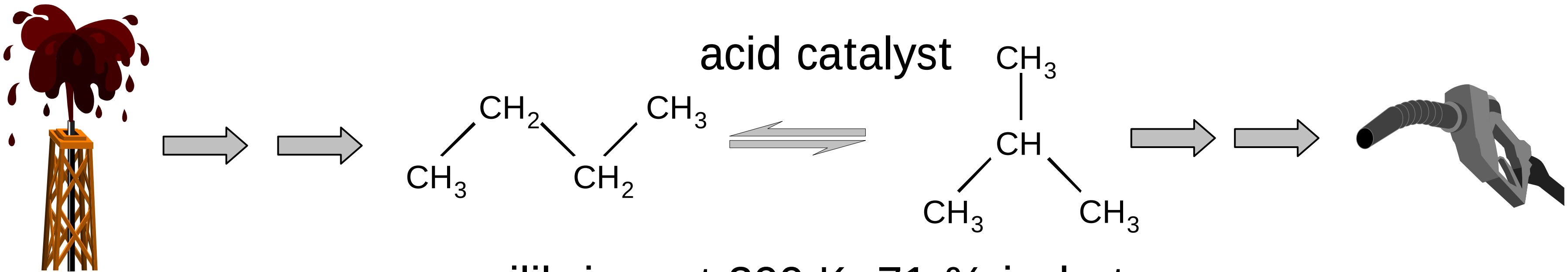
Abteilung Anorganische Chemie
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4-6, 14195 Berlin

A Fundamental Approach to the Development of Novel Alkane Isomerization Catalysts

Friederike C. Jentoft

University of Reading
June 4, 2007

Alkane Skeletal Isomerization



equilibrium at 300 K: 71 % isobutane

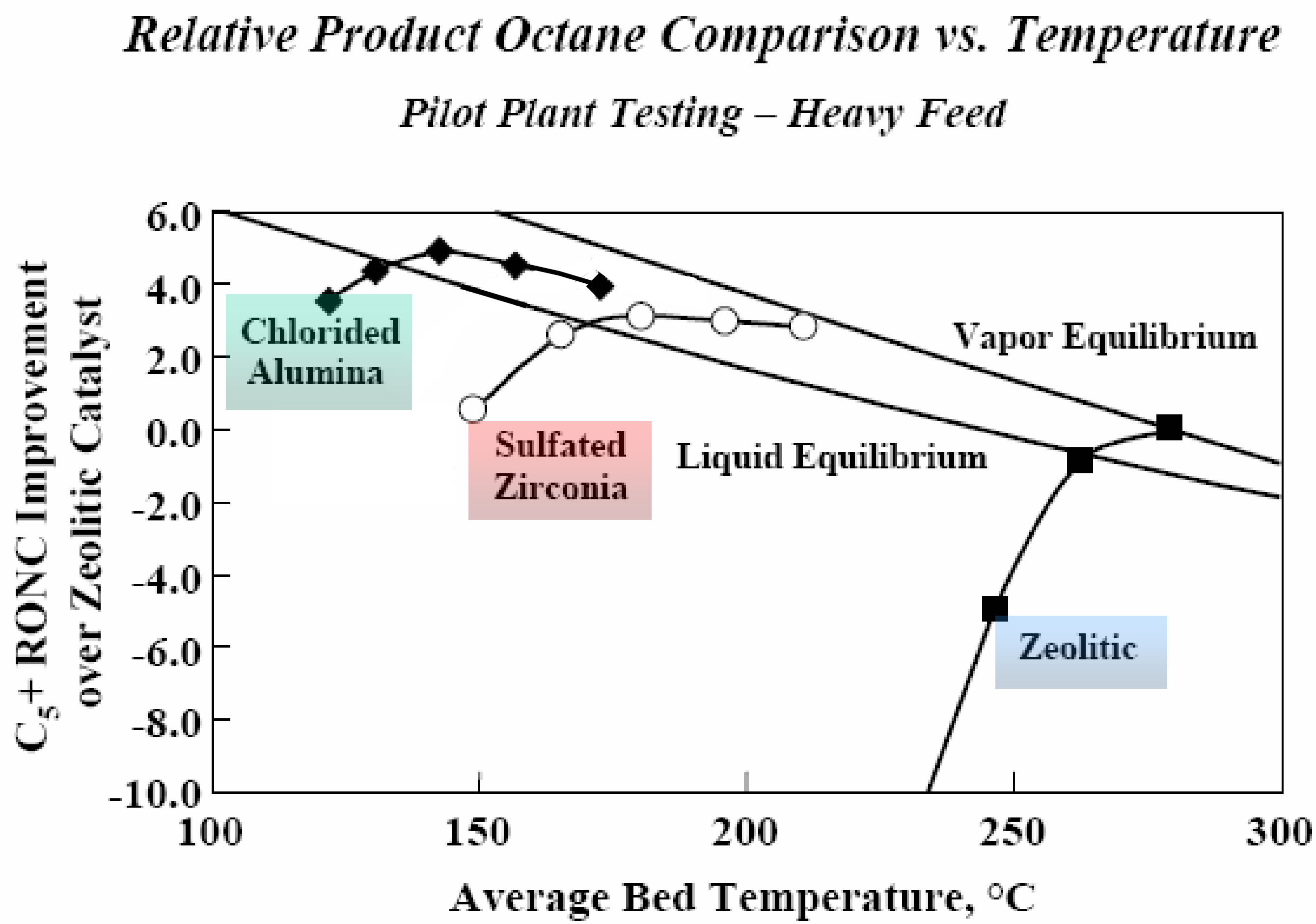
Common solid acid catalysts

- Pt/$AlCl_3$-Al_2O_3: 393-453 K, problems with Cl and H_2O
- Pt/zeolite: 533 K, unfavorable equilibrium

“New” low temperature isomerization catalyst

- Pt/sulfated zirconia

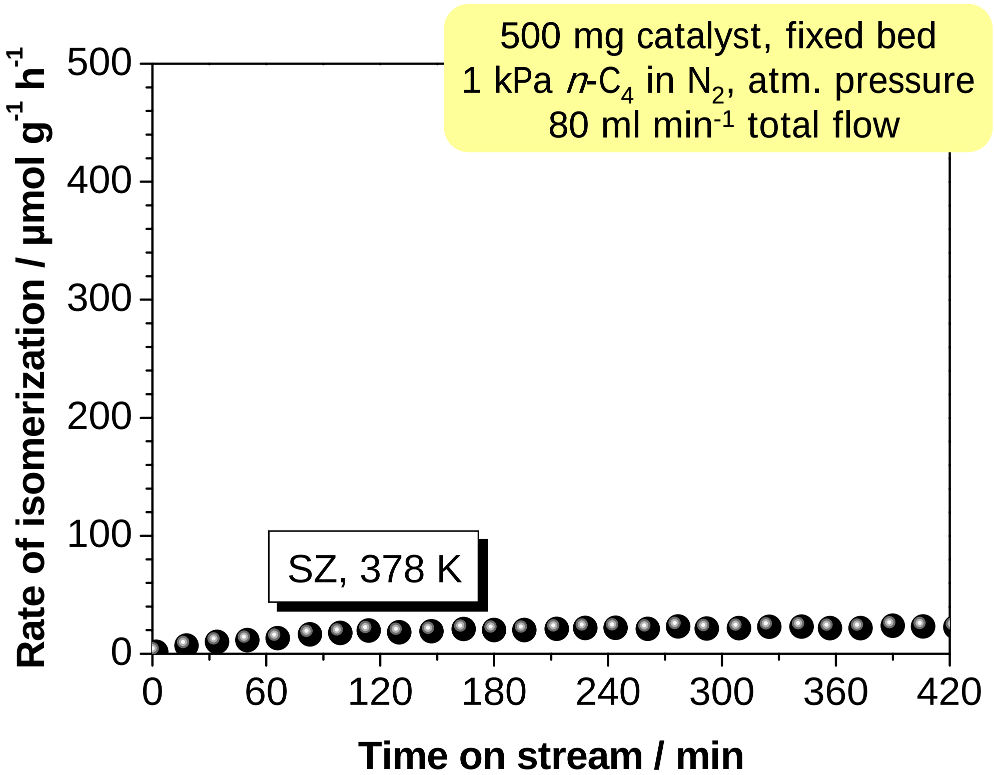
Catalyst Comparison



after G.C. Anderson, R.R. Rosin, M.A. Stine, M.J. Hunter, UOP 2004

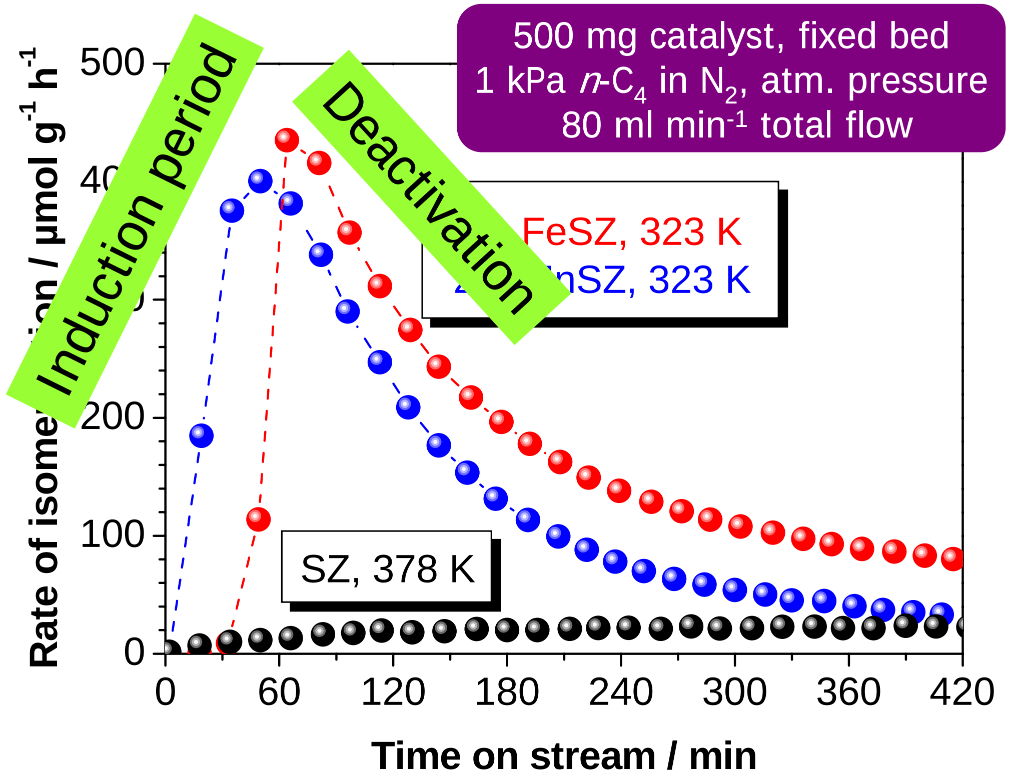
Promotion of Sulfated Zirconia

- Pt/sulfated zirconia: 353 K
  Holm, Bailey 1962, US Patent 3,032,599
- "SZ" isomerizes *n*-butane at RT
  Hino, Arata, JACS 1979 & Chem. Comm. 1980



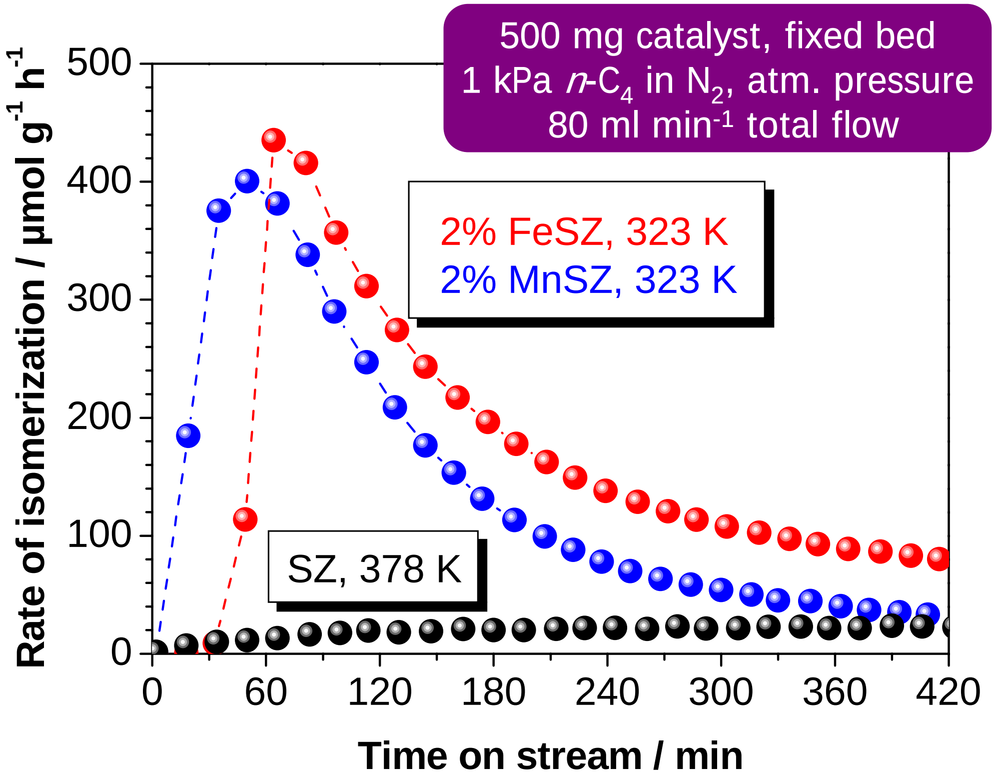
Promotion of Sulfated Zirconia

- Pt/sulfated zirconia: 353 K
  Holm, Bailey 1962, US Patent 3,032,599
- "SZ" isomerizes *n*-butane at RT
  Hino, Arata, JACS 1979 & Chem. Comm. 1980
- Fe and Mn act as promoters of SZ
  Hollstein et al., US Patent 4,918,041 1990
  Hsu et al., Chem. Comm. 1992
  Lange et al., Catal. Lett. 1996



Promotion of Sulfated Zirconia

- Pt/sulfated zirconia: 353 K
  Holm, Bailey 1962, US Patent 3,032,599
- "SZ" isomerizes *n*-butane at RT
  Hino, Arata, JACS 1979 & Chem. Comm. 1980
- Fe and Mn act as promoters of SZ
  Hollstein et al., US Patent 4,918,041 1990
  Hsu et al., Chem. Comm. 1992
  Lange et al., Catal. Lett. 1996

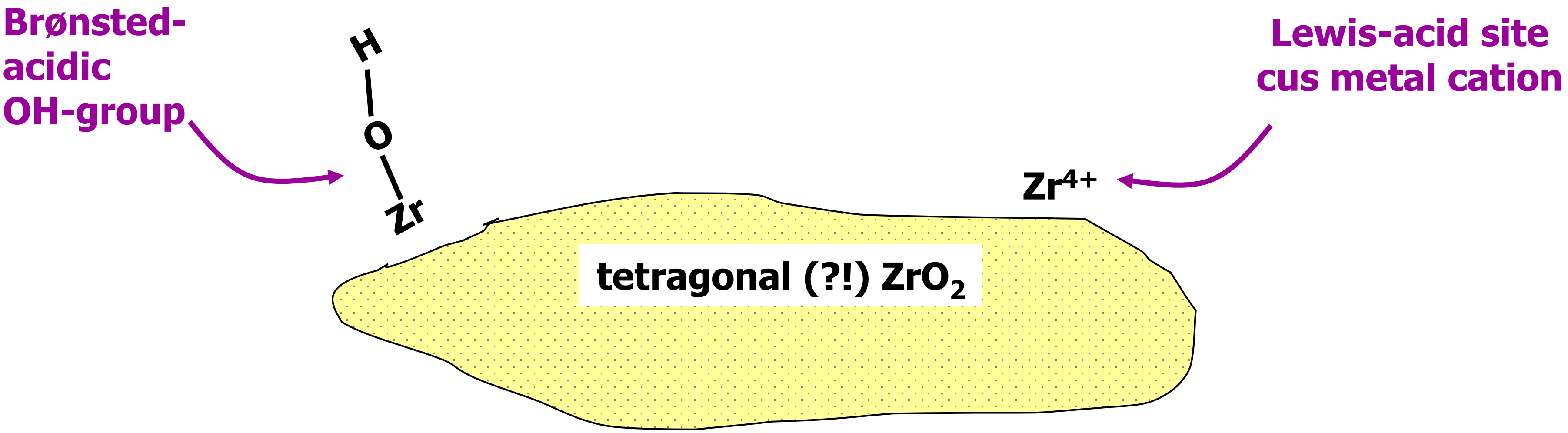


- SZ catalyzes cracking, alkylation, condensation, etherification, acylation, esterification, nitration, and oligomerization

  G.D. Yadav, J.J. Nair, Microporous Mesoporous Mat. 33 (1999) 1-48

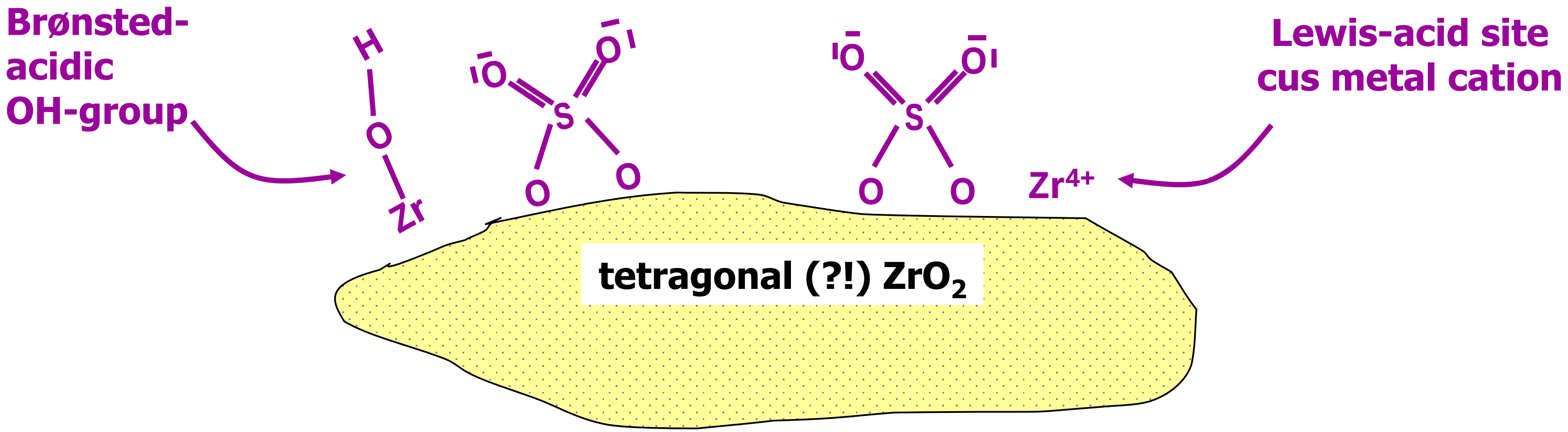
➡ sulfated zirconia a solid superacid (>100% H_2SO_4) ?

