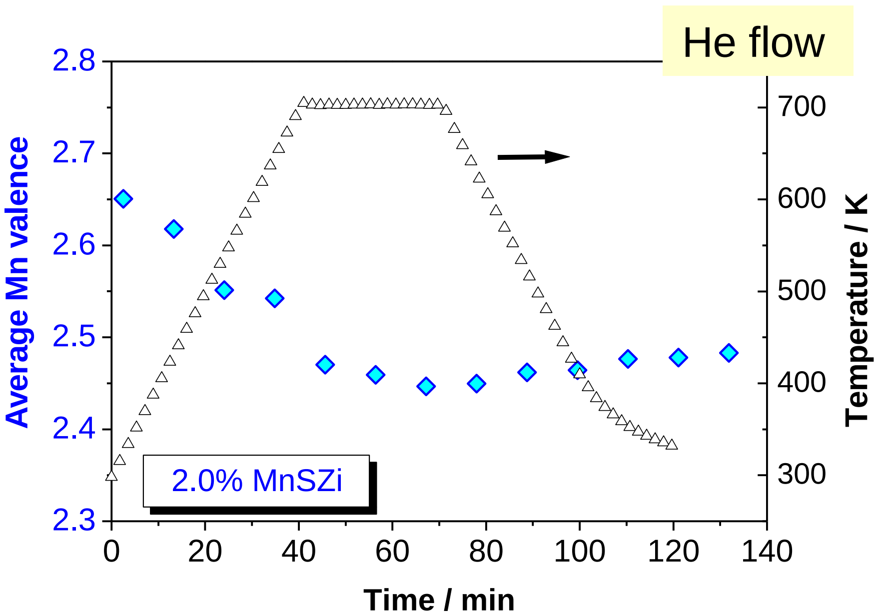


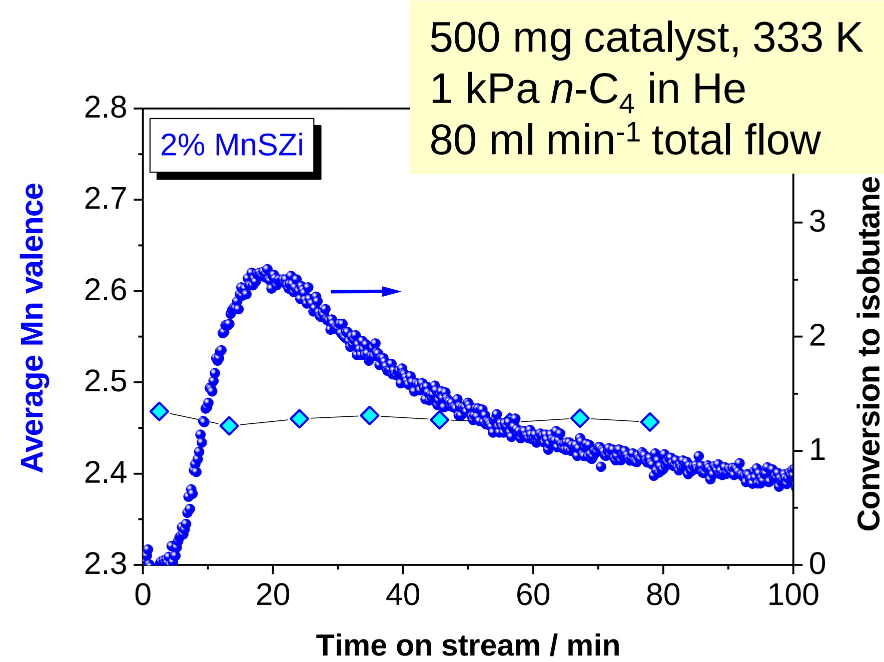
Fe K edge XANES



- ❖ 42% Fe removed removed by oxalic acid, Fe_2O_3
- ❖ sulfate also removed in washing

