Modern Methods in Heterogeneous Catalysis Research

Probing the Catalyst Surface by FTIR Spectroscopy of Adsorbed Molecules

Part I

28 November 2014

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LECTURE SERIES
HETEROGENEOUS CATALYSIS

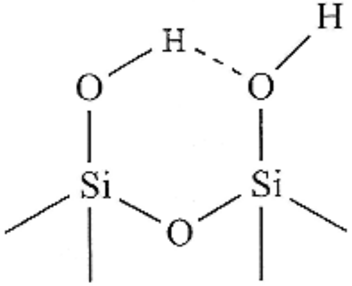
Solid structures and termination

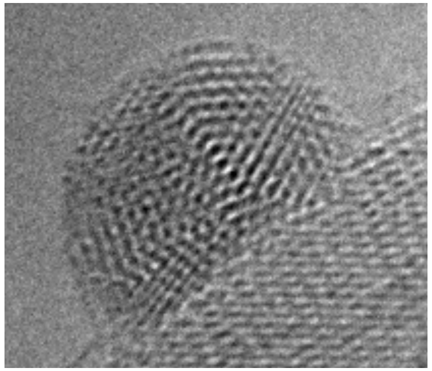
- Most of the materials of interest in heterogeneous catalysis are polycrystalline / amorphous solids or polydispersed surface species
- Termination may result in the exposure of several crystal planes (or several surface species) simultaneously
- The surface usually differs from the ideal bulk structure due to surface defects, reconstruction, adsorption from the environment
- Surface arrangements cannot be deduced staightforward from the bulk structure, which complicates the identification of active sites

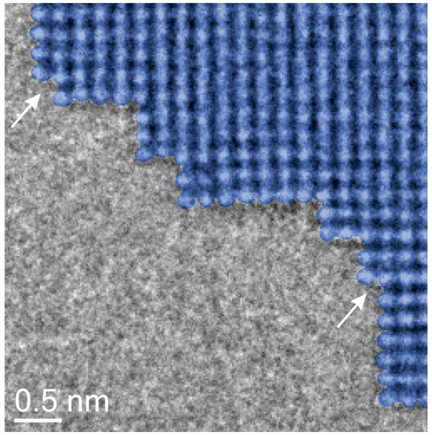
What is an active site?

- Microscopic group of atoms, which determines the specific catalytic activity of the surface
- At the active sites, electron transfer between the catalyst surface and the reacting molecule happens that leads to structural rearrangement of the substrate molecule
- The active sites are formed during catalyst activation and undergoe structural and electronic changes during the catalytic cycle
- Adsorption of probe molecules on the fresh catalyst gives information about the nature of ***surface sites*** on the catalyst precursor, generally ***not about the active site***

Surface sites / functionalities







- Hydroxyl-hydrate cover

Brønsted acid-base sites

- Surface sites of supported metal particles

Metal sites

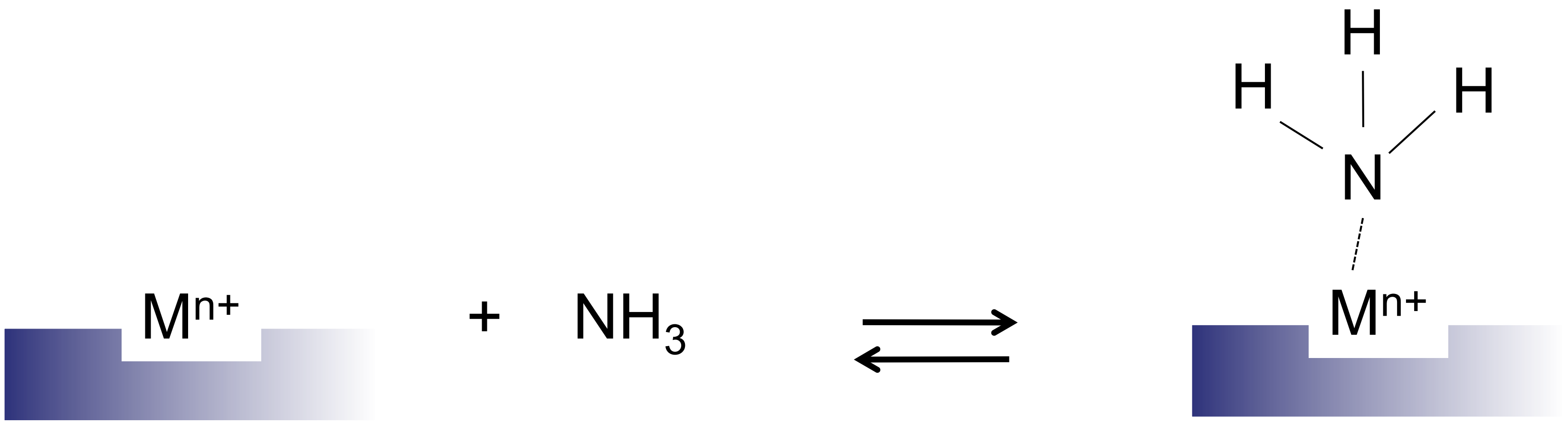
- Electron donating (oxygen) atoms

Lewis base sites

- Coordinatively unsaturated metal cations

Lewis acid sites

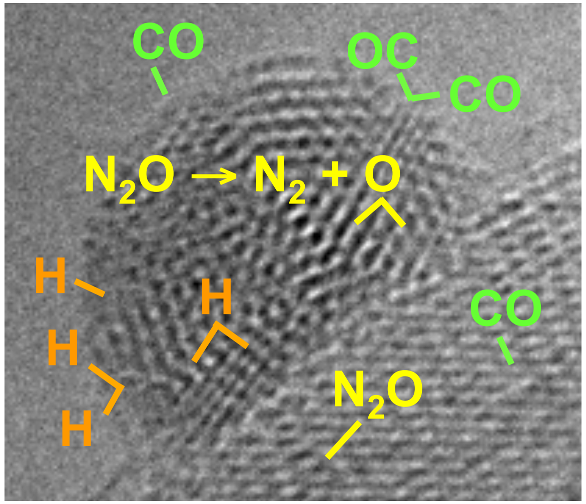
Probing surface sites by adsorption



experiment	physical quantity	method
adsorption	n_{ads}, ΔH_{ads}	microcalorimetry, volumetric, gravimetric methods
desorption	T_{des}	TPD, TDS
band shift	Δ..., T_{des}	IR, NMR, UV-vis, PL, XPS, ...