Initial Ideas



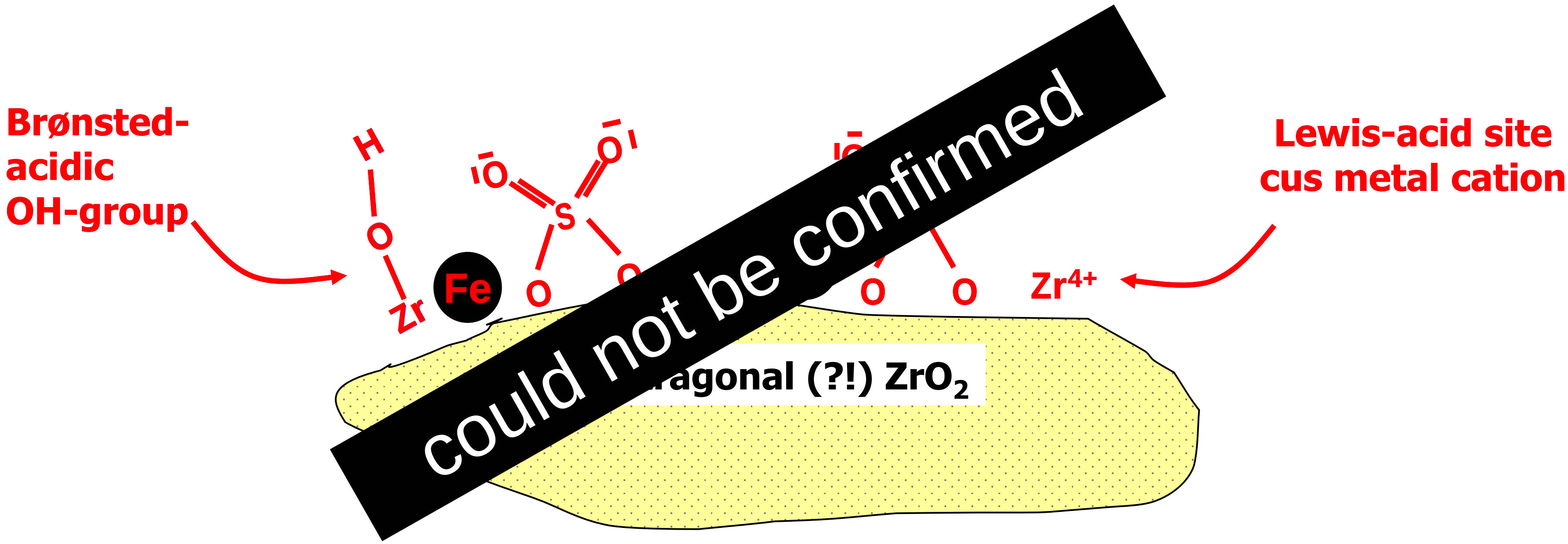
- "ZrO_2 (mp 2700°C) is a white, chemically, thermally, and mechanically stable compound"
  Riedel, Anorganische Chemie, deGruyter 2002, p. 776

Initial Ideas



- "ZrO_2 (mp 2700°C) is a white,
  chemically, thermally, and mechanically stable compound"
  Riedel, Anorganische Chemie, deGruyter 2002, p. 776
- sulfate generates acidity

Initial Ideas



- "ZrO_2 (mp 2700°C) is a white,
  chemically, thermally, and mechanically stable compound"
  Riedel, Anorganische Chemie, deGruyter 2002, p. 776

- sulfate generates acidity

- Mn and Fe increase acidity of the "solid superacid" sulf. ZrO_2
  evidence: activity, TPD with (subst.) benzenes
  Hsu et al., Chem. Comm. 1992; Lin et al., Chem. Comm. 1992

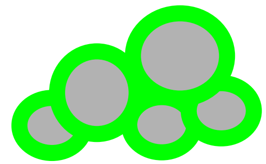
- ...extremely acidic sites can not be identified
  Adeeva et al., J. Catal. 1995; Wan et al., J. Catal. 1996

Outline

1. Preparation: calcination chemistry
2. Zirconia metastability
3. Zirconia - promoter interaction
4. Surface sites and reactivity
5. Summary
6. Outlook

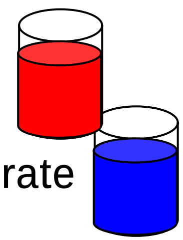
Addition of Promoters

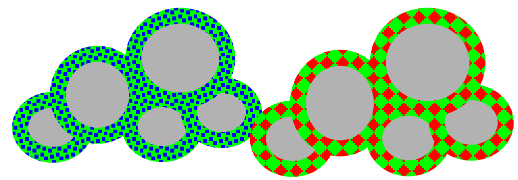
commercial hydrous zirconia
X-ray amorphous
sulfated with $(NH_4)_2SO_4$
dried at 383 K



Incipient wetness

Fe(III),
Mn(II) nitrate





Calcination

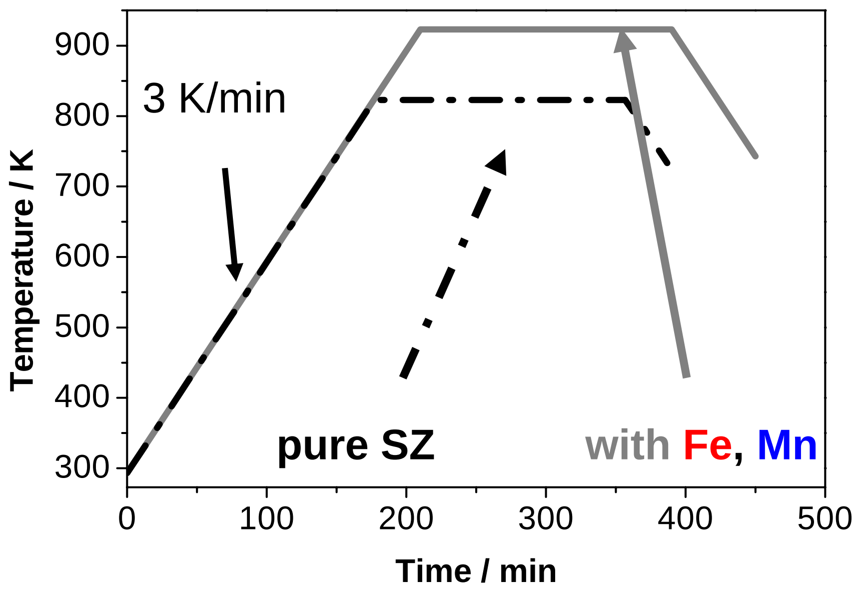
sulf. ZrO_2
"SZ"

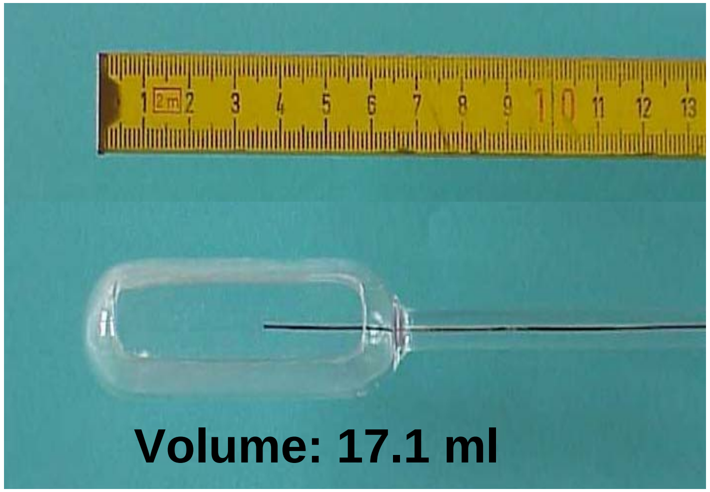
Mn-sulf. ZrO_2
"MnSZ"

Fe-sulf. ZrO_2
"FeSZ"

sulfate content: 4.5 wt% SO_3 promoter content: 0.5-5.0 wt% metal

Calcination Chemistry

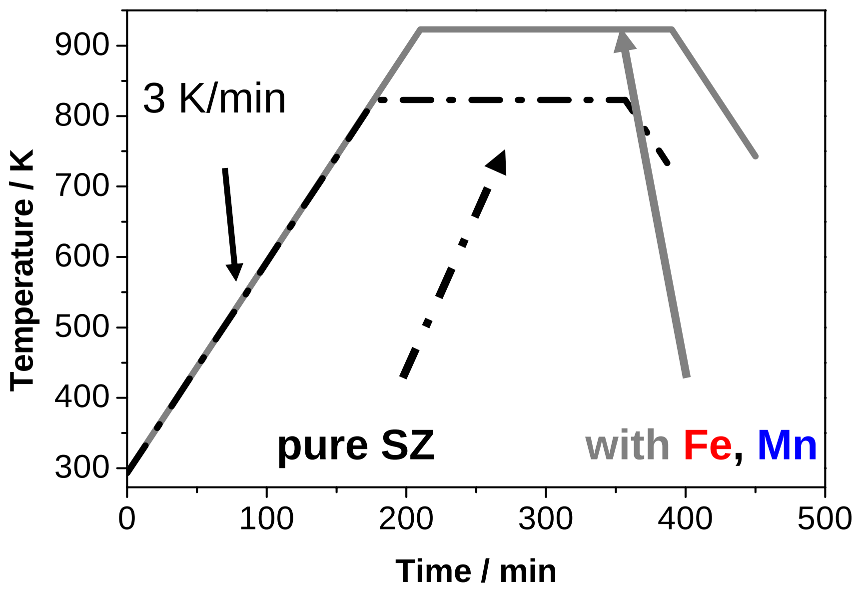


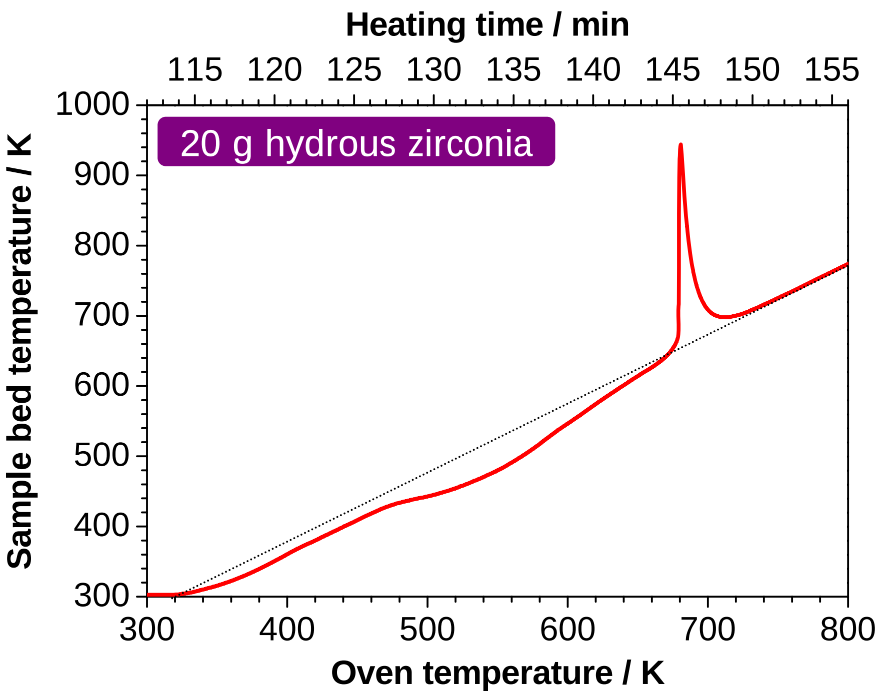


- Water loss
- Decomposition of NO_3^- and NH_4^+
- Crystallization / sintering of ZrO_2

Endo-/exothermic reactions

Calcination Chemistry and Engineering

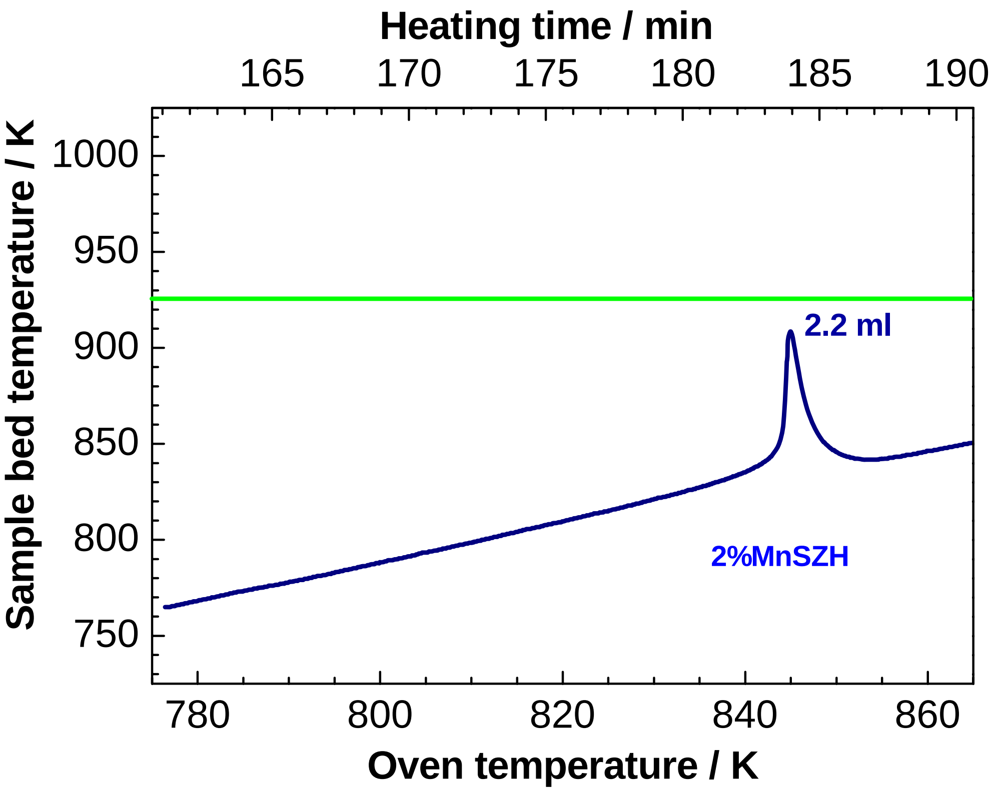


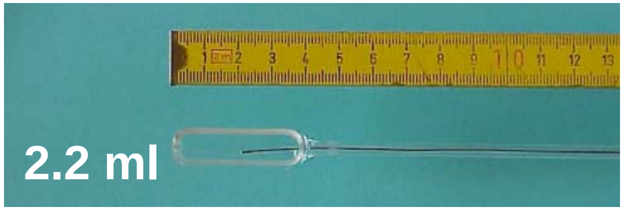


- Water loss
- Decomposition of NO_3^- and NH_4^+
- Crystallization / sintering of ZrO_2