Oxidation State of Mn in MnSZi

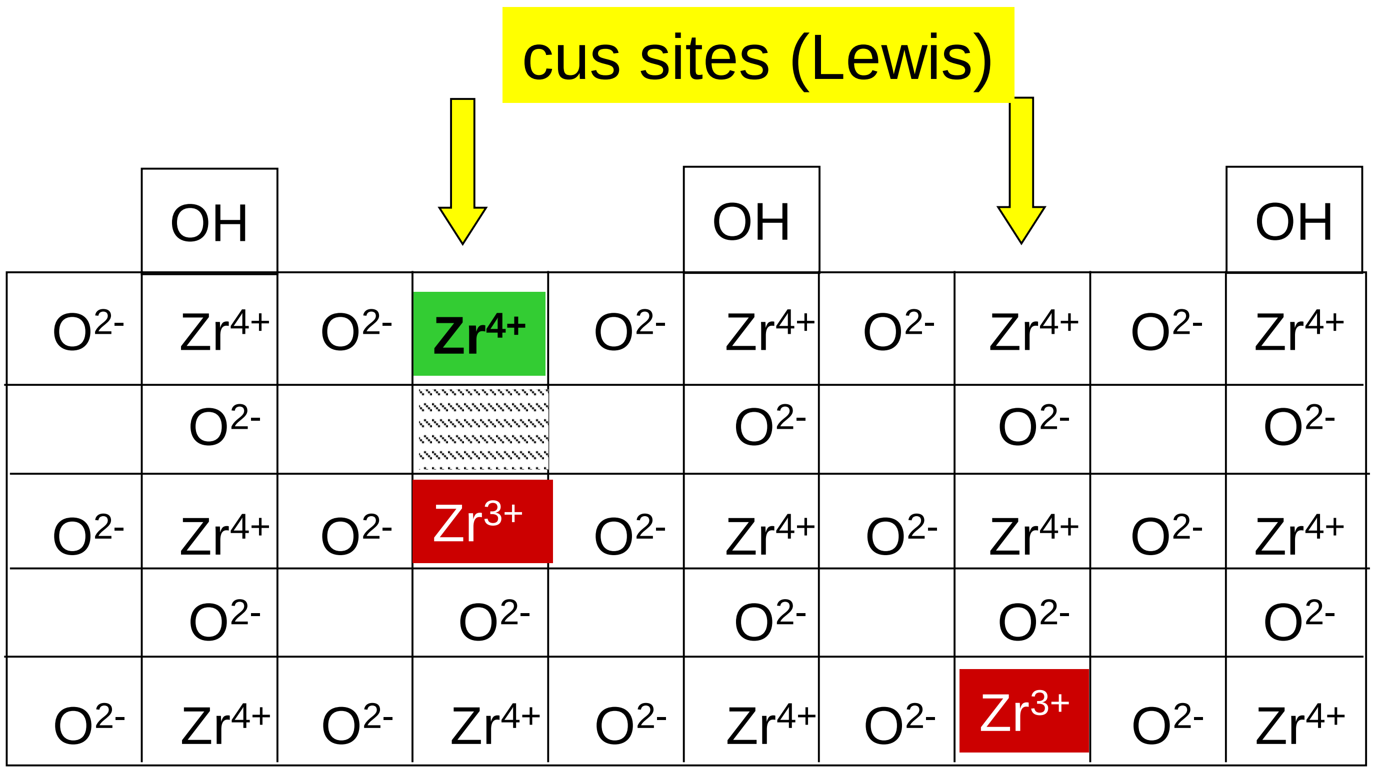




Analysis of Mn valence by in situ X-ray absorption spectroscopy (XAS)