Retrievable information

- Type of sites
    - Coordination number
    - Electronic structure
- Number of sites
- Relative abundance
- Site distribution



Criteria for selection of probe molecules

- Specific interaction of the probe molecule with certain sites
  (preferable adsorption of the reacting molecule at $T < T_r$)
- Sufficient sensitivity with respect to the differences in the electronic structure of various surface sites
- Only small pertubation of the whole system
- No „corrosive“ adsorption (reconstruction of the surface due to adsorption)
- No side reactions

See also H. Knözinger, IRS for Characterization of Surface Acidity and Basicity, Handbook of Heterogeneous Catalysis

Selection of probe molecules – HSAB concept

	hard	**soft**
acids	H^+, Li^+, Na^+, K^+ Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Mn^{2+} Sc^{3+}, Ga^{3+}, In^{3+}, La^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+}, As^{3+}, Ge^{3+}, Si^{4+}, Zr^{4+}, Th^{4+}, Ru^{4+}, UO_2^{2+}, $(CH_3)_2Sn^{2+}$, VO^{2+}, MoO^{3+} RCO^+, CO_2, NC^+	Cu^+, Ag^+, Au^+, Tl^+, Hg^+ Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}, CH_3Hg^+, $Co(CN)_5^{2-}$, Pt^{4+}, Te^{4+} M^0 (metal atoms)
	Boundary: Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Sn^{2+}, Sb^{3+}, Bi^{3+}, Rh^{3+}, Ir^{3+}, SO_2, NO^+, Ru^{2+}, Os^{2+}, R_3C^+, $C_6H_5^+$	
bases	Ammonia, pyridine	CO, olefins, aromatics

A. Davydov, Molecular Spectroscopy of Oxide Catalyst Surfaces, p. 77

Typical probes

metals	**acid sites**	**basic sites**
H_2 **CO** N_2 NO N_2O	piperidine n-butylamine **ammonia** **pyridine** acetone pyvalonitrile acetonitrile 2,6-dimethylpyridine (lutidine) benzene CO NO H_2, D_2 N_2	**CO_2** SO_2 CO pyrrole chloroform acetonitrile alcohols thiols boric acid trimethyl ether ammonia pyridine

How to measure FTIR spectra of solid catalysts?

Sample preparation	geometry	remarks
KBr technique	transmission	Quantitative measurements difficult Chemical interaction with KBr may happen Differences in refractive index Particle size effect of embedded material, differences in refractive index (Christiansen effect) No pretreatment, no adsorption
Suspension in paraffin oil (Nujol®)	transmission	
Self supported wafer	transmission	Pretreatment and adsorption possible
powder	DR	Used in *in-situ* FTIR spectroscopy
Powder or suspension	ATR	Used to study solid-liquid interface

How to measure FTIR spectra of solid catalysts?

Transmission and DR can be used to study catalysts *in situ*

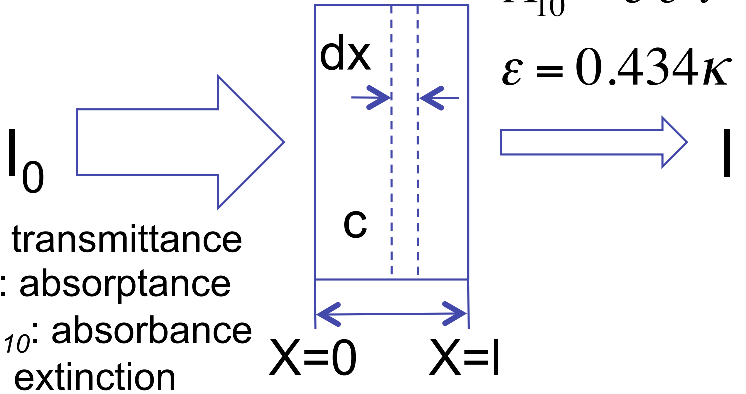
Infrared region	**Wavelength (nm)**	**Wavenumber (cm^{-1})**	**Energy (meV)**	**Vibrations**
far	1×10^6 - 5×10^4	10-200	1.2-25	lattice
mid	5×10^4 - 2500	200-4000	25-496	molecular
near	2500 - 1000	4000-10000	496-1240	overtones