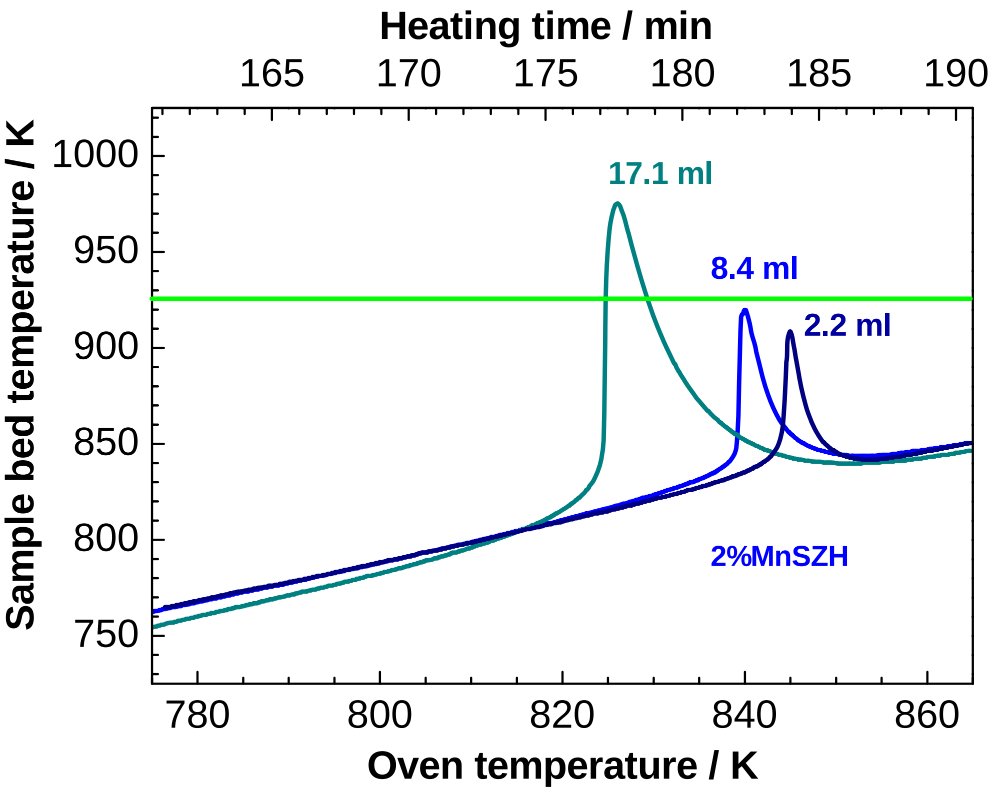
- Rapid overheating (up to 40-50 K/s)
- Overshoot up to 300 K
- "Glow phenomenon" not unique to formation of ZrO_2: Ti, Fe, Cr oxides

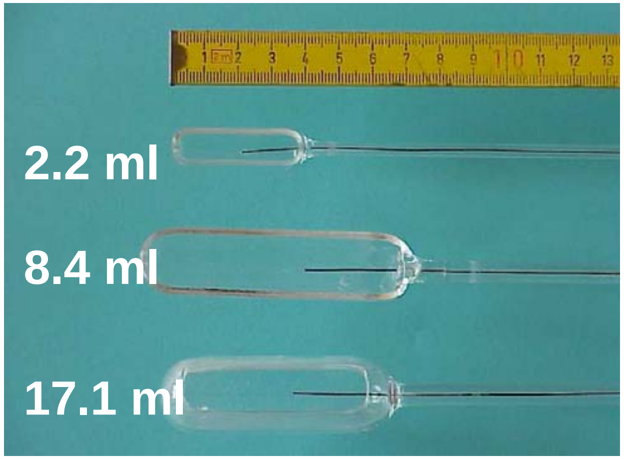
Effect of the Calcined Amount: MnSZ and FeSZ





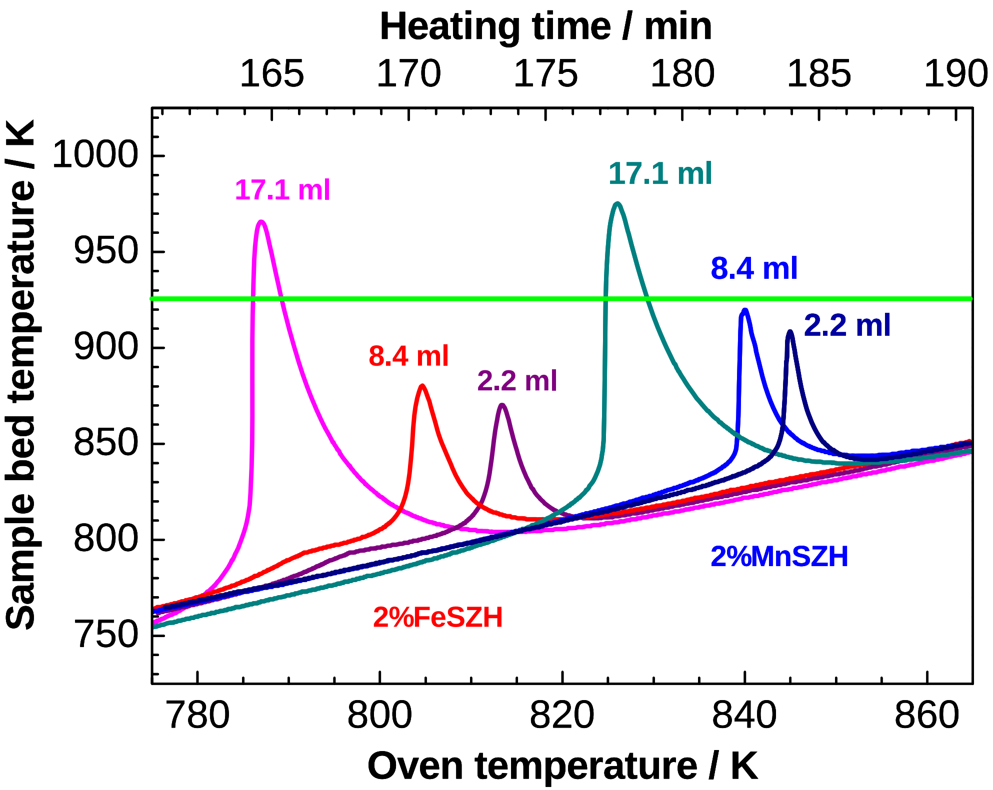
Effect of the Calcined Amount: MnSZ and FeSZ

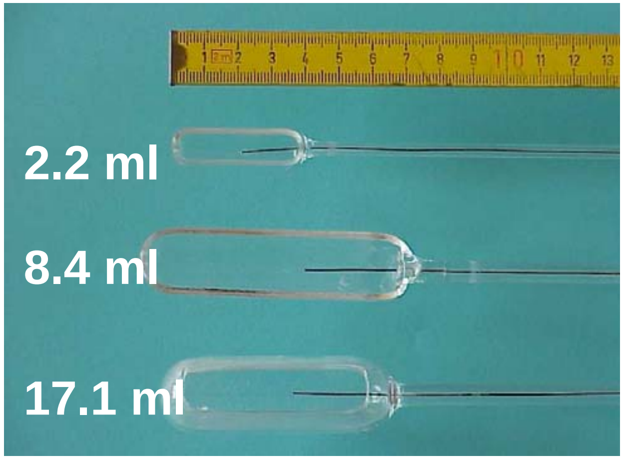




- Strong effect of batch size
- Planned T_{max} may be exceeded

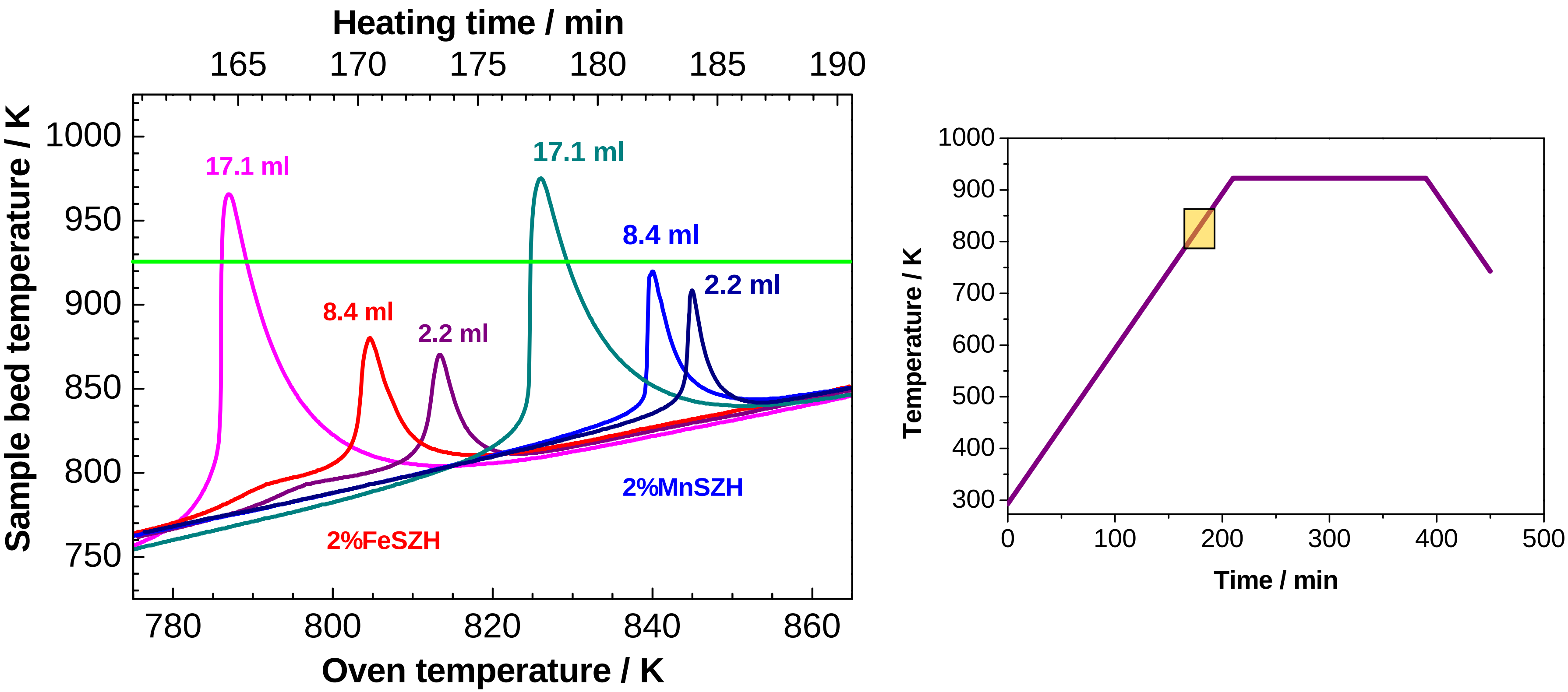
Effect of the Calcined Amount: MnSZ and FeSZ





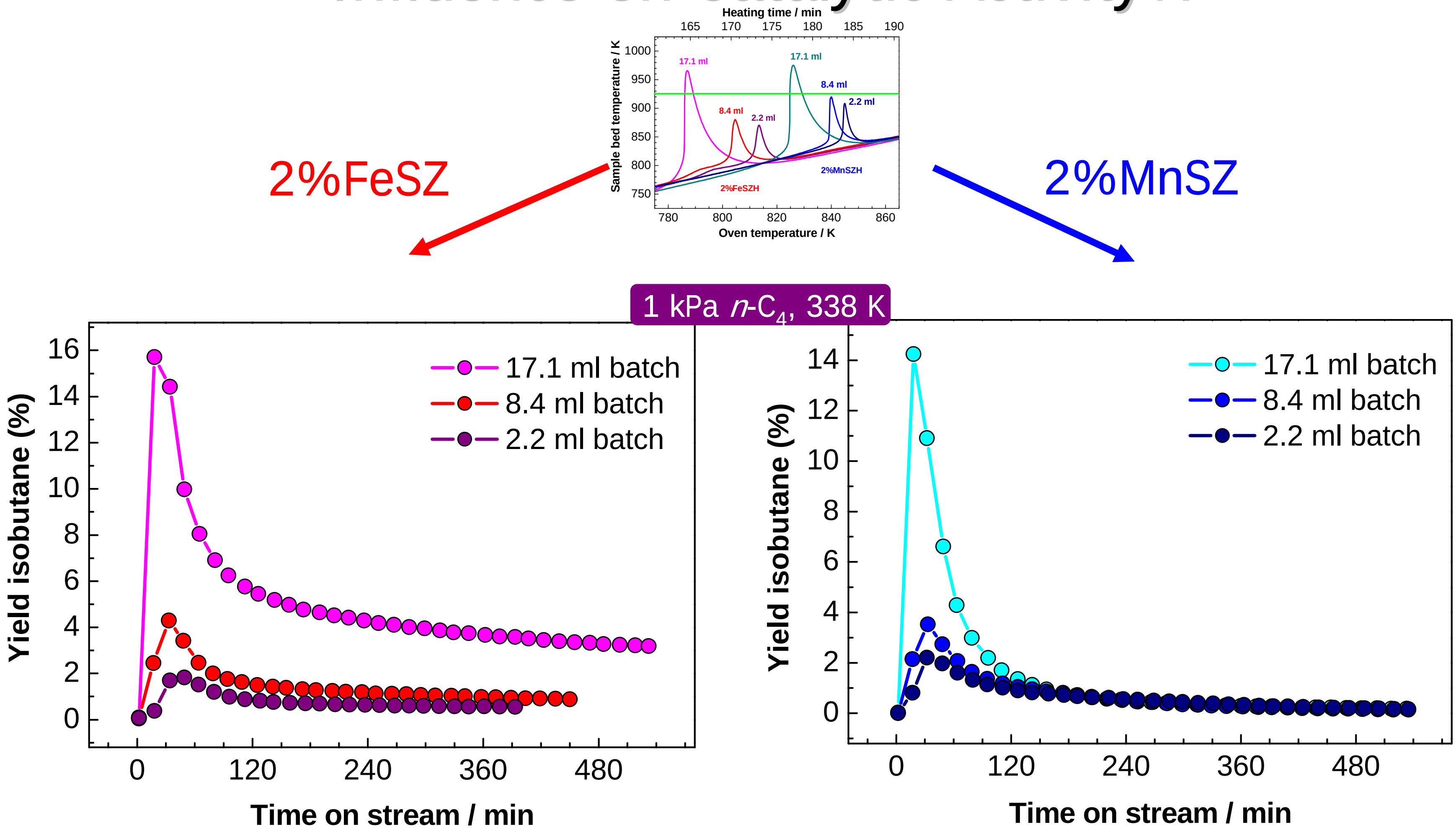
- Strong effect of batch size
- Planned T_{max} may be exceeded
- Promoters: influence calcination chemistry, Fe different than Mn

Effect of the Calcined Amount: MnSZ and FeSZ



- Strong effect of batch size
- Planned T_{max} may be exceeded
- Promoters: influence calcination chemistry, Fe different than Mn

Influence on Catalytic Activity?!



➢ Samples calcined in large batches more active

➡ Active phase formed during overheating – non equilibrium state

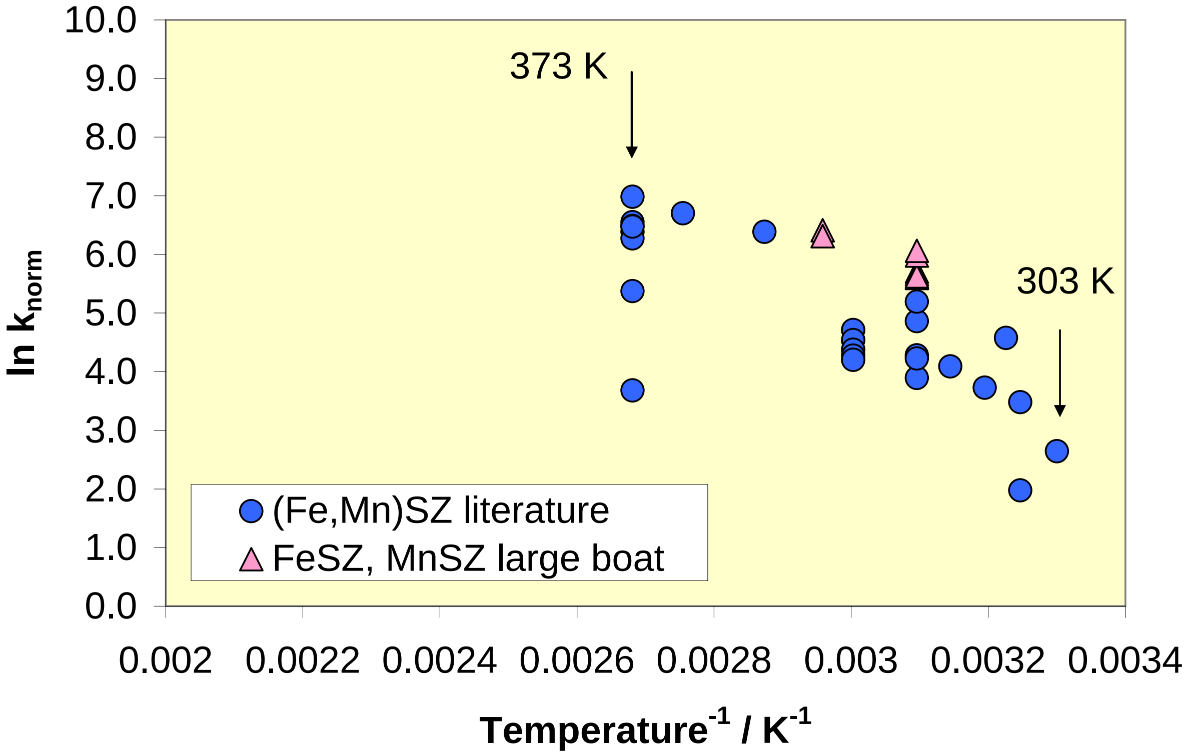
A. Hahn, F.C. Jentoft et al., Chem. Commun. 2001

Calcination - Summary

- Improved reproducibility; extrinsic parameter decisive: calcined amount
- Rapid genesis of active phase during overheating
- Large batch calcination produce most active catalysts