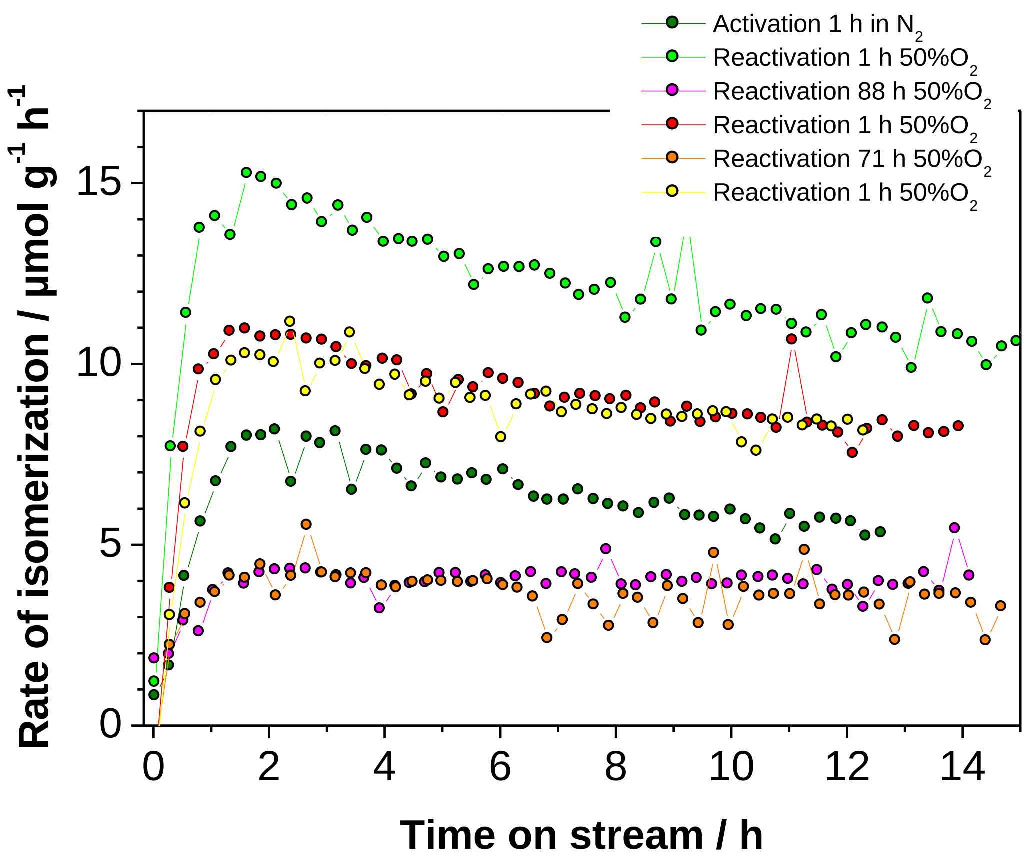
- ❖ mixed valence for Mn, slightly reduced during activation in inert gas: Mn participates in reactions
- ❖ no change of Mn oxidation state detectable during reaction

Model for Surface Sites



- cations with a valence < +IV in zirconia lattice essential
- role of sulfate?