Lambert-Beer Law

$$\tau = \frac{I}{I_0} = e^{-\kappa c l} = 1 - \alpha$$

$$A_{10} = \varepsilon\, c\, l \quad = -\log(\tau)$$

$$\varepsilon = 0.434\kappa$$

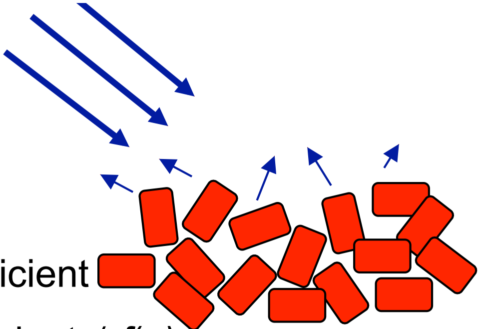


τ: transmittance
α: absorptance
A_{10}: absorbance
ε: extinction coefficient

Transmission

Kubelka-Munk function $R_\infty(v) \rightarrow K(v)$

$$F(R_\infty) = \frac{(1-R_\infty)^2}{2R_\infty} = \frac{K}{S}$$



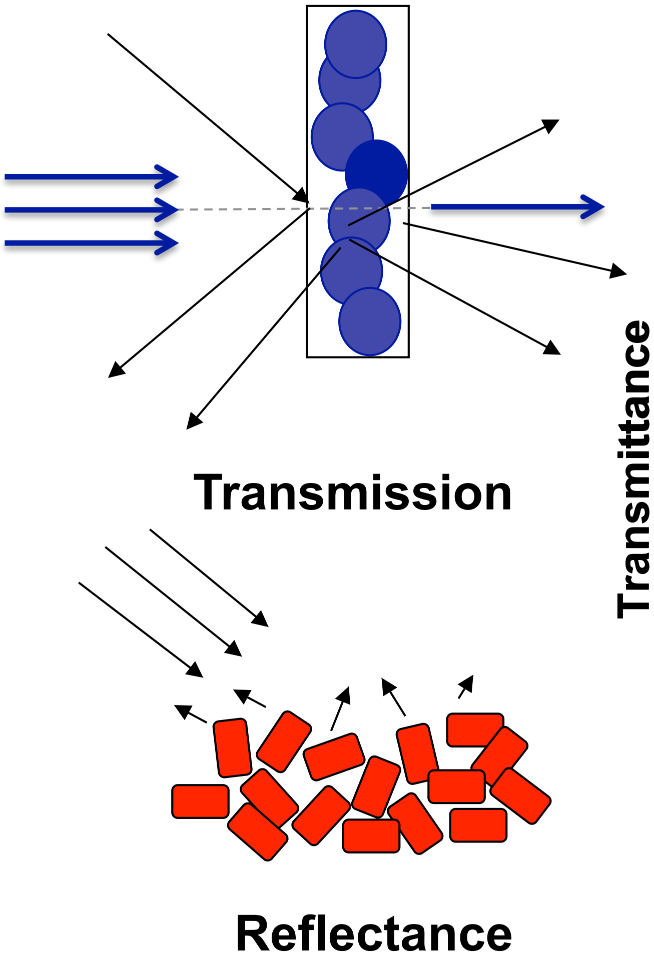
K: absorption coefficient

S: scattering coefficient ≠ $f(v)$

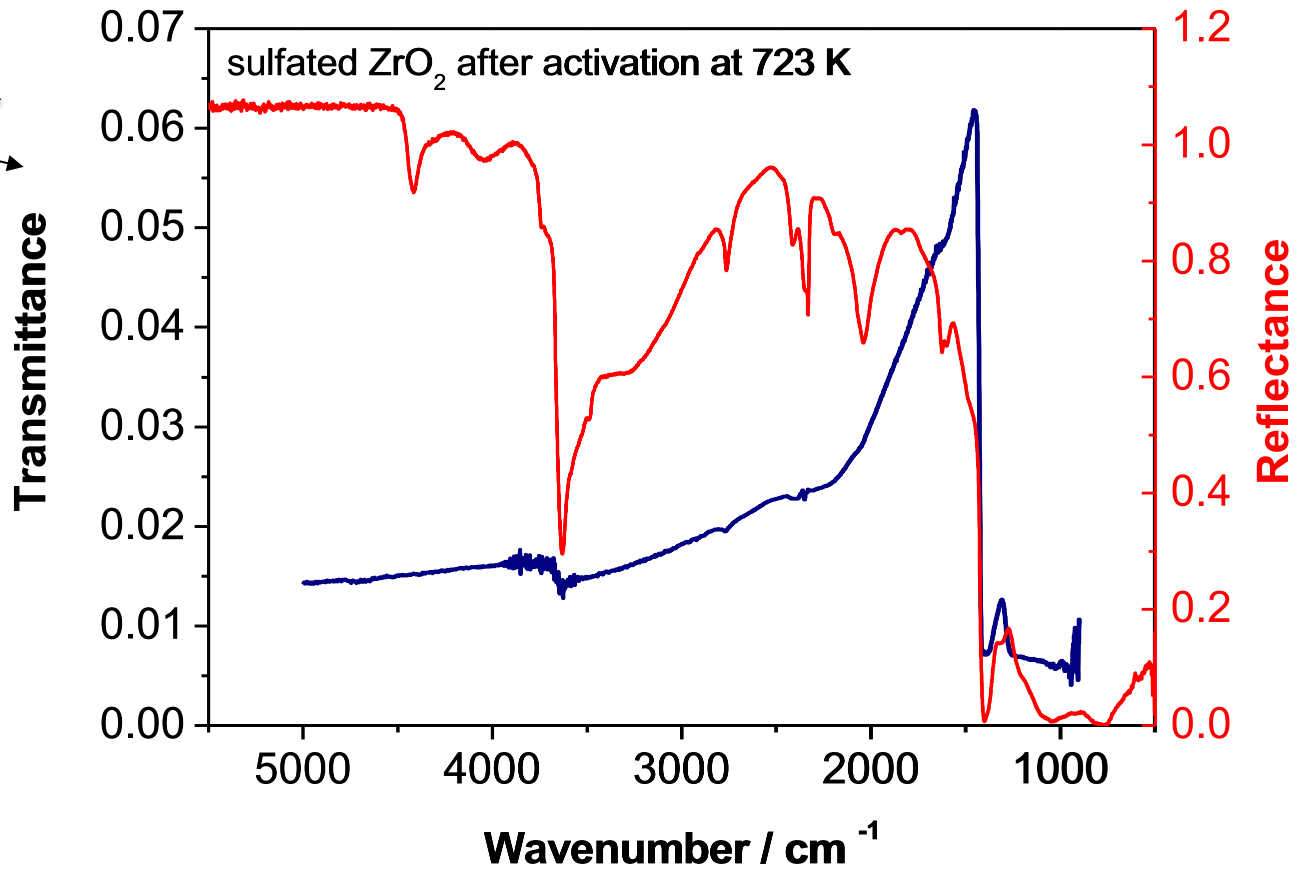
R: measured reflectivity

Reflectance

Infrared spectroscopy of powders



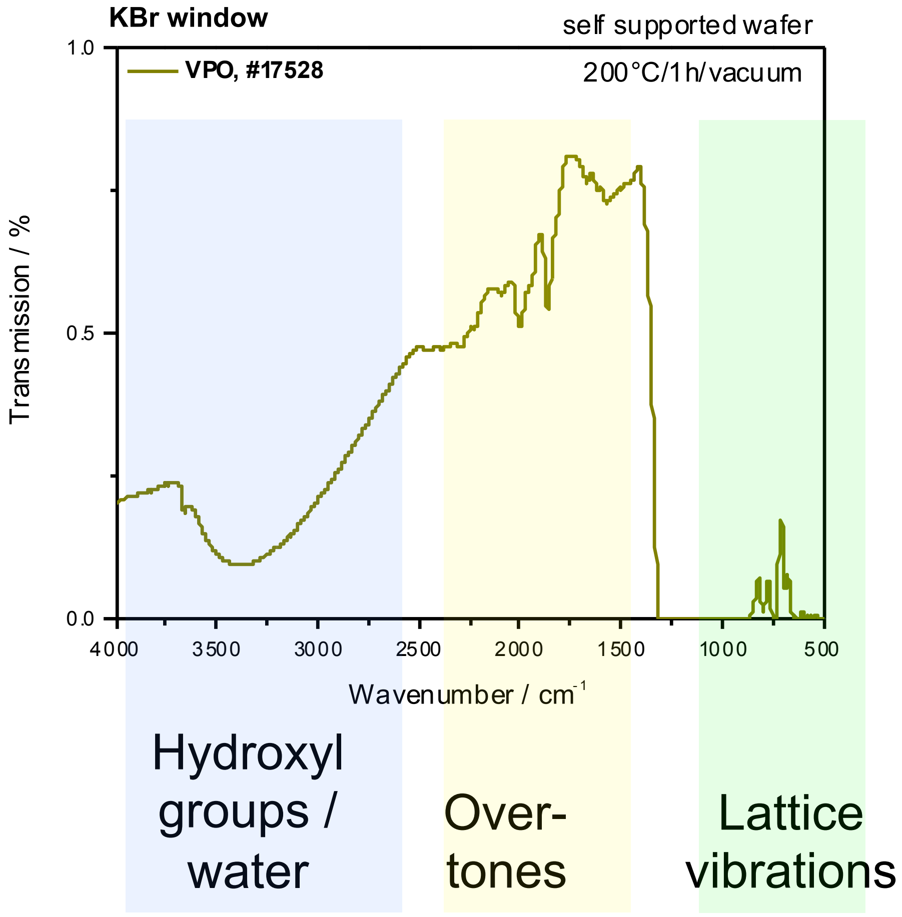
Transmission: self-supporting wafer
Reflectance: powder bed