Calcination - Summary

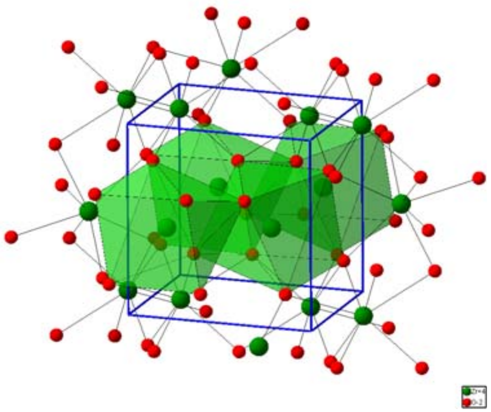
- Improved reproducibility; extrinsic parameter decisive: calcined amount
- Rapid genesis of active phase during overheating
- Large batch calcination produce most active catalysts

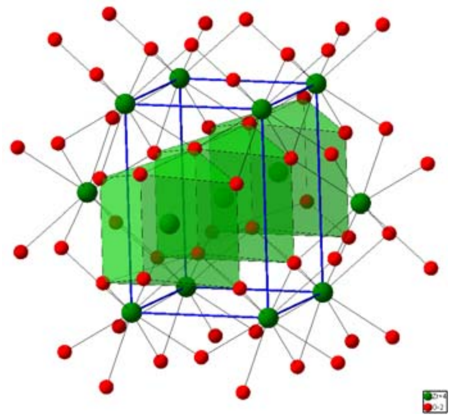


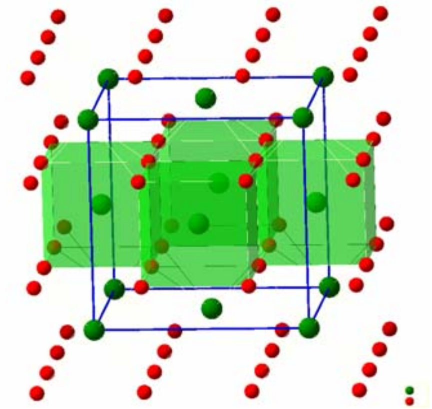
- Arrhenius-type graph
- Rate constants from literature
- Assuming 1st order in *n*-butane

F.C. Jentoft et al., invited article in preparation for Angew. Chemie

Zirconia Phase Chemistry







1223 - 1473 K **>2473 K**

monoclinic ⇌ **tetragonal** ⇌ **cubic**

- Tetragonal / cubic phase stabilized by doping with of Y^{3+}, Mg^{2+}, Ca^{2+}
- Sulfate also stabilizes tetragonal phase
- Tetragonal phase more active than monoclinic phase

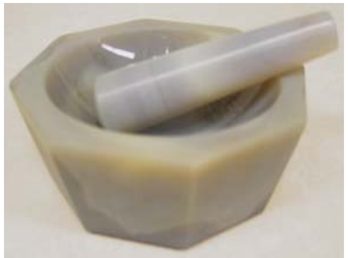
  C. Morterra, G. Cerrato, F. Pinna, M. Signoretto, J. Catal. 157 (1995) 109

  W. Stichert and F. Schüth, J. Catal. 174 (1998) 242

Metastable Nature of Active Sites

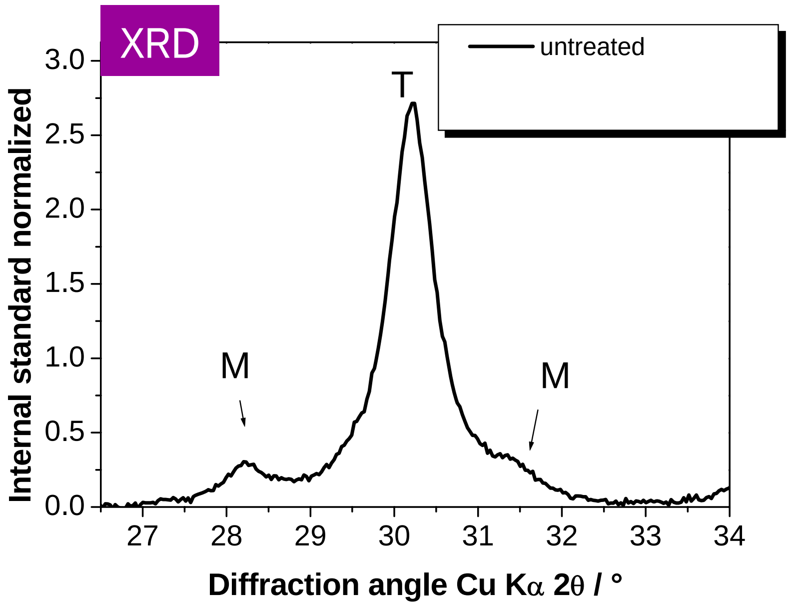
- After calcination, powders are clumped together

- Samples are being ground or milled to obtain fine powder

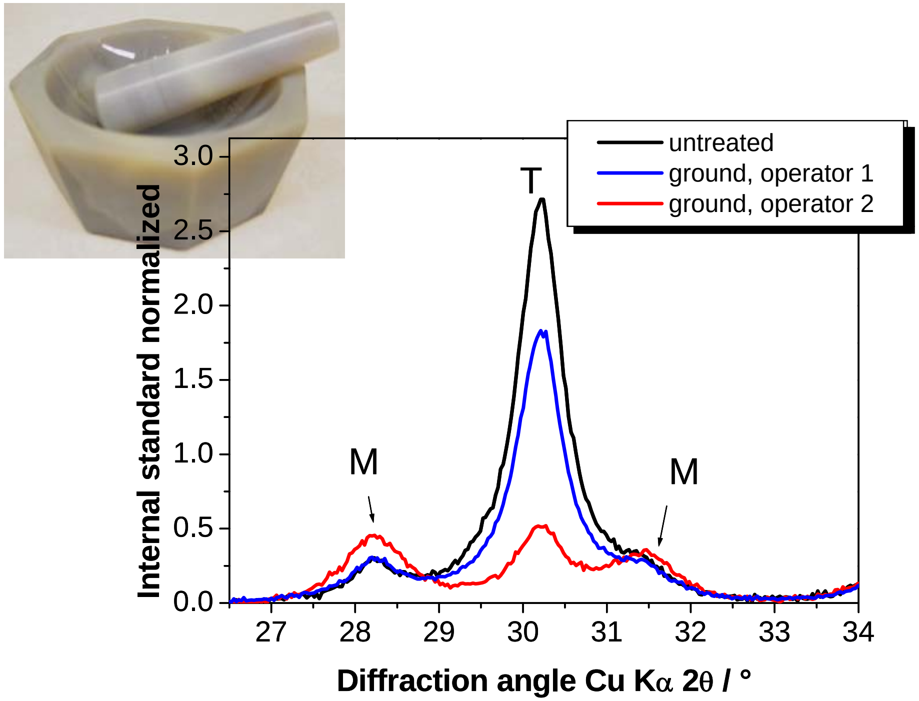


- Samples are pressed for catalysis, transmission spectroscopy, vacuum methods

Grinding of 0.5% MnSZ: XRD and Catalysis

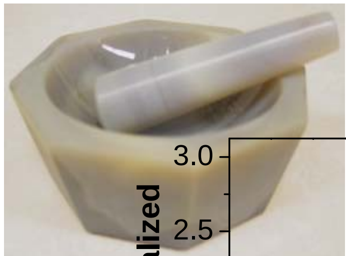


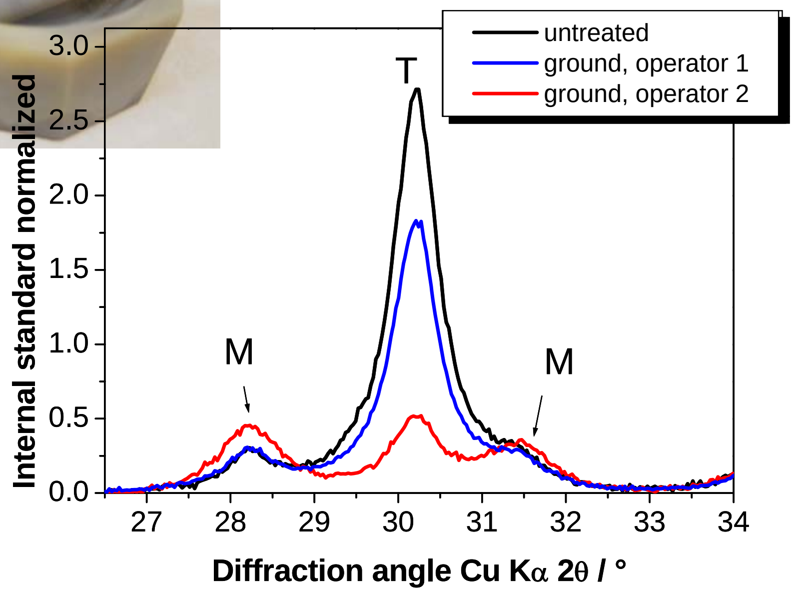
Grinding of 0.5% MnSZ: XRD and Catalysis

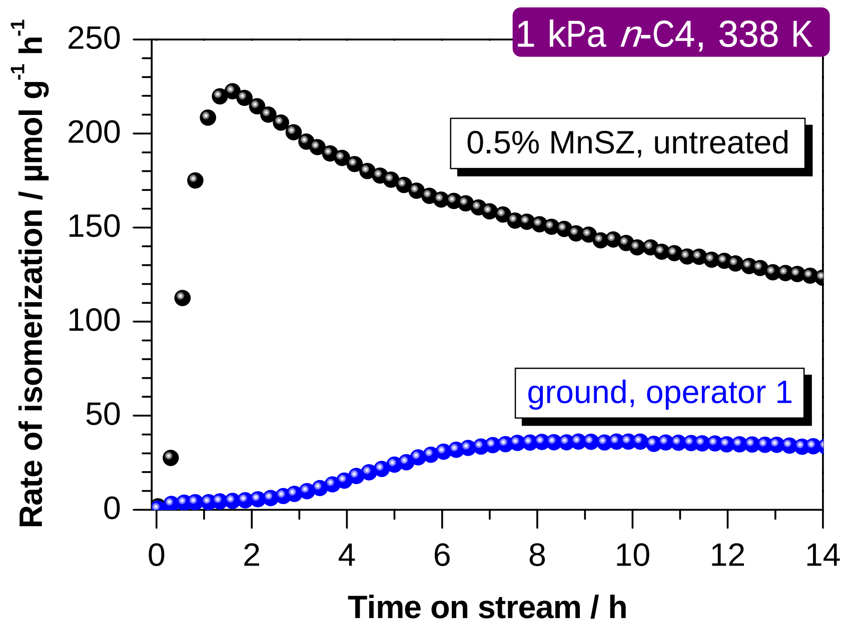


- ZrO_2 affected by mechanical stress, transformation of t-ZrO_2 to m-ZrO_2
  E.D. Whitney, Trans. Faraday. Soc. 1965 (footnote!)
- Grinding: strong operator influence

Grinding of 0.5% MnSZ: XRD and Catalysis







- ➢ ZrO_2 affected by mechanical stress, transformation of t-ZrO_2 to m-ZrO_2
  E.D. Whitney, Trans. Faraday. Soc. 1965 (footnote)
- ➢ Grinding: strong operator influence
- ➢ Catalytic performance also altered!

B. Klose, F.C. Jentoft et al., J. Catal. 2003

Stability during Long-Term Storage

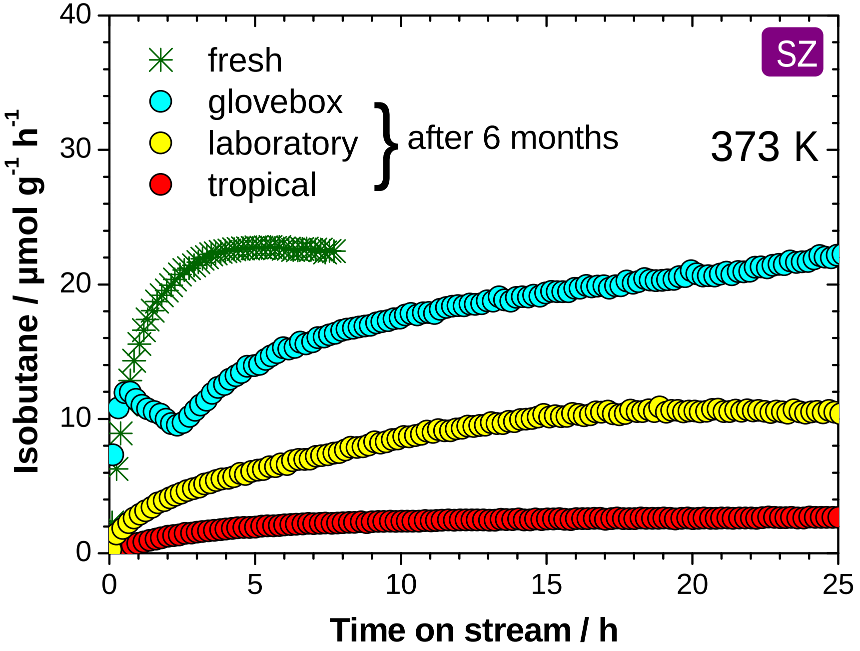
Storage Conditions

Laboratory
"Berliner Luft"

glovebox

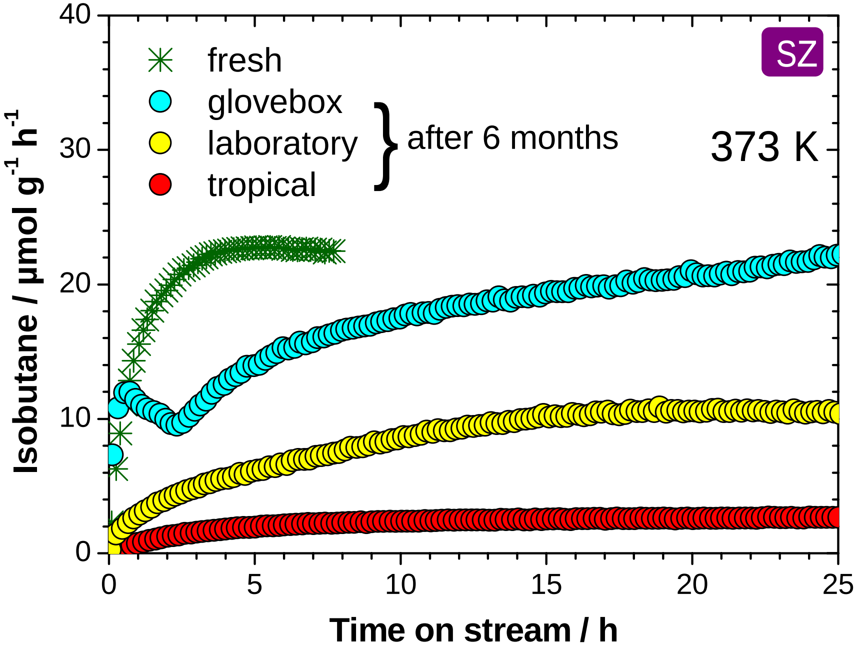
"tropical" 313 K,
saturated H_2O vapor

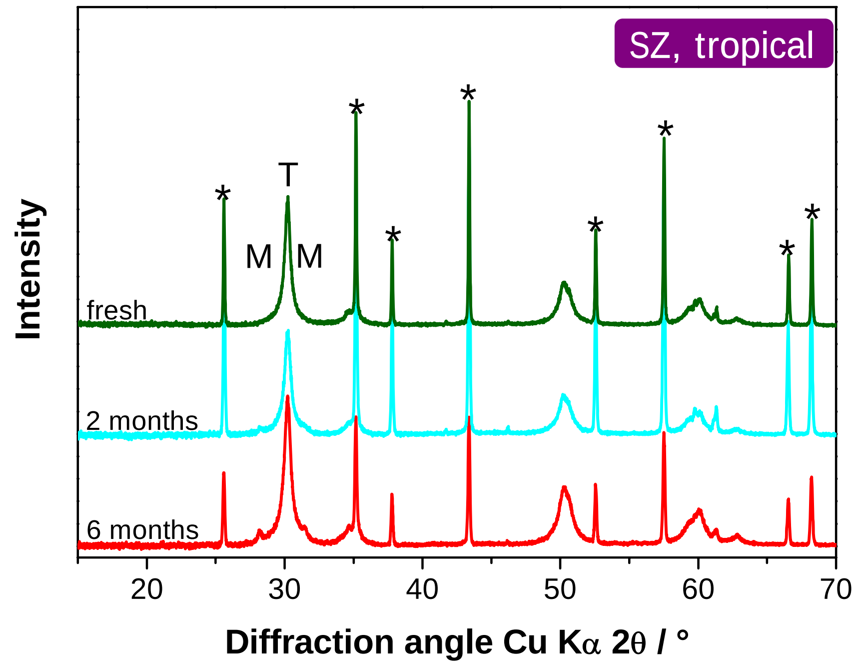
Stability of Sulfated Zirconia



B.S. Klose, F.C. Jentoft et al., in preparation

Stability of Sulfated Zirconia



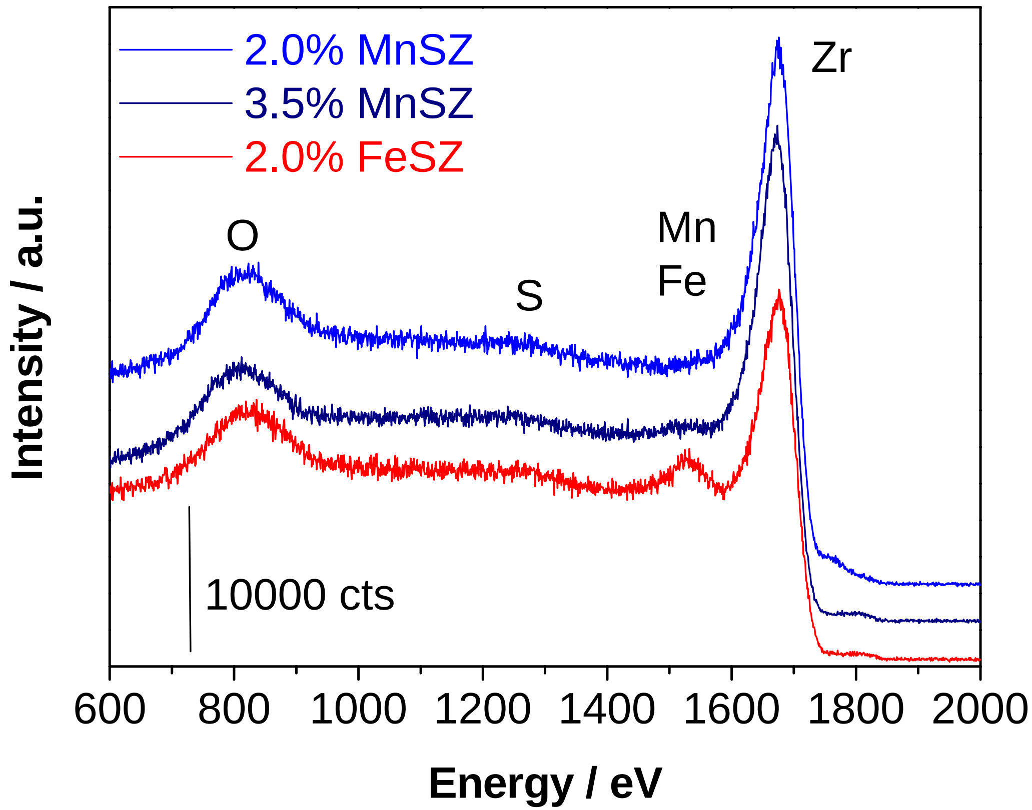


- Tropical, 6 months: loss of 90% activity, 21% monoclinic phase

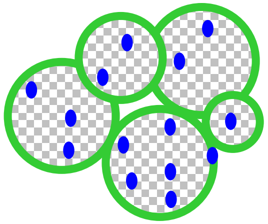
➡ Only fraction of tetragonal material active, particularly prone to phase transformation