Regeneration of SZ



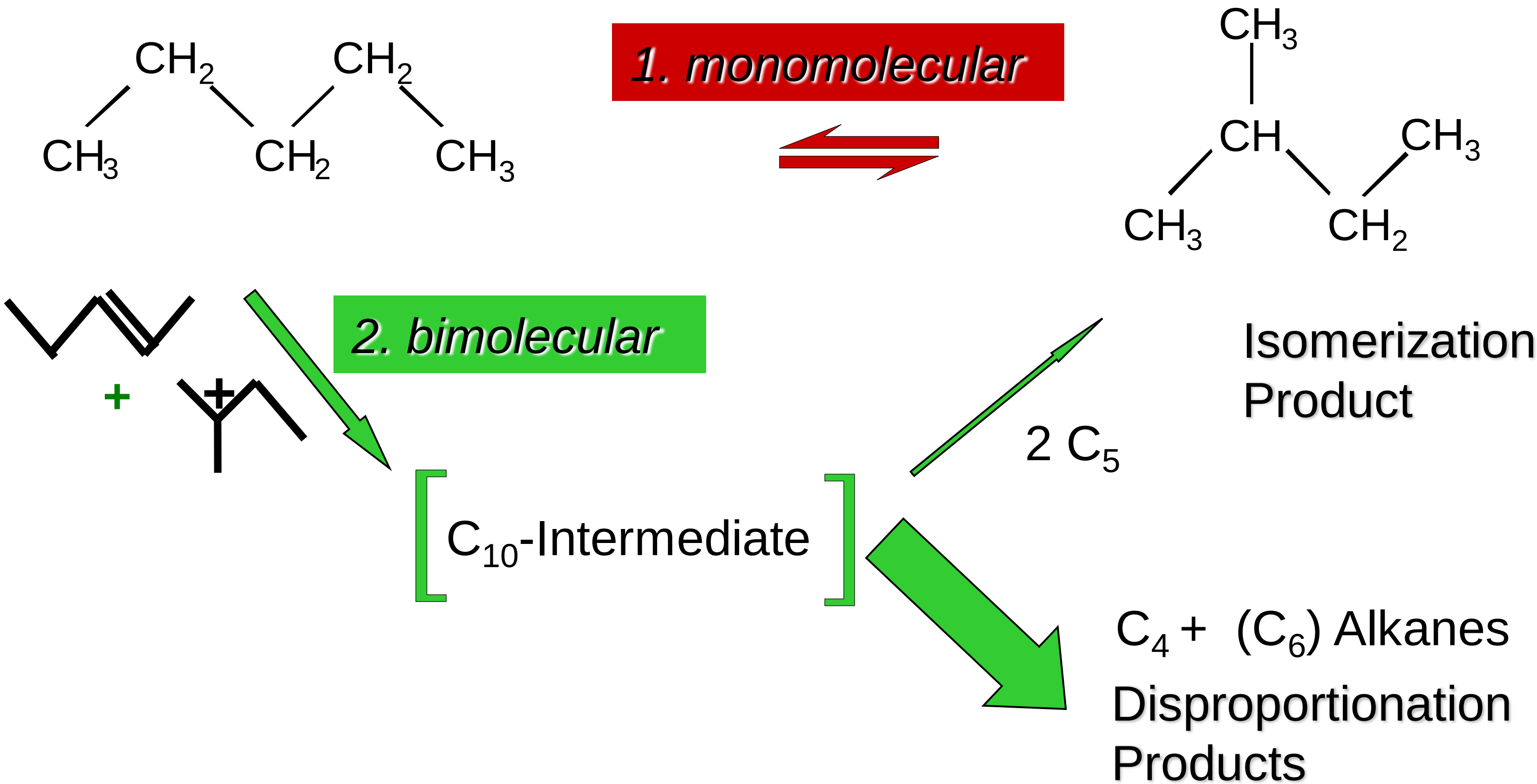
500 mg SZ, 1 kPa n-C_4
reaction at 338 K
regeneration at 723 K

- „conditioning in O_2“?