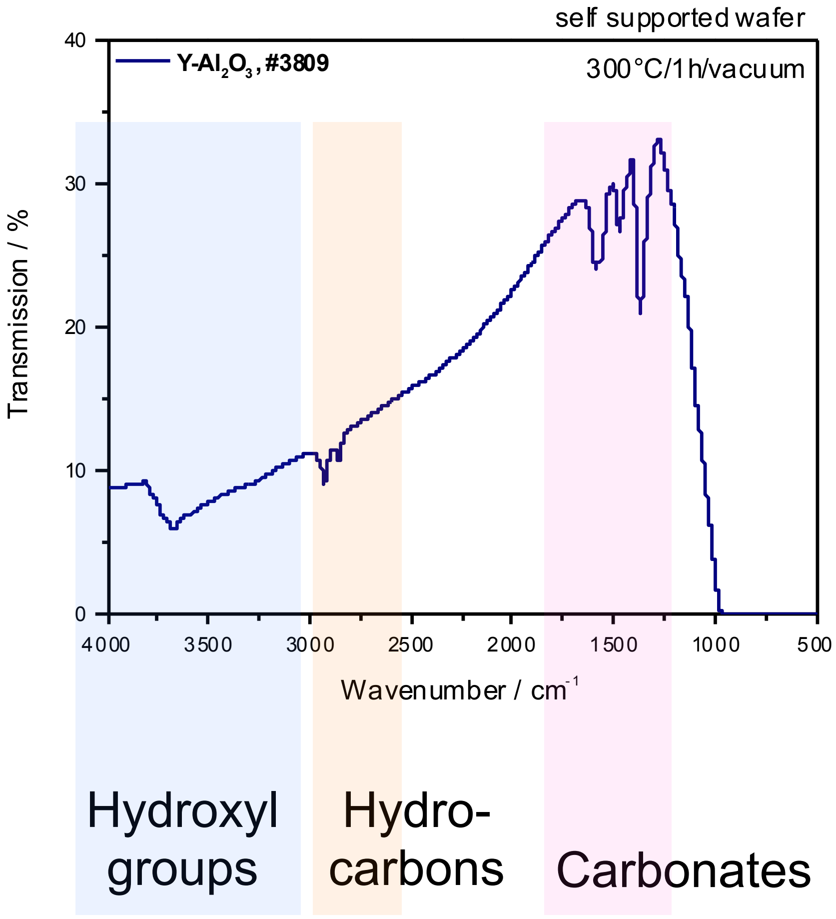


- Scattering is considerable for colloids and solids when the wavelength is in the order of magnitude of the particle size – DRIFTS beneficial
- Transmission provides advantage in terms of quantification

The transmission spectrum of the catalyst

- Prior to adsorption the catalyst is measured as background
- The probe molecule may interact with surface functional groups and cause artefacts





Jutta Kröhnert

Infrared spectra of oxides

- Surface M-O stretching vibrations appear at higher wavenumbers compared to fundamental modes (materials with > 1 m^2/g can be studied)
- Surface M-O bonds are of greater strength due to different coordination of surface metal atoms
- Sometimes, the adsorption frequencies of M-O bonds at the surface are correlated with the order of the M-O bond
- Combination vibrations of fundamental absorption frequencies of the lattice may appear in this region as well!