B.S. Klose, F.C. Jentoft et al., in preparation

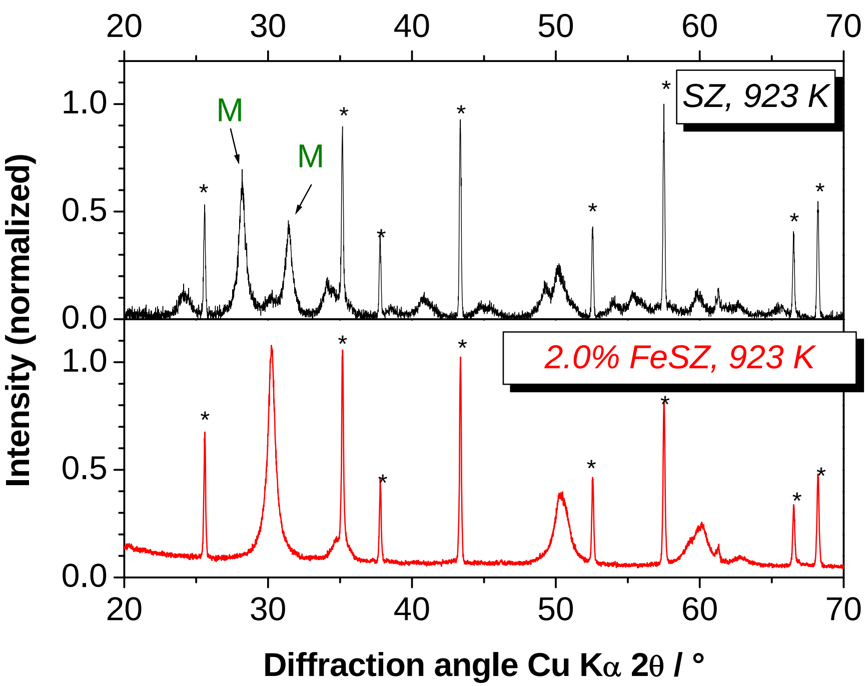
Ion Scattering Spectroscopy: Surface Composition



- No Mn on surface at typical promoter contents



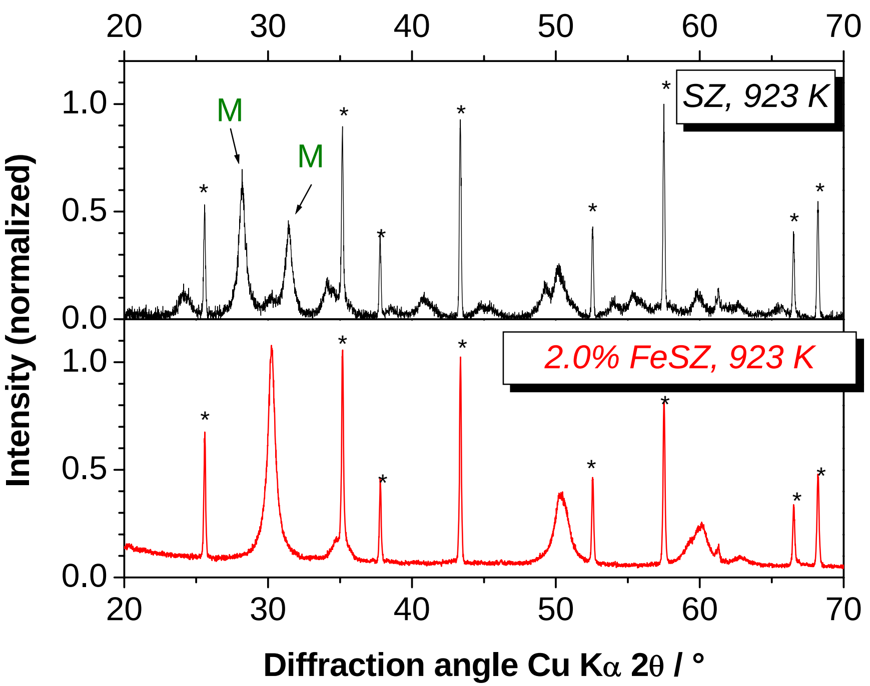
XRD: Phase Composition and Promoters

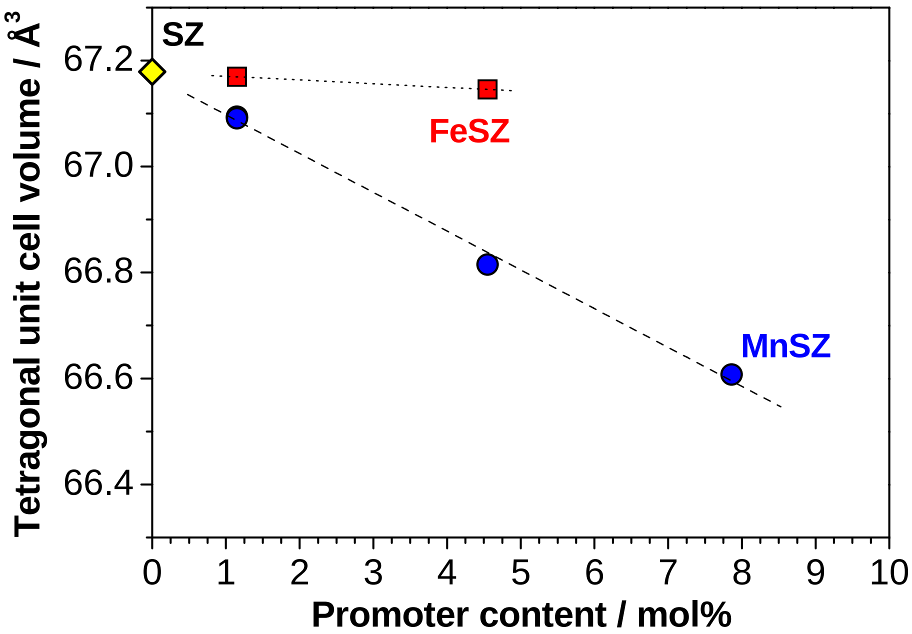


- Fe, Mn stabilize tetragonal / cubic phase

J. Stöcker, Ann. Chim. 1960

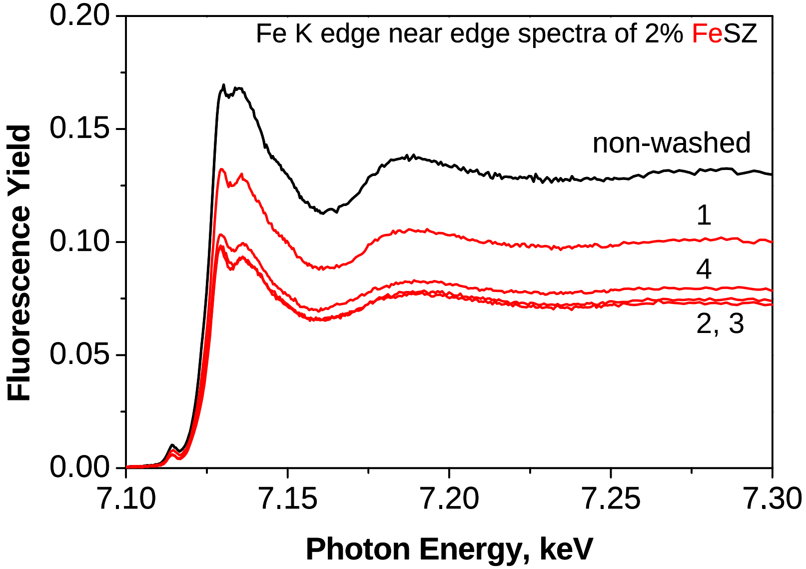
XRD: Phase Composition and Promoters

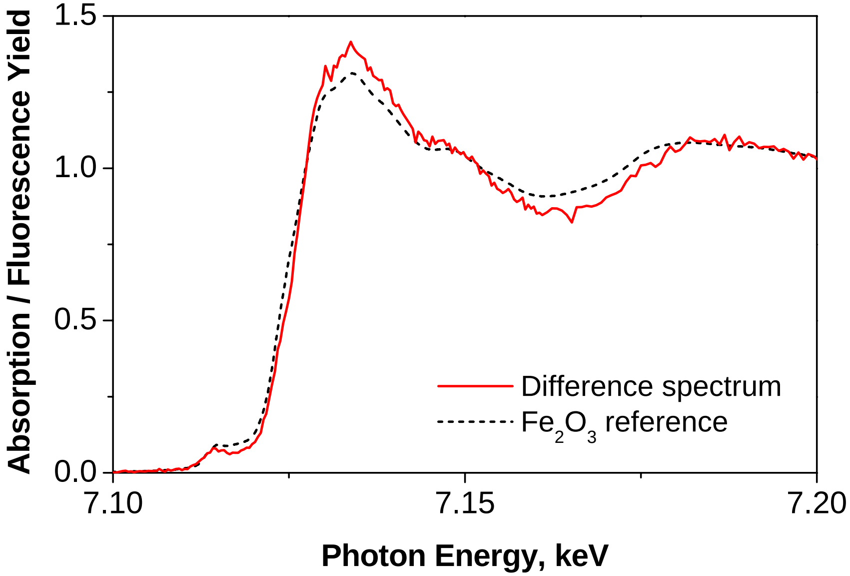




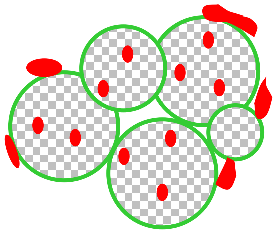
- Fe, Mn stabilize tetragonal / cubic phase
  J. Stöcker, Ann. Chim. 1960
- Unit cell of tetragonal ZrO_2 shrinks with increasing Mn content, isolated Mn^{2+} in EPR spectrum

Analysis of Fe-Species in FeSZ with XANES





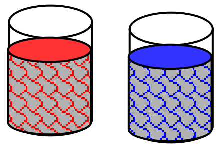
- Surface species can be washed off with oxalic acid, ca. 42%
- EPR and Mössbauer: only Fe^{3+}
  3-4 species, Fe_2O_3 and isolated Fe^{3+}



model FeSZ

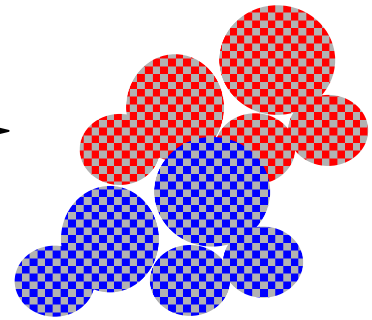
F.C. Jentoft et al., J. Catal. 2004

Preparation Method and Distribution of Promoters

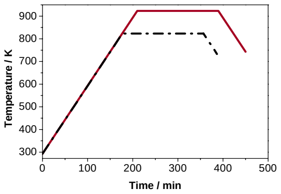


coprecipitation

NH_4OH



calcination 923 K

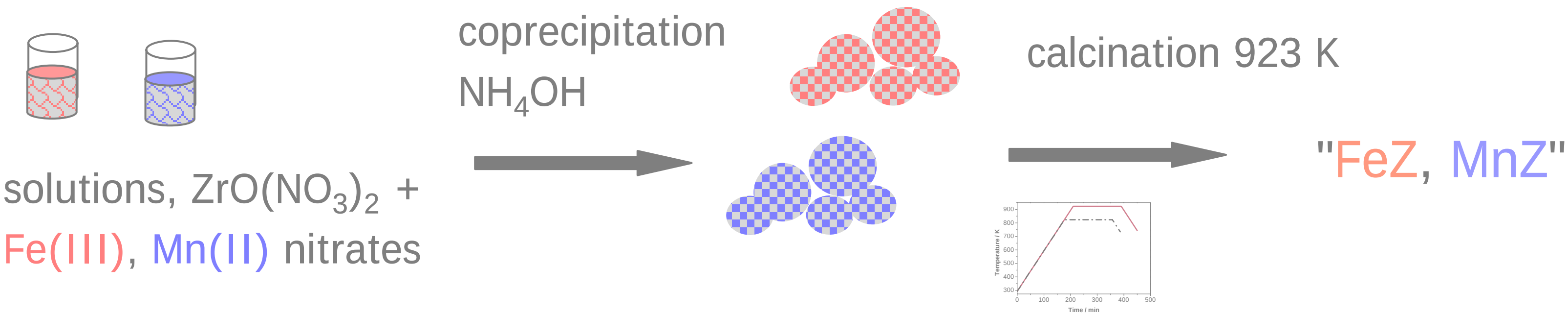


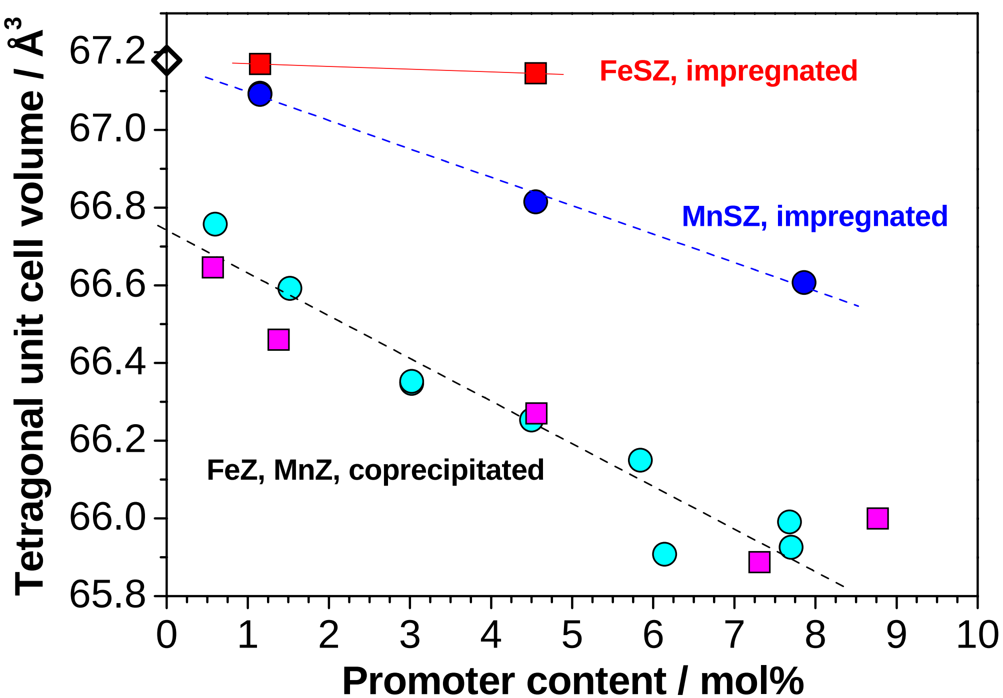
"FeZ, MnZ"