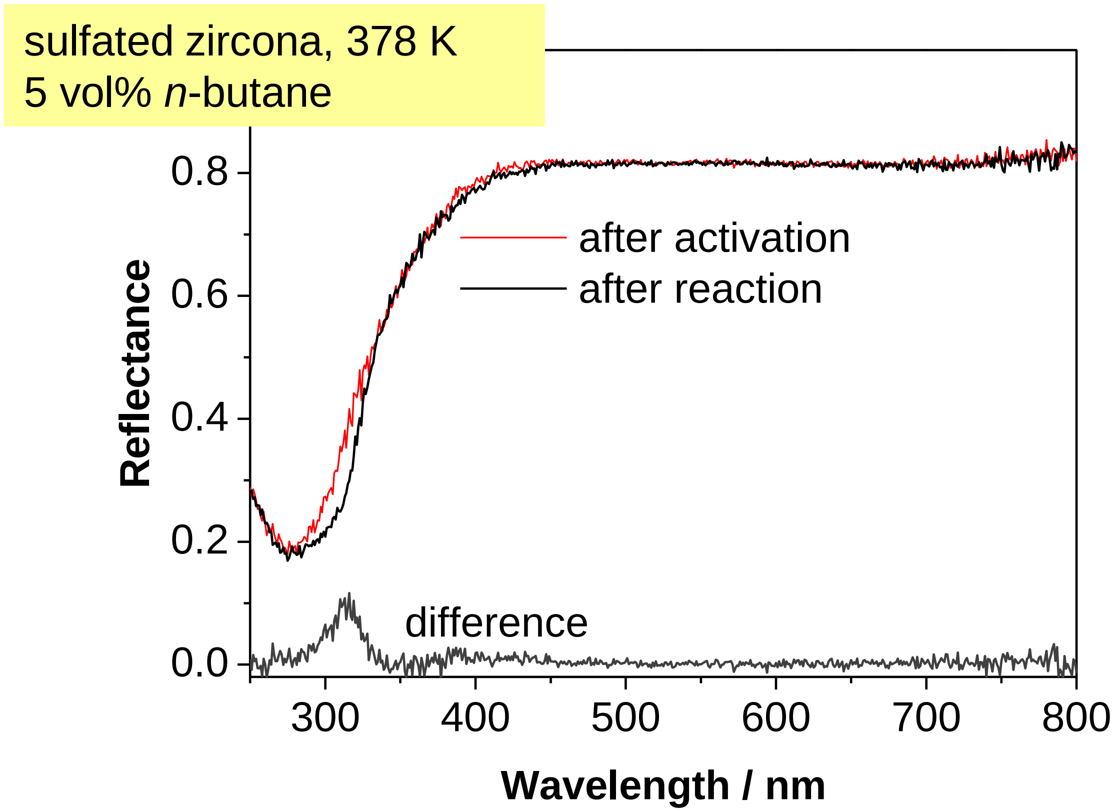
➡ a model that holds for SZ **and** promoted SZ

5. Deactivation of Sulfated Zirconia

Isomerization can proceed through 2 different mechanisms – does only one lead to surface deposit formation?