Infrared spectra of oxides

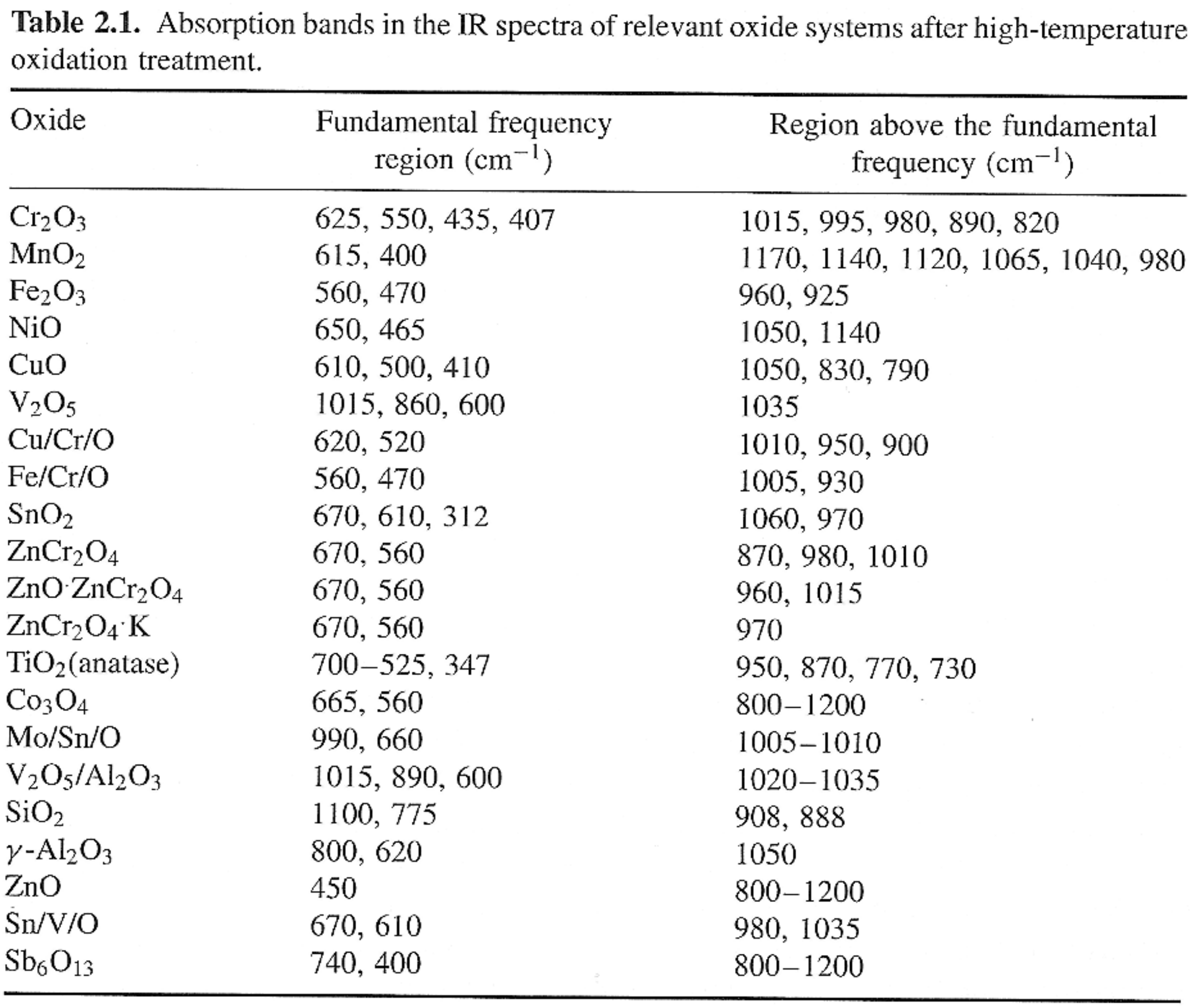
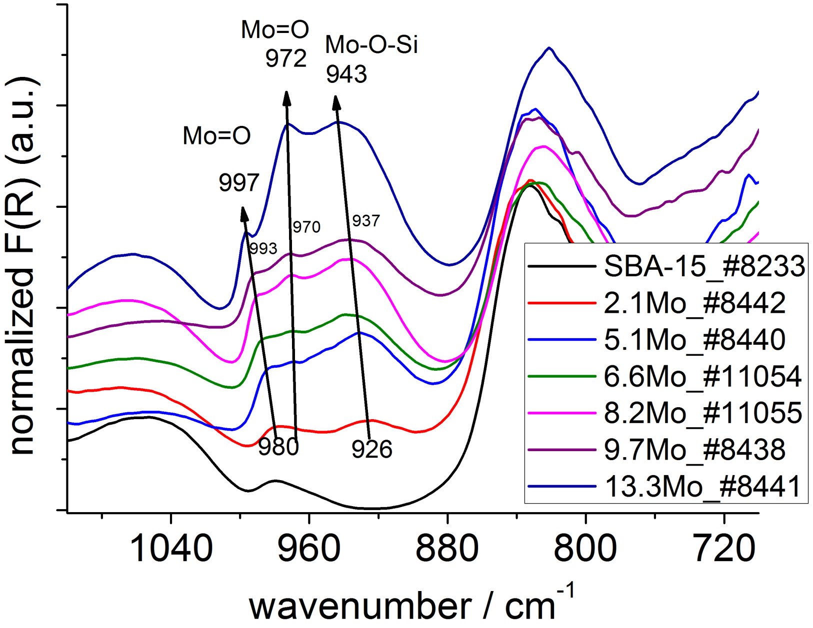


Table 2.1. Absorption bands in the IR spectra of relevant oxide systems after high-temperature oxidation treatment.

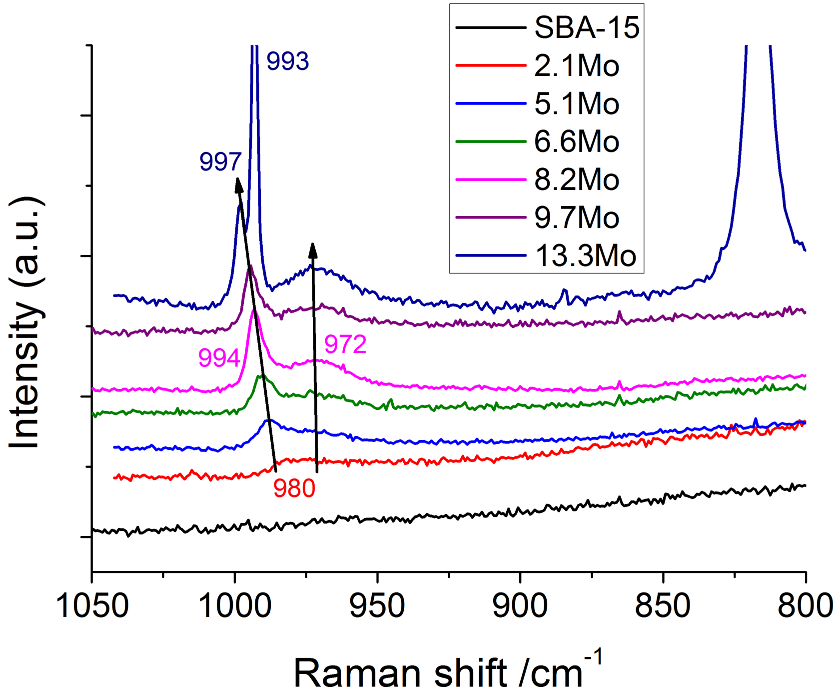
Oxide	Fundamental frequency region (cm^{-1})	Region above the fundamental frequency (cm^{-1})
Cr_2O_3	625, 550, 435, 407	1015, 995, 980, 890, 820
MnO_2	615, 400	1170, 1140, 1120, 1065, 1040, 980
Fe_2O_3	560, 470	960, 925
NiO	650, 465	1050, 1140
CuO	610, 500, 410	1050, 830, 790
V_2O_5	1015, 860, 600	1035
Cu/Cr/O	620, 520	1010, 950, 900
Fe/Cr/O	560, 470	1005, 930
SnO_2	670, 610, 312	1060, 970
$ZnCr_2O_4$	670, 560	870, 980, 1010
$ZnO \cdot ZnCr_2O_4$	670, 560	960, 1015
$ZnCr_2O_4 \cdot K$	670, 560	970
TiO_2(anatase)	700–525, 347	950, 870, 770, 730
Co_3O_4	665, 560	800–1200
Mo/Sn/O	990, 660	1005–1010
V_2O_5/Al_2O_3	1015, 890, 600	1020–1035
SiO_2	1100, 775	908, 888
γ-Al_2O_3	800, 620	1050
ZnO	450	800–1200
Sn/V/O	670, 610	980, 1035
Sb_6O_{13}	740, 400	800–1200