solutions, $ZrO(NO_3)_2$ +

Fe(III), Mn(II) nitrates

Preparation Method and Distribution of Promoters

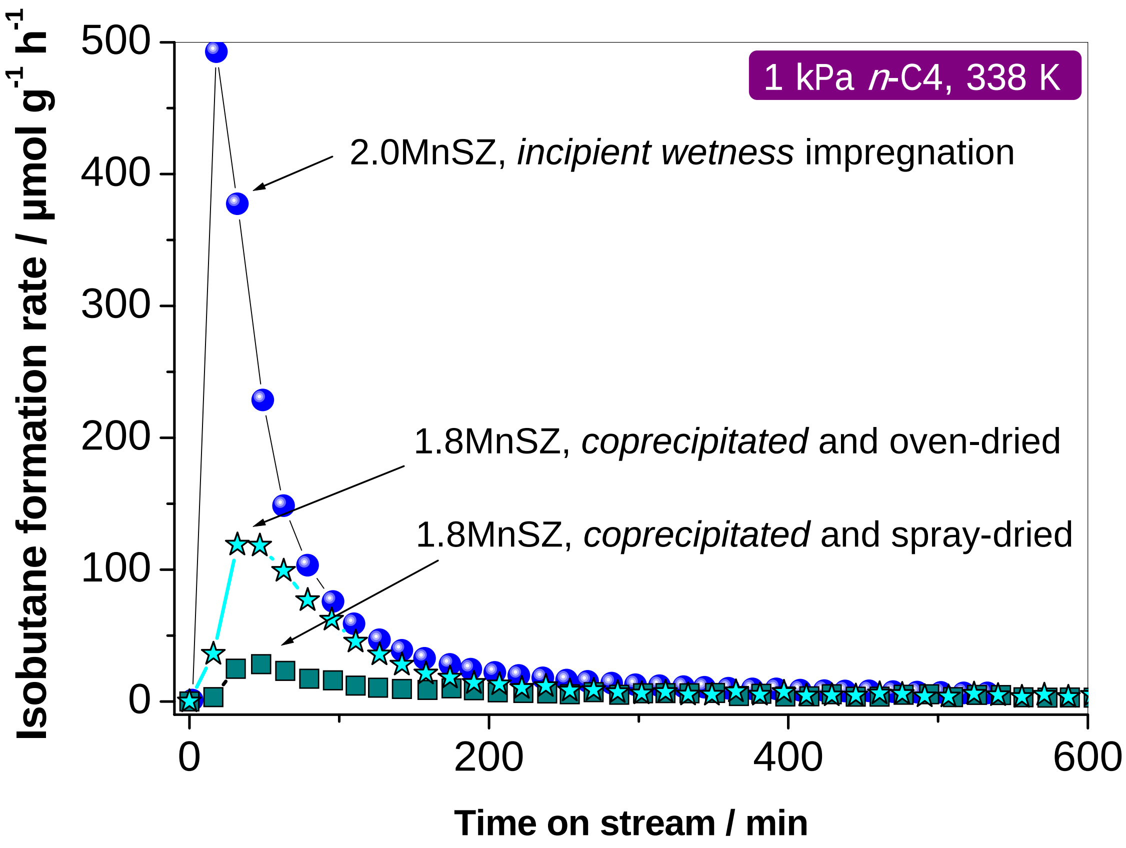




- Distribution of promoters on surface and into zirconia lattice strongly preparation dependent
- Promoter valences, zirconia crystallite size also influence unit cell

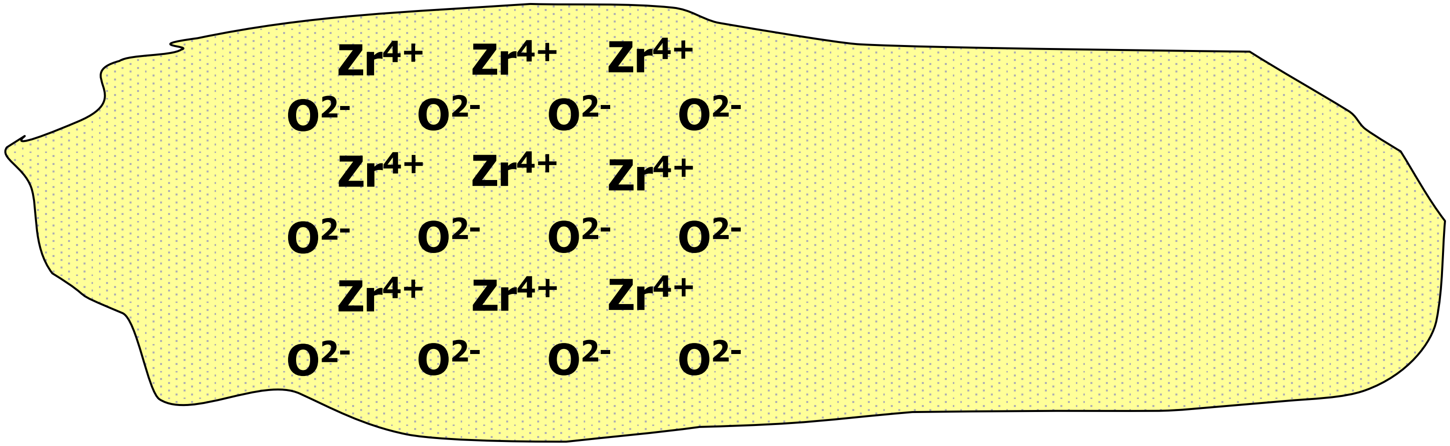
F.C. Jentoft et al., J. Catal. 2004

Sulfation of Coprecipitated Materials & Catalysis



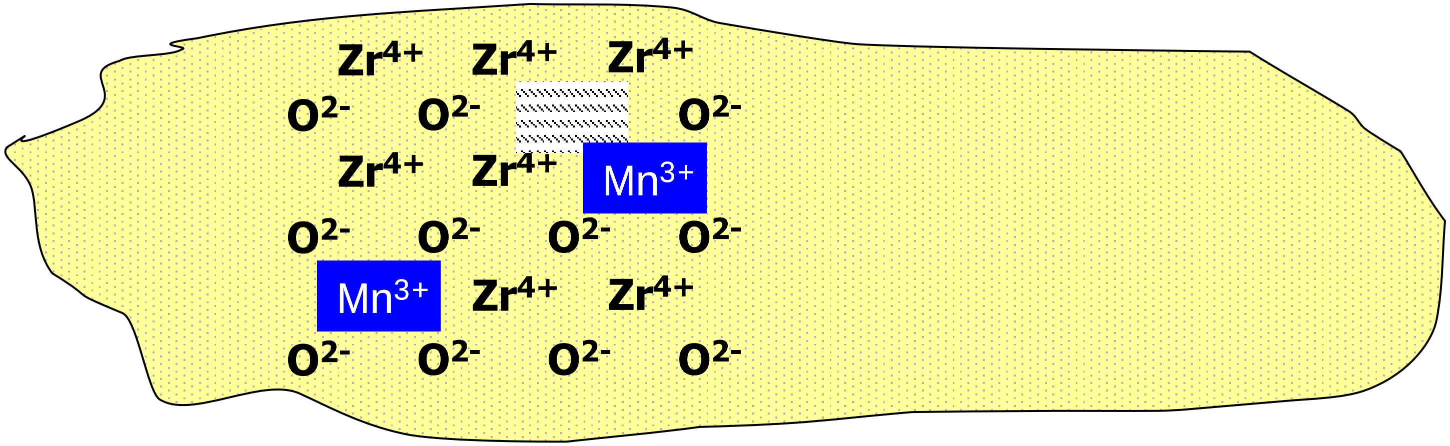
- Active material can be generated via coprecipitation

Zirconia Solid State Chemistry Summary



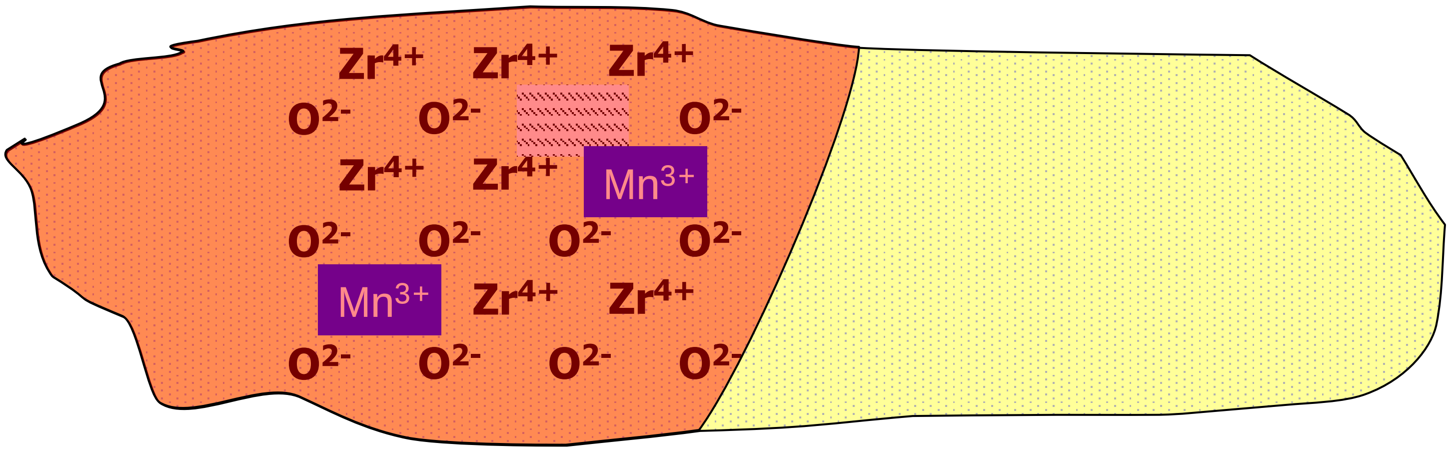
- Active tetragonal phase formed during glow - defects? O vacancies?

Zirconia Solid State Chemistry Summary



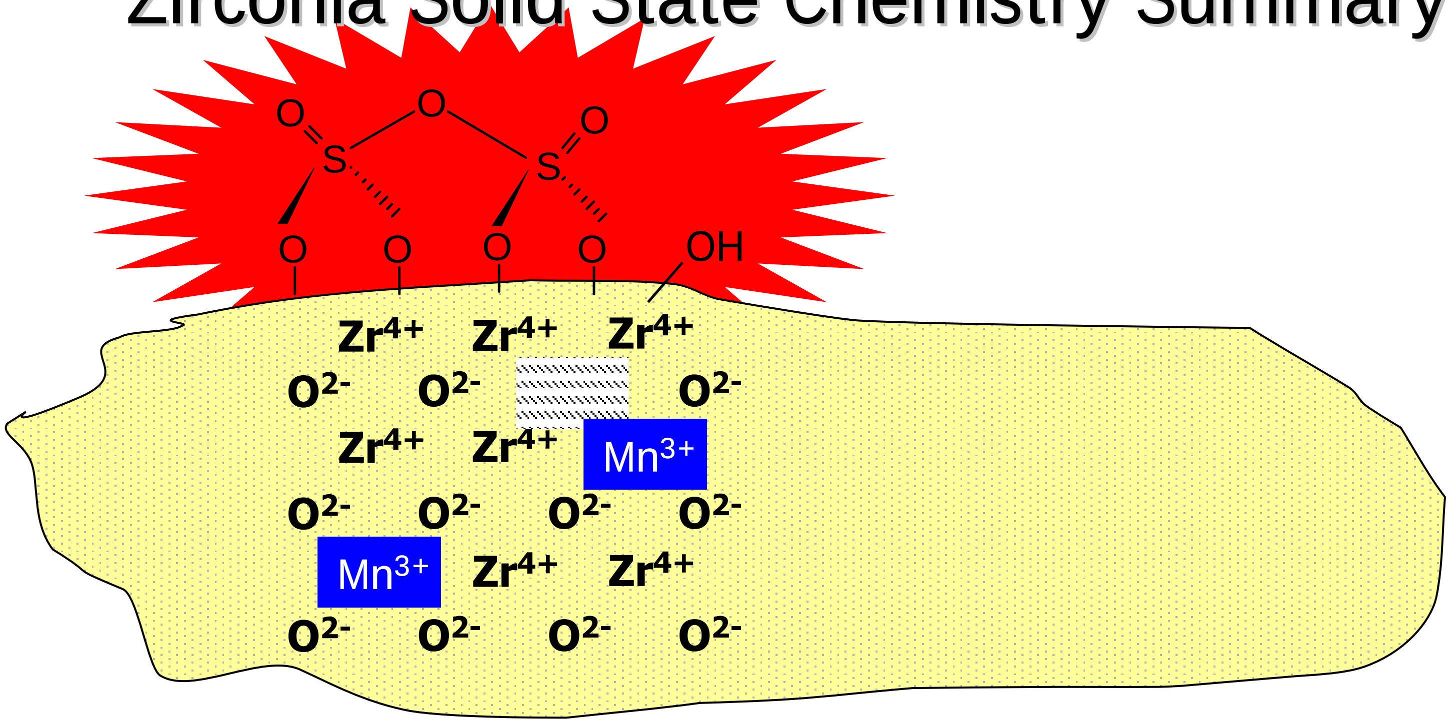
- Active tetragonal phase formed during glow - defects? O vacancies?
- Incorporation of promoters M^{x+} with x<4 into lattice: O vacancies
- Many M^{x+} promoters known: Cr, Mn, Fe, Co, Ni, Al, Ga

Zirconia Solid State Chemistry Summary



- Active tetragonal phase formed during glow - defects? O vacancies?
- Incorporation of promoters M^{x+} with $x<4$ into lattice: O vacancies
- Many M^{x+} promoters known: Cr, Mn, Fe, Co, Ni, Al, Ga
- Active phase metastable (monoclinization)

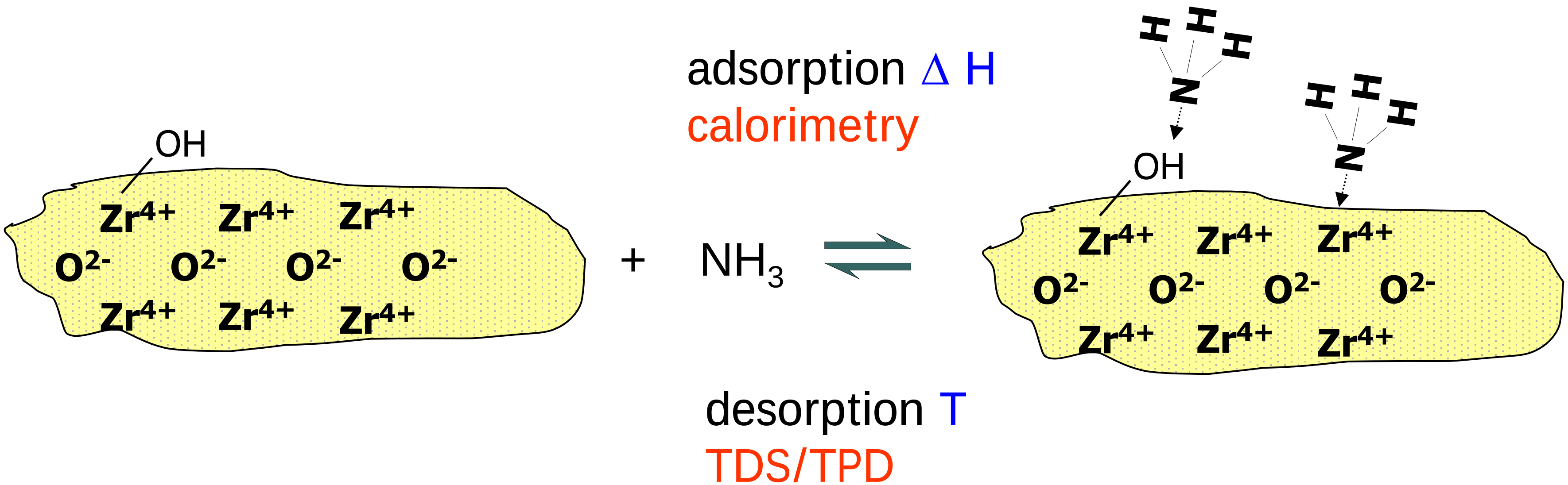
Zirconia Solid State Chemistry Summary



- Active tetragonal phase formed during glow - defects? O vacancies?
- Incorporation of promoters M^{x+} with x<4 into lattice: O vacancies
- Many M^{x+} promoters known: Cr, Mn, Fe, Co, Ni, Al, Ga
- Active phase metastable (monoclinization)

How is the surface chemistry affected?