In Situ UV-vis Spectroscopy

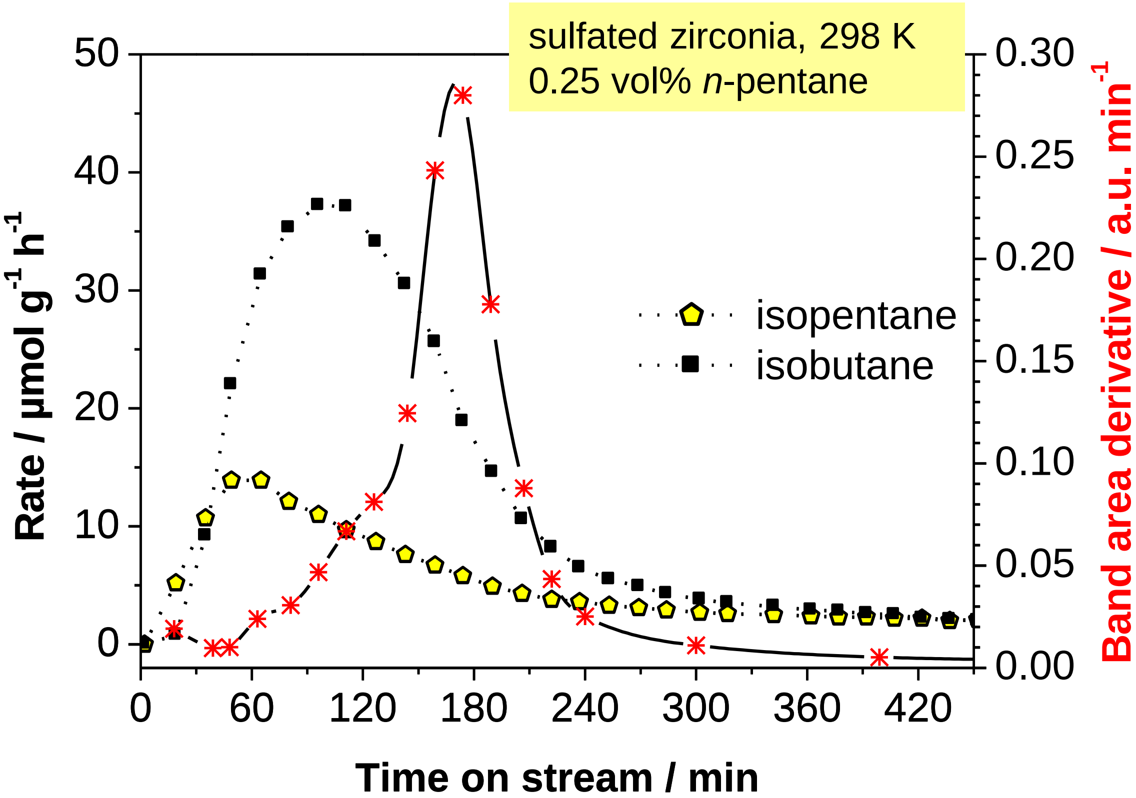


❖ band at 310 nm after *n*-butane reaction: allylic cations
Spielbauer et al., Catal. Lett. 1996

➡ monitor band growth and catalytic performance

Reaction Profile during Pentane Isomerization

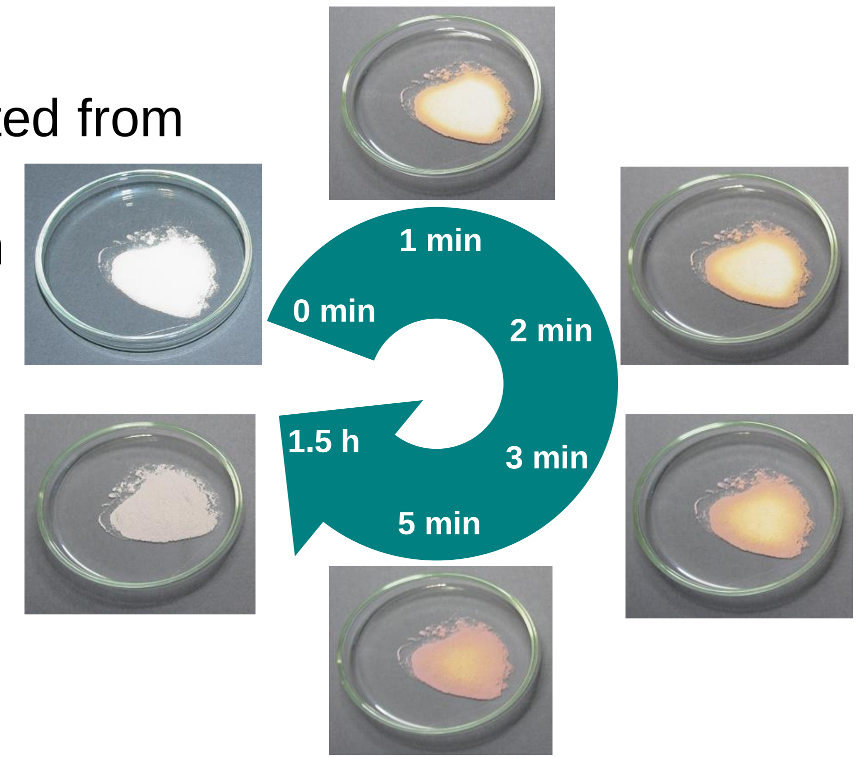
Ahmad, Jentoft et al.
J. Catal. 2003



- unsaturated species are not intermediates
- not a result of monomolecular isomerization
- result of bimolecular mechanism, competing reaction to formation of gas phase products

Reaction of Surface Deposits with Air

SZ, deactivated from *n*-pentane isomerization



- ❖ reaction of surface deposits with components of air (O_2, H_2O?)
- ❖ volatilization?