A. Davydov, Molecular Spectroscopy of Oxide Catalyst Surfaces, p. 32

Vibrational spectra of MoO_x/SiO_2



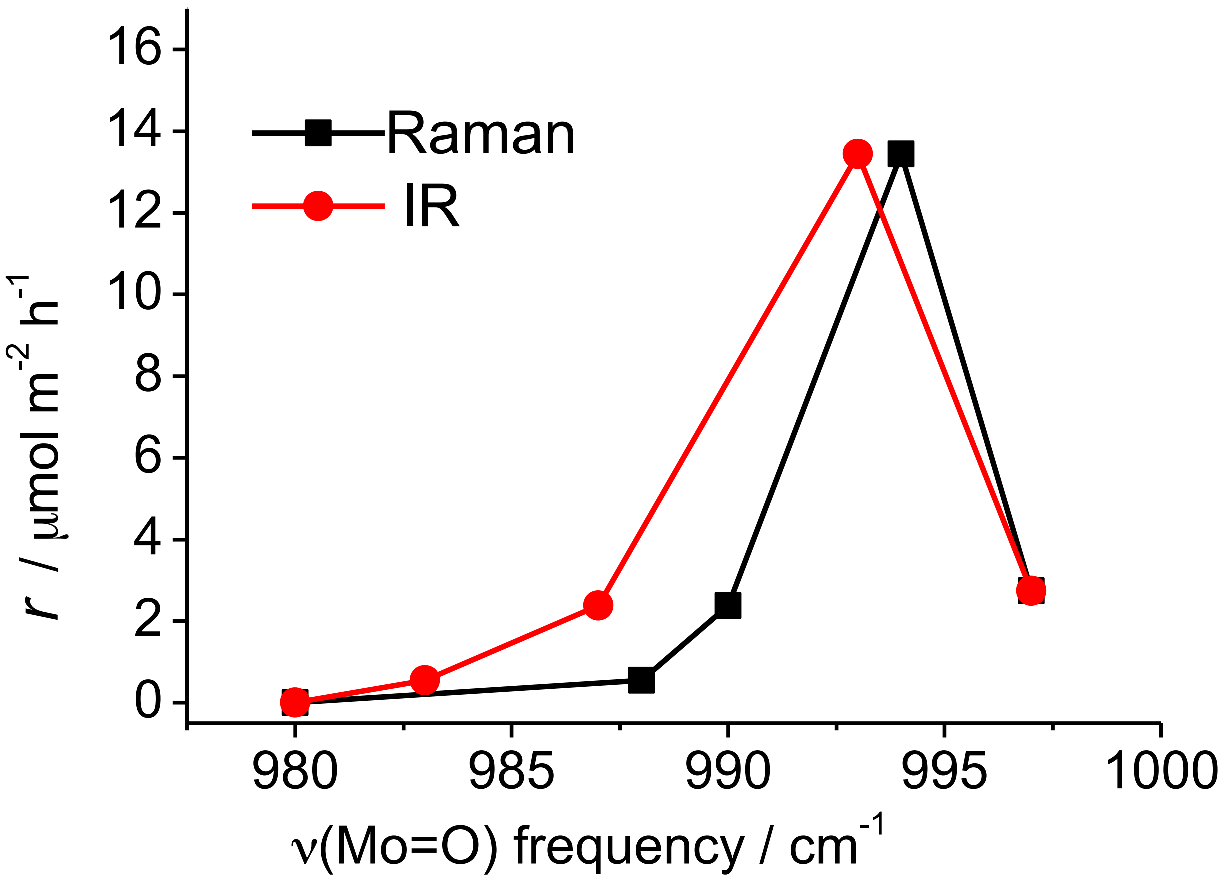
DRIFTS



Raman, E_{ex}=1.96 eV

Jutta Kröhnert, Kazuhiko Amakawa

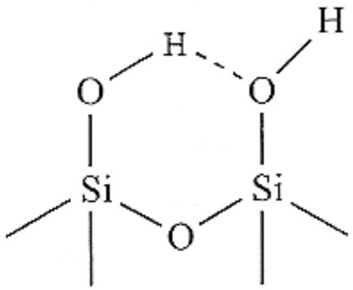
Vibrational spectra of MoO_x/SiO_2



Correlation between the ν(Mo═O) frequency detected in Raman/IR analysis and propene metathesis activity of MoO_x/SBA-15 at 323 K and at 15-21 h time on stream. The catalysts were pretreated or regenerated in 20% O_2 at 823 K for 0.5 h.

Kazuhiko Amakawa

Surface sites



Hydroxyl-hydrate cover

Surface hydroxyl groups

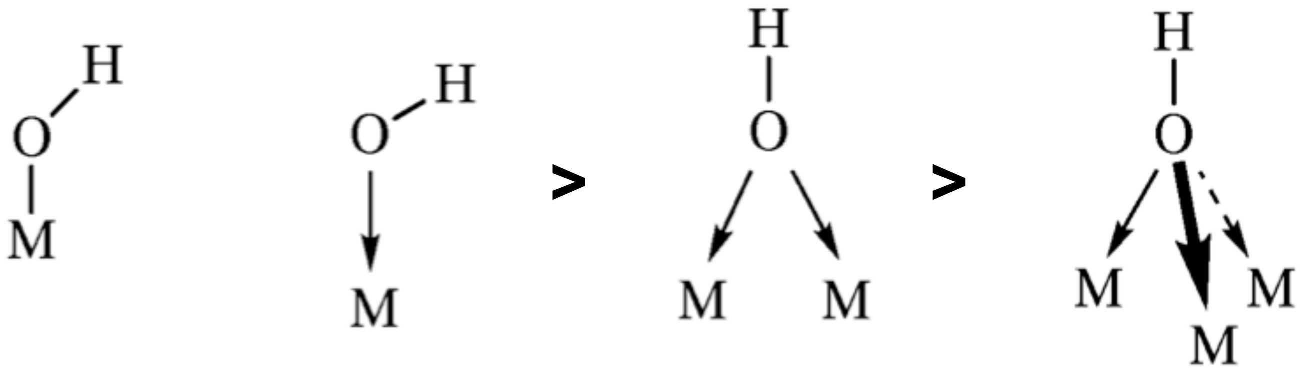
The position and shape of the OH bands of surface hydroxyl groups is informative of their coordination

- Covalent oxide components usually give rise to very typical strong sharp peak
- In covalent oxides coordination of oxygen is mostly two and this also occurs at the surface where the OHs are, consequently, terminal
- On ionic oxides the coordination of oxygen is higher than two, so that bridging and triply bridging hydroxy groups are formed at the surface

G. Busca, PCCP 1 (1999) 723.

Surface hydroxyl groups

- Isolated hydroxyl groups are responsible for discrete absorption bands in the range 3800-3600 cm^{-1} (if not involved in hydrogen bonding)

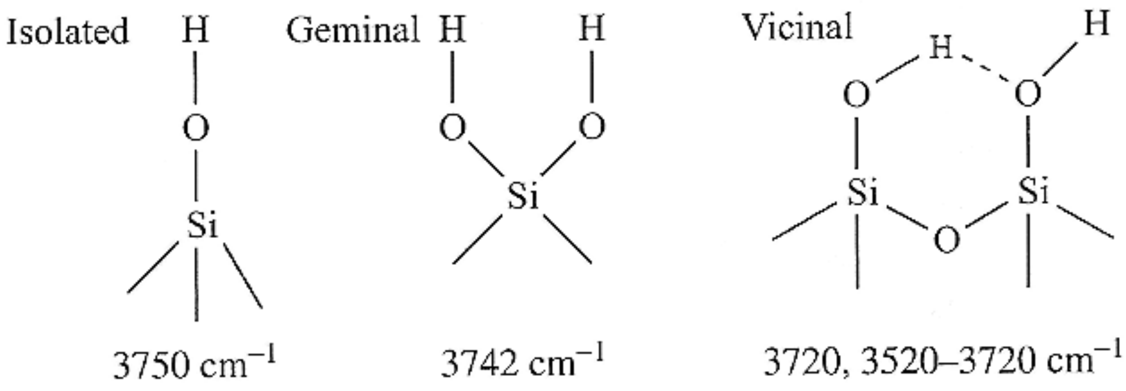


- Hydrogen bonding:

✓ shift to lower wavenumber (3650-3200 cm^{-1})
✓ strengthened integrated intensity
✓ broadened peak shape

G. Busca, PCCP 1 (1999) 723.

Silanol groups (only terminal!)

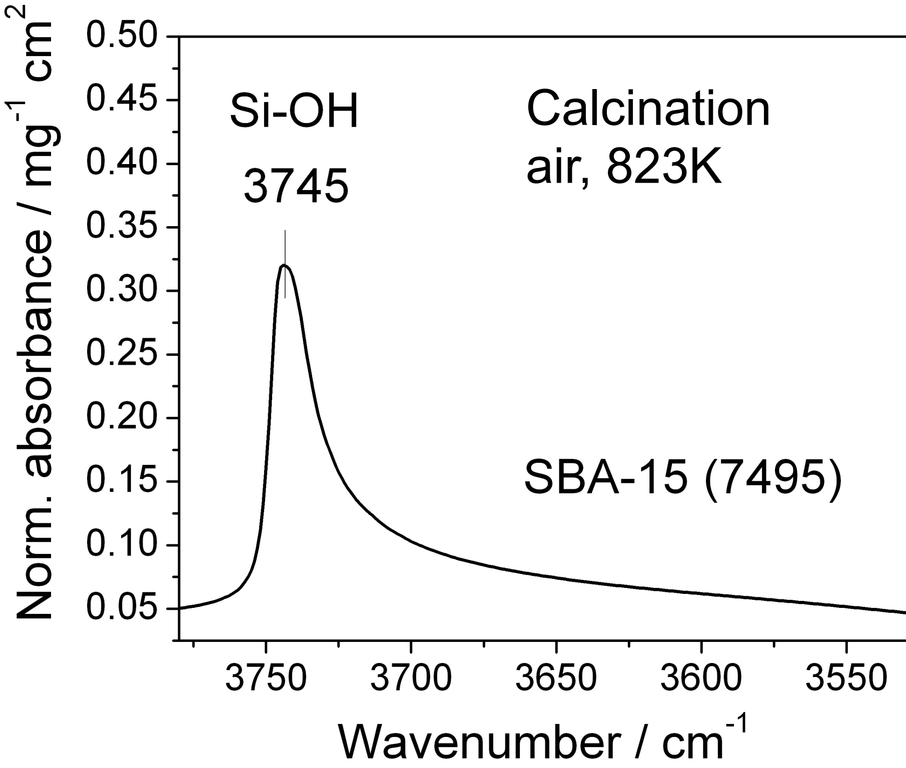


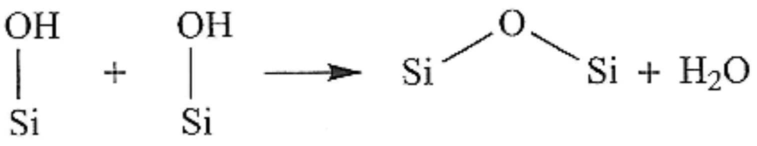
vOH+δOH = 4550 cm^{-1}

(no combination band for molecular water in this range,

H_2O v$_1$+v$_2$=5100-5300 cm^{-1})

ρ = 3 – 5 OH nm^{-2}

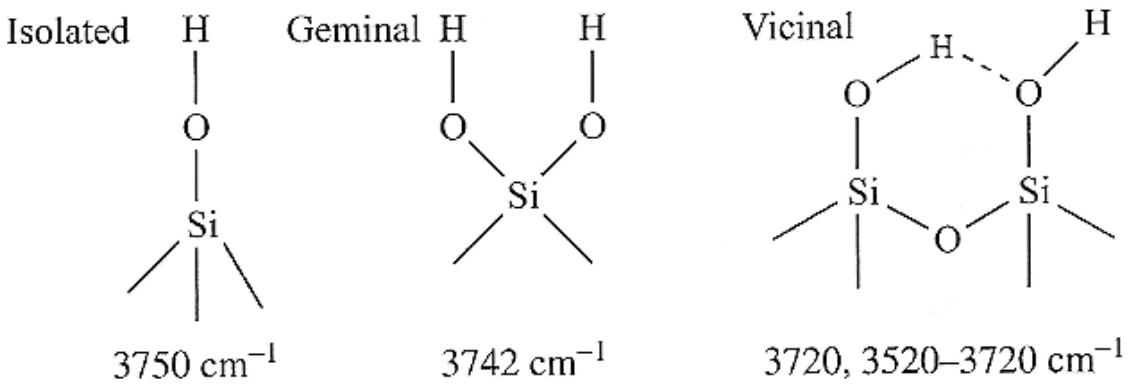


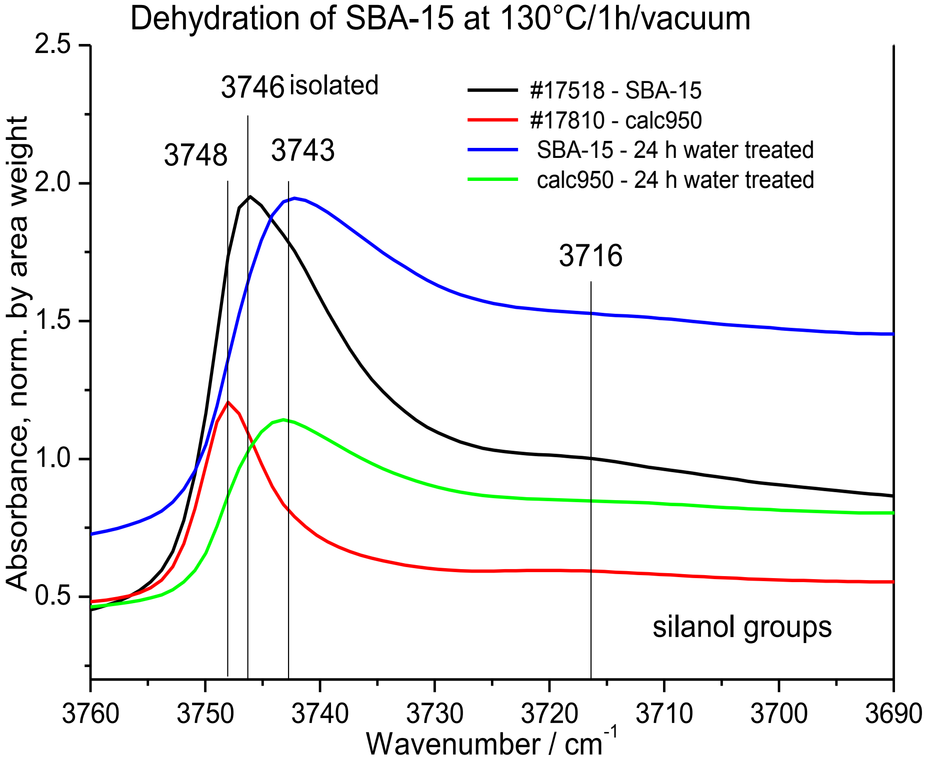


The newly formed siloxane groups are very reactive due to strain caused by dehydration

Jutta Kröhnert

Silanol groups (only terminal!)

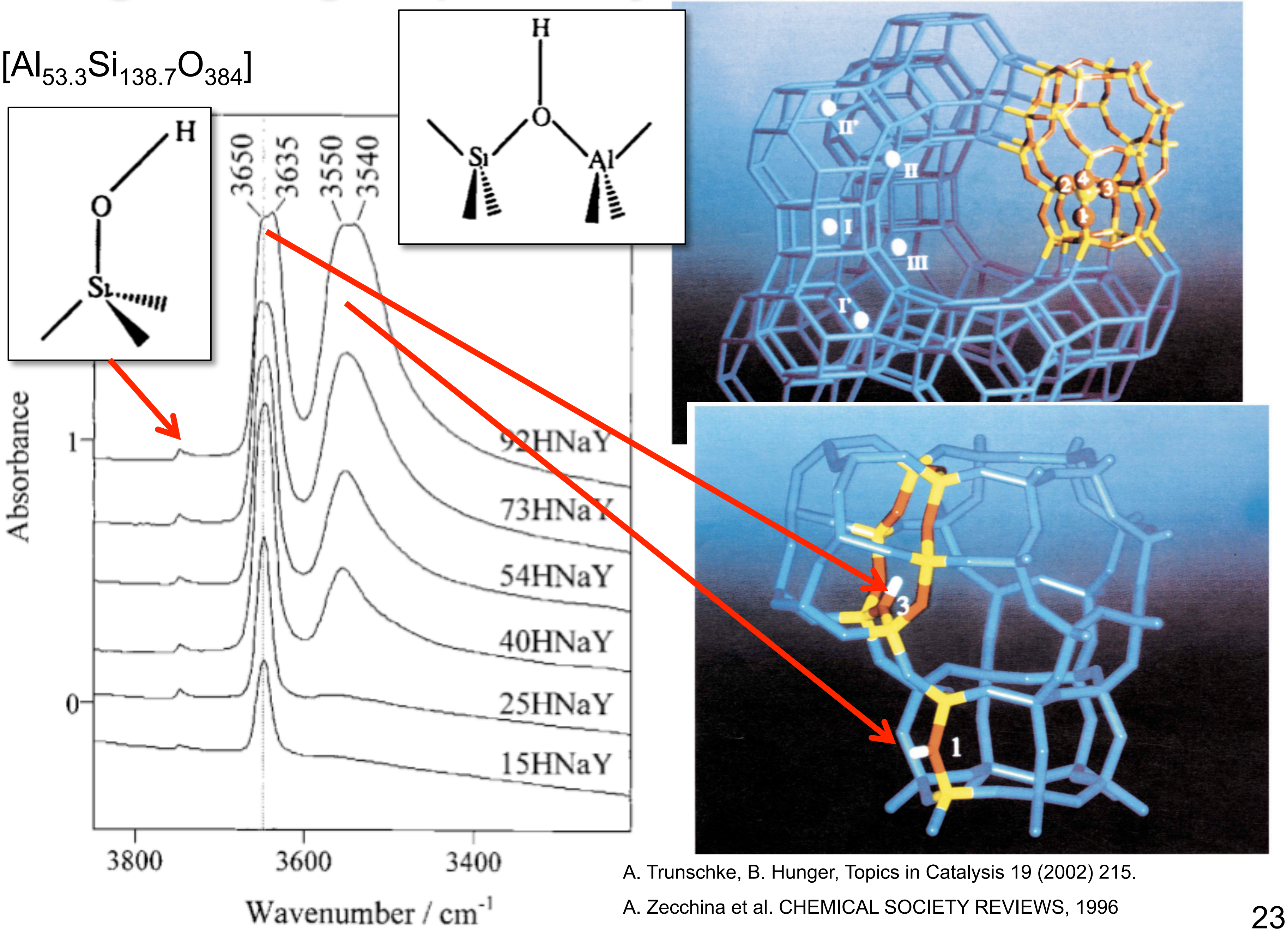




Jutta Kröhnert, Margherita Macino

Bridged OH groups in crytalline alumosilicates