Probing Sites by Chemisorption

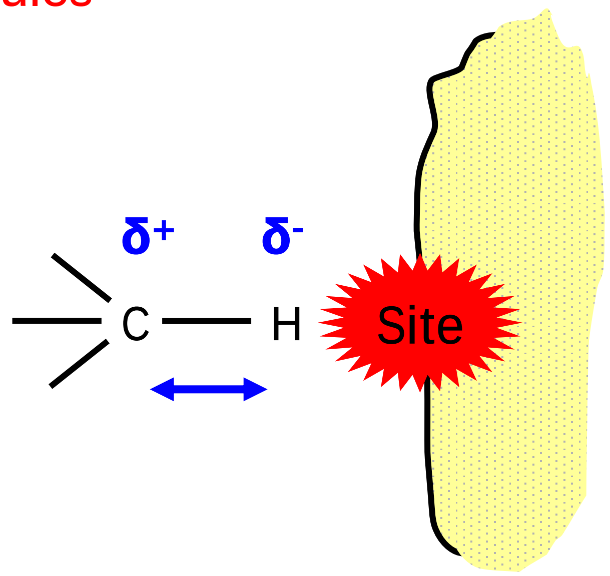


IR, XPS, NMR, UV/Vis…
shift of bands (probe/surface)

Novel Concept: Evaluation of IR Intensities

1. Hydrocarbons as probe molecules
2. Evaluation of IR Intensities

$$I \propto \left(\frac{\partial \mu}{\partial r} \right)^2$$

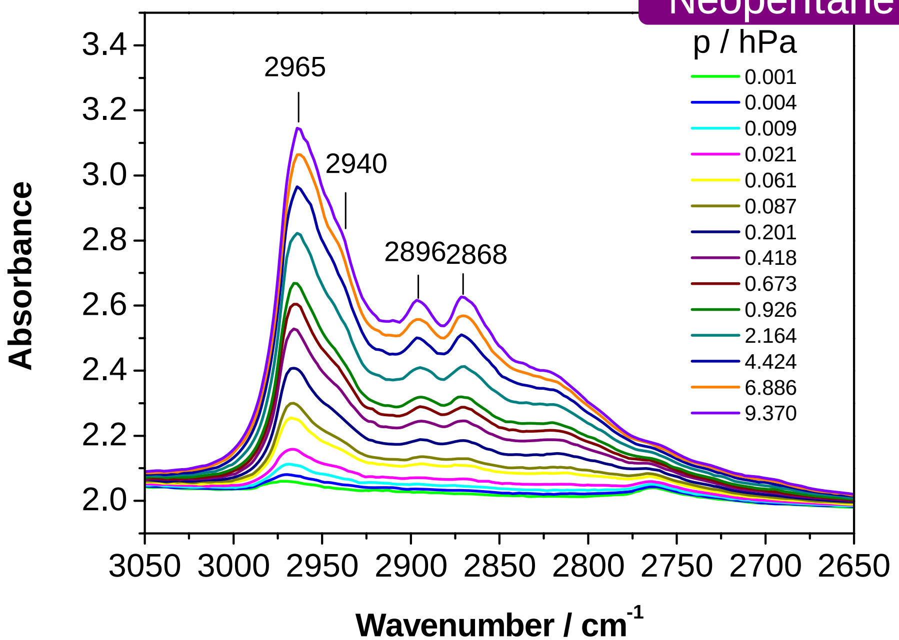


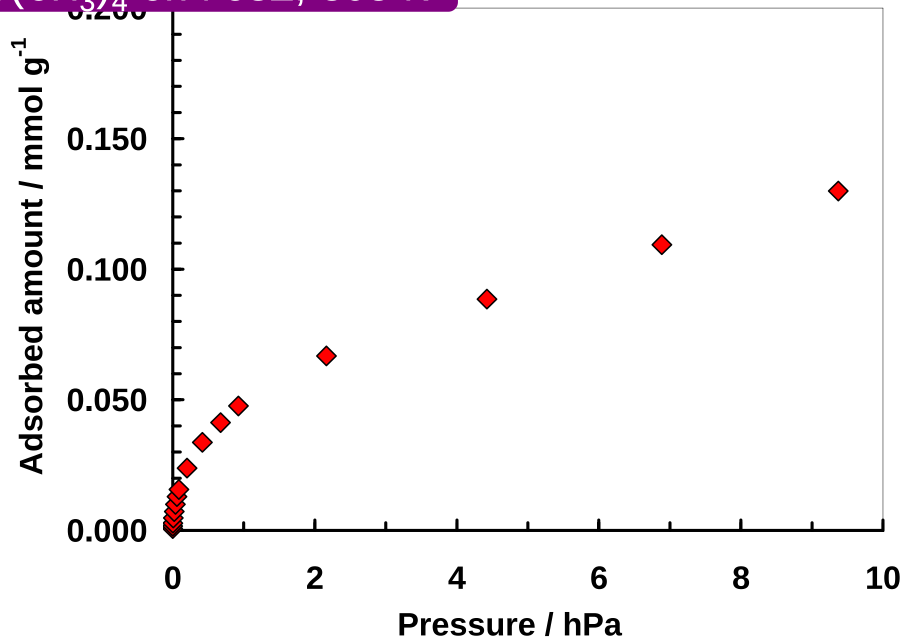
- Extinction coefficients as a measure of polarization of adsorbed molecule
- Intensified vibrations ↔ activated bonds (reaction begin)

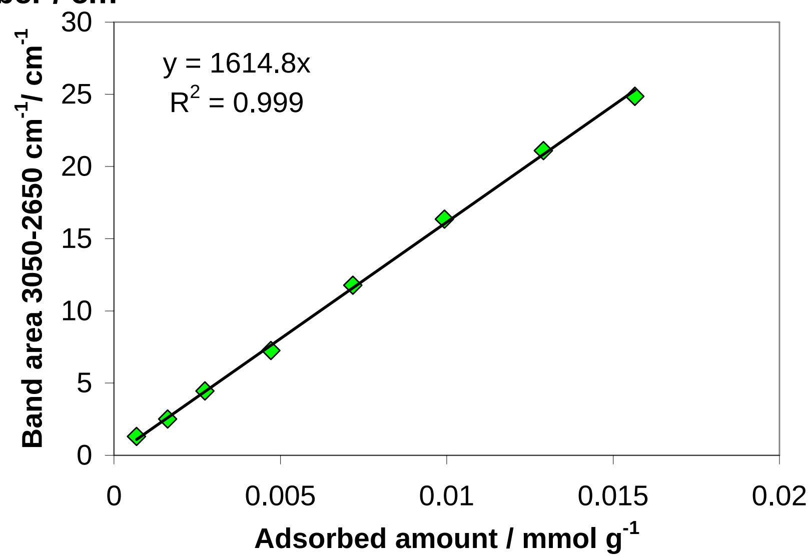
V.B. Kazansky, I.R. Subbotina, A.A. Pronin, R. Schlögl, F.C. Jentoft, J. Phys. Chem. B 110 (2006) 7975
V.B. Kazansky, I.R. Subbotina, F.C. Jentoft, J. Catal. 240 (2006) 77
V.B. Kazansky, I.R. Subbotina, F.C. Jentoft, R. Schlögl, J. Phys. Chem. B 110 (2006) 17468

Spectroscopic and Adsorption Data

Neopentane $C(CH_3)_4$ on FeSZ, 308 K







- Measurement on SZ catalysts obscured by scattering effects

Activation of Hydrocarbons by Zeolites

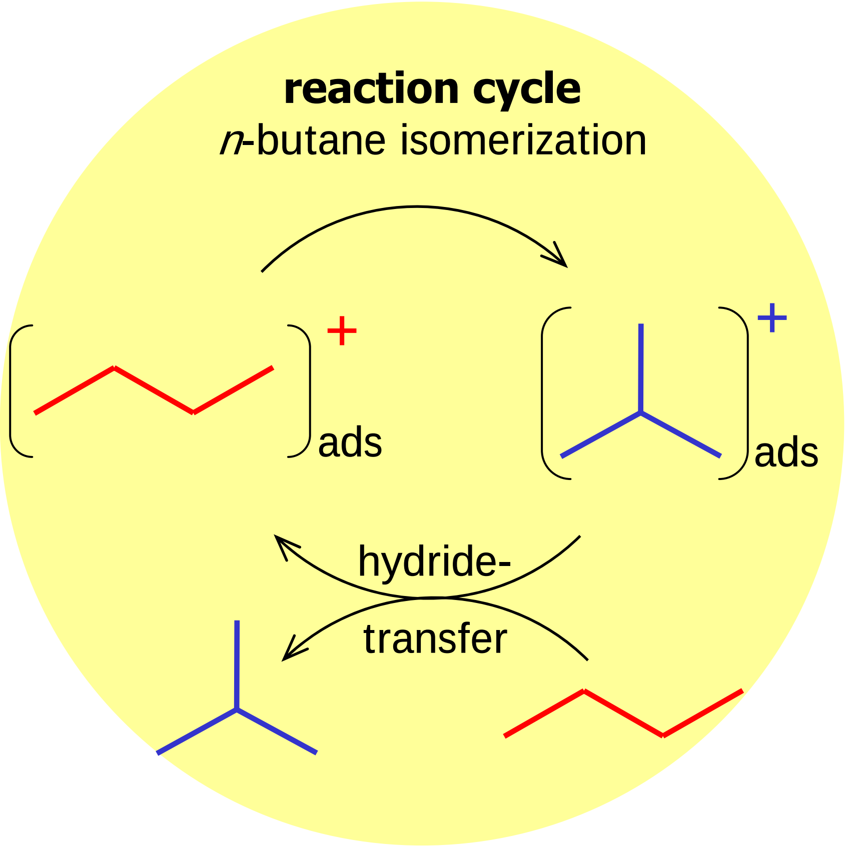
Ethane, CH stretching vibrations

	IMEC in km/mol
gas phase	169
NaY	100
CaY	260

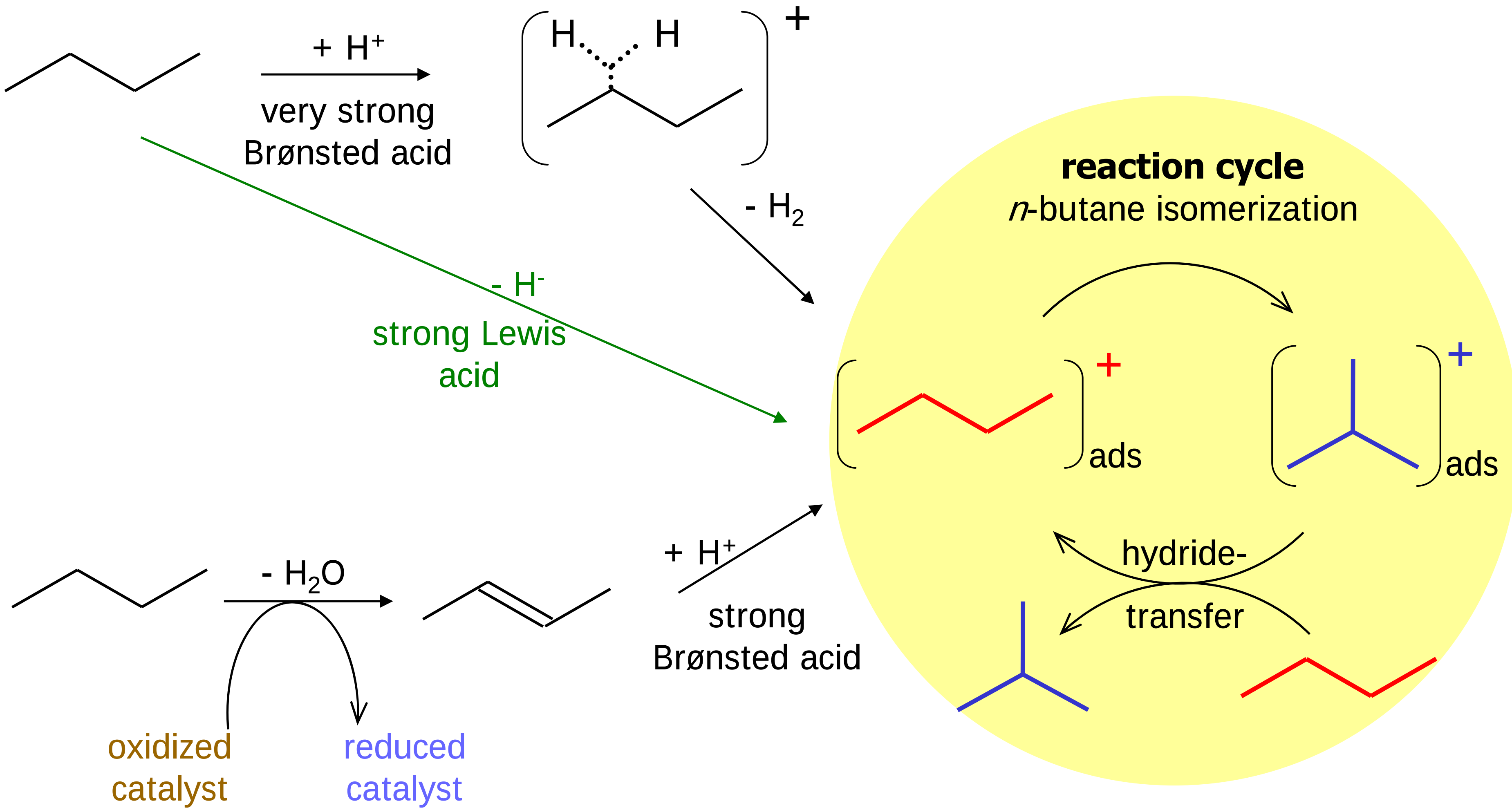
- Activation of hydrocarbon by cations in zeolite (faujasite)

➡ IR intensities can be used as new criterion to evaluate activation of hydrocarbons on surfaces

Possibilities for Reaction Initiation

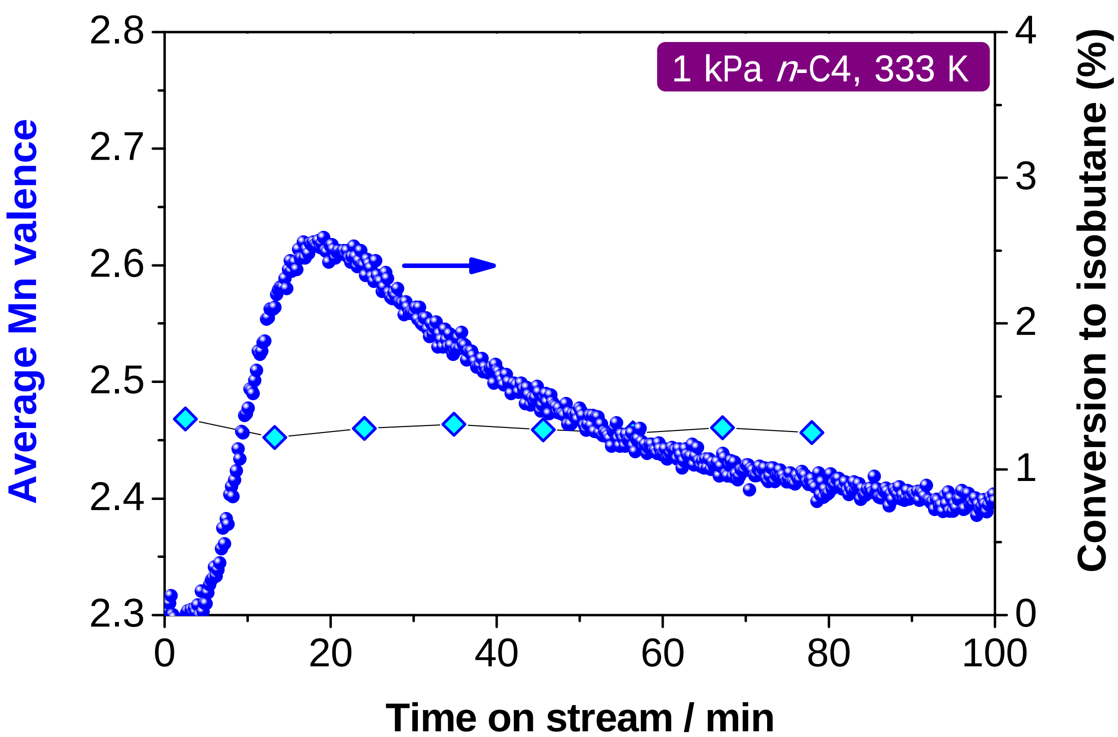


Possibilities for Reaction Initiation



oxidative dehydrogenation (stoichiometric?)
possible oxidizing agents: S, Zr, promoters

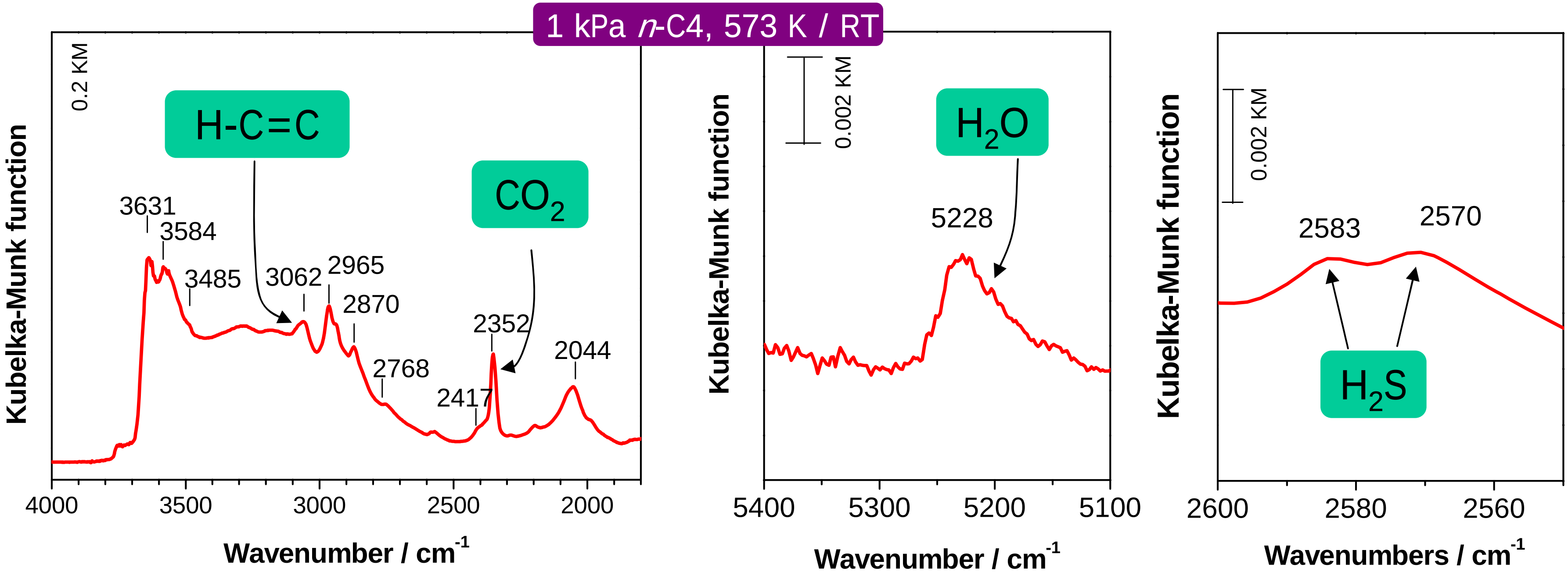
n-Butane Isomerization over MnSZ: In Situ XAS



- No change of Mn valence during reaction (after activation in He)
- No correlation of Mn valence to catalytic performance
- No stoichiometric redox reaction involving Mn

R.E. Jentoft, F.C. Jentoft et al., PCCP 2005

Diffuse Reflectance IR Spectroscopy
Reaction of SZ with *n*-Butane

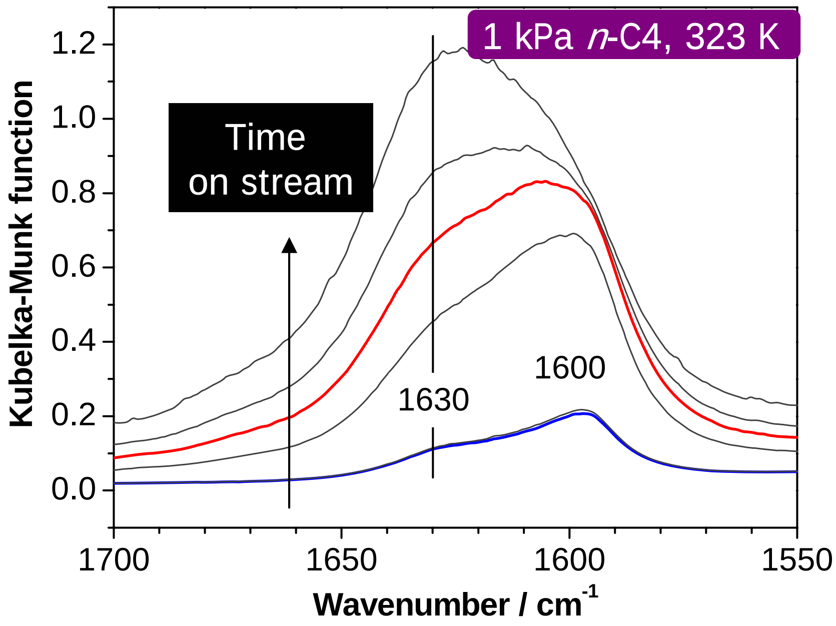


- Batch mode experiment: heating of SZ in *n*-butane, spectra recorded at RT
- Formation of H_2O, CO_2, H_2S, and unsaturated hydrocarbons

➡ Redox chemistry involving sulfate!

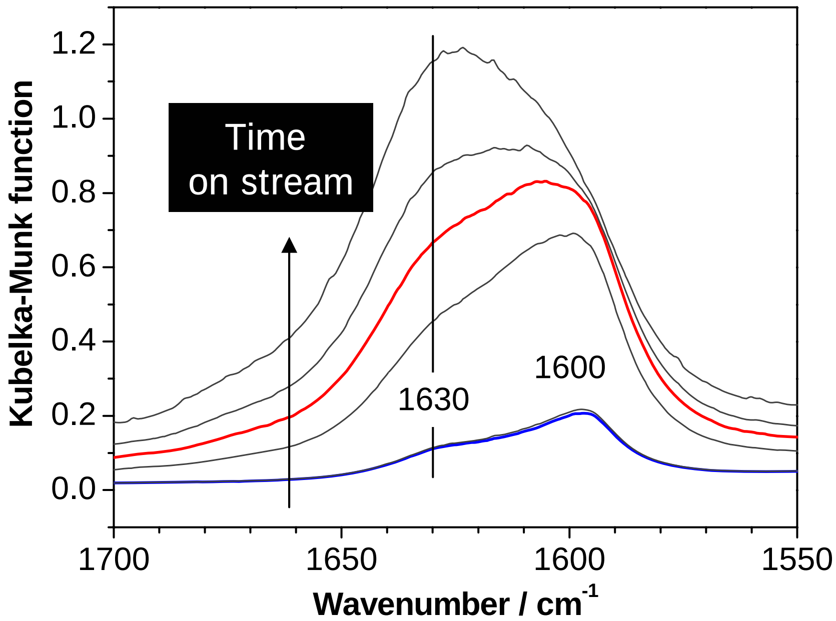
B.S. Klose, F.C. Jentoft, I.R. Subbotina, V.B. Kazansky, R. Schlögl, Langmuir 2005

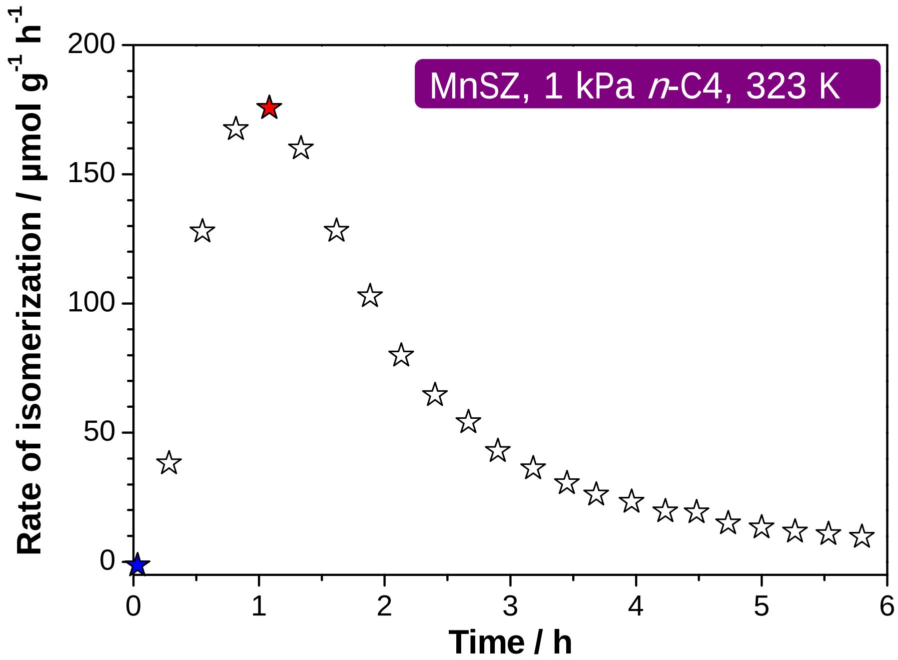
In Situ DRIFTS: Flow Experiments

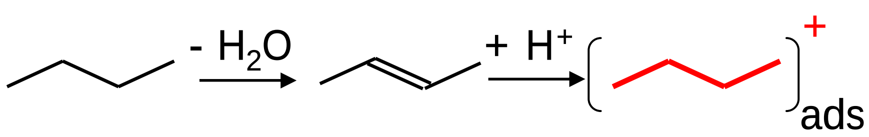


- Bands at 1600, 1630 cm^{-1} increase
- Range of C=C stretching vibrations, but corresponding CH vibrations not observed
- Water bending vibration

Spectral and Catalytic Information



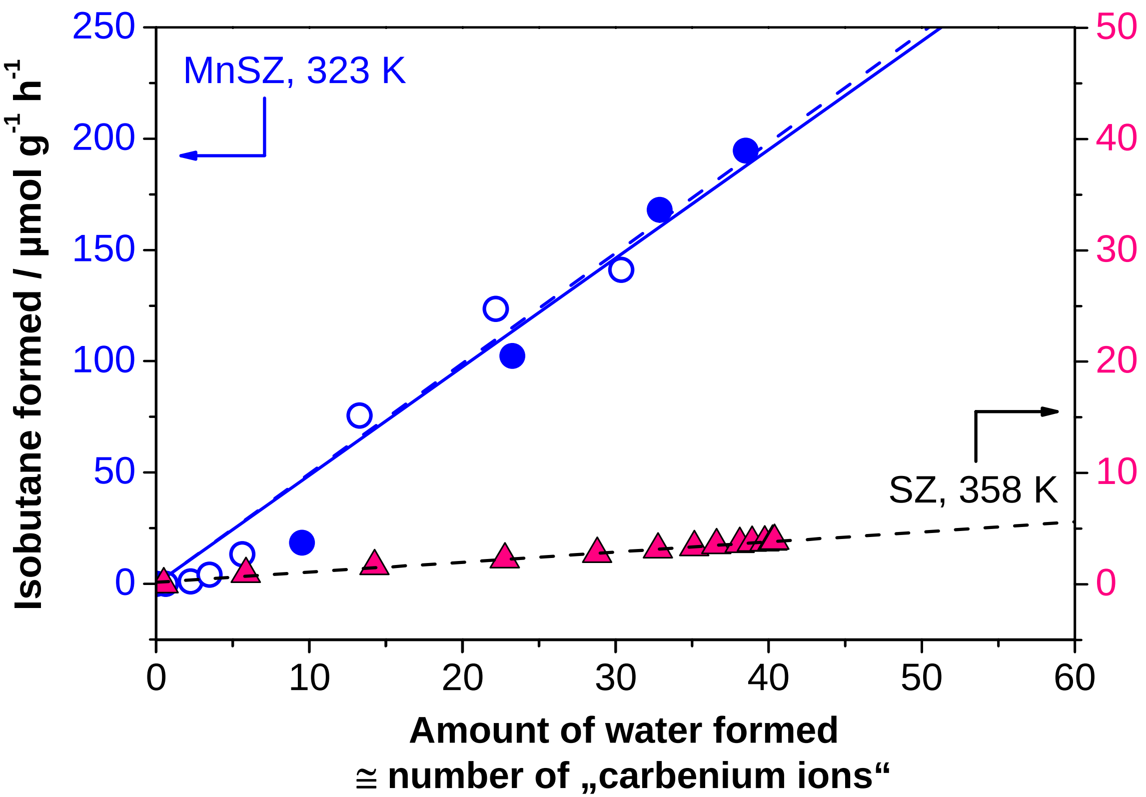




- Bands at 1600, 1630 cm^{-1} increase
- Range of C=C stretching vibrations, but corresponding CH vibrations not observed
- Water bending vibration

- Rate proportional to number of intermediates?
- Estimate number of intermediates from band area

Correlation of Spectral and Catalytic Information

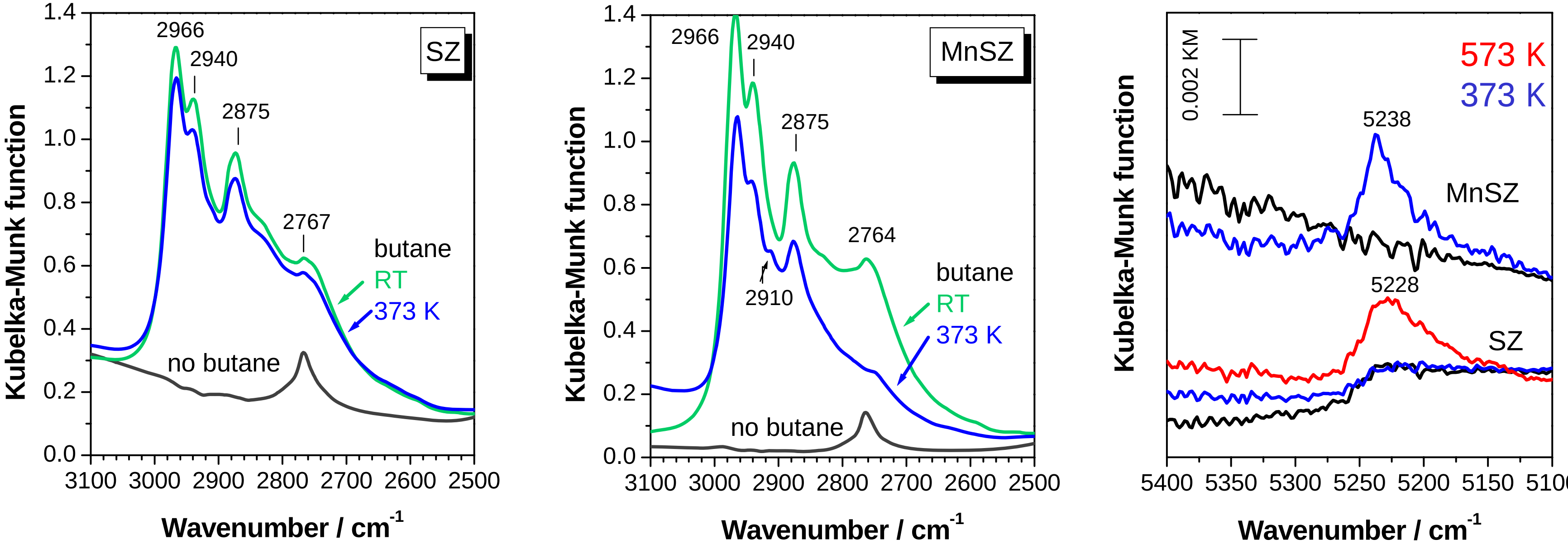


- Rate of isomerization proportional to amount of water formed (induction period)

➡ ODH <u>one</u> activation pathway

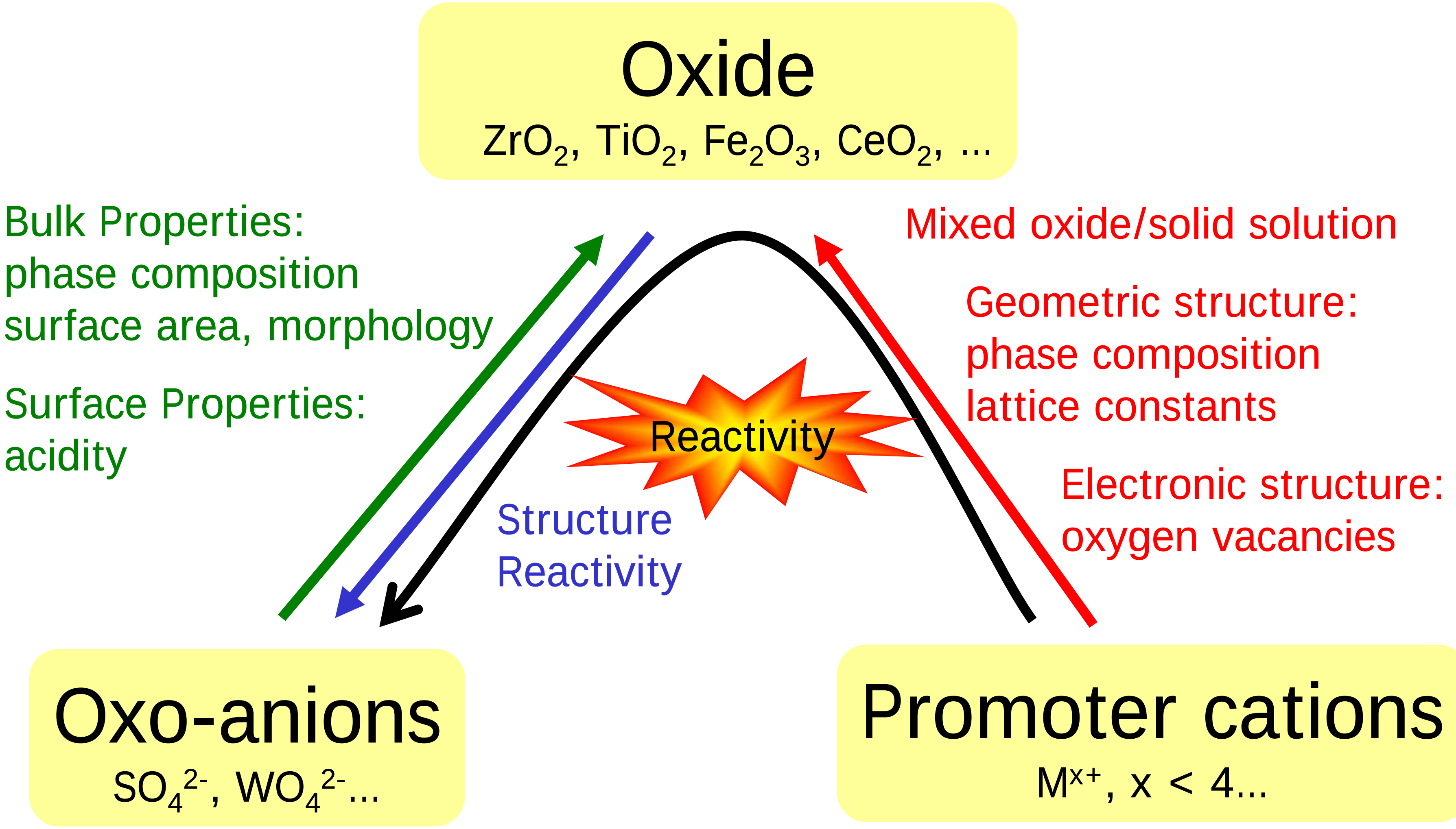
B.S. Klose, F.C. Jentoft et al., J. Catal. 2005

Diffuse Reflectance IR: Effect of Promoters



➡ Promoters (Mn) increase reducibility = oxidizing power of sulfate

Summary: Catalyst Development



Current Work & Outlook

Novel catalysts

- Preparative efforts to vary defect chemistry of zirconia
- Promotion by Ga (et al.)
- In situ electron paramagnetic resonance (TU Munich)

Deactivation phenomena

- Stabilization of catalytic activity through Pt & H_2
- Identification of carbonaceous deposits
- In situ UV-vis spectroscopy