➡ study "coke" in situ without exposure to air

Conclusions I

Role of sulfate

- only a minority of sulfate participates

➡ active species will be difficult to identify

Preparation of sulfated zirconia catalysts

- calcination parameters essential; batch size (extensive quantity) and packing have influence on catalytic activity

➡ explains differences between preparations from different groups

Handling of sulfated zirconia catalysts

- ZrO_2 not "inert": succumbs to mechanical stress

➡ handle with care...

Conclusions II

Effect of promoters

- Fe, Mn stabilize tetragonal (cubic) phase through incorporation in lattice
- promoters: on surface + in lattice, distribution depends on preparation
- Mn is not involved in stoichiometric redox reactions
- lower valence of Fe, Mn (other promoters) vs. Zr^{4+}: oxygen vacancies

→ a common model for promoted and unpromoted SZ

Deactivation and regeneration

- deactivation result of bimolecular mechanism
- surface deposits are reactive in air, may be volatilized?

→ surface species must be studied in situ

Outlook

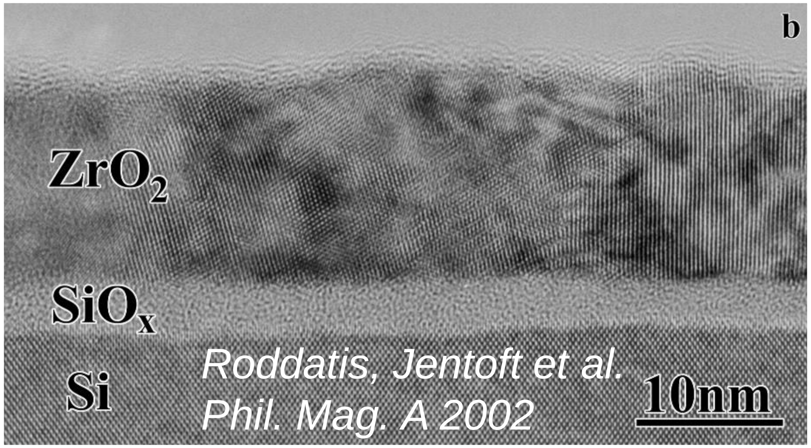
Materials

- "improved preparation"
- other anions (tungstated zirconia)
- other promoters (periodic table)
- supported sulfated zirconia (SiO_2, MCM-41, Al_2O_3)
- nano- and mesostructured zirconia

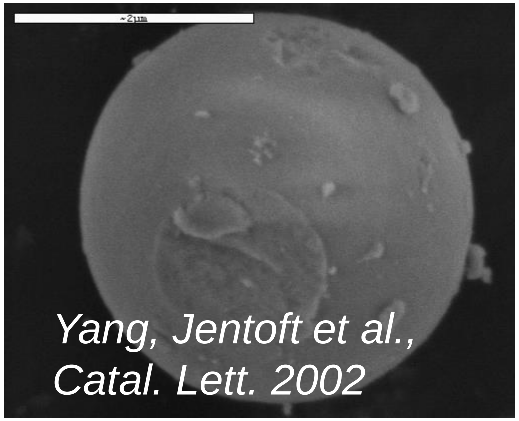
Catalysis

- prevention of deactivation by Pt/H_2
- other reactions
  Yadav & Nair, Microp. Mesop. Mater. 1999

…and Understanding???



Roddatis, Jentoft et al.
Phil. Mag. A 2002


Yang, Jentoft et al.,
Catal. Lett. 2002

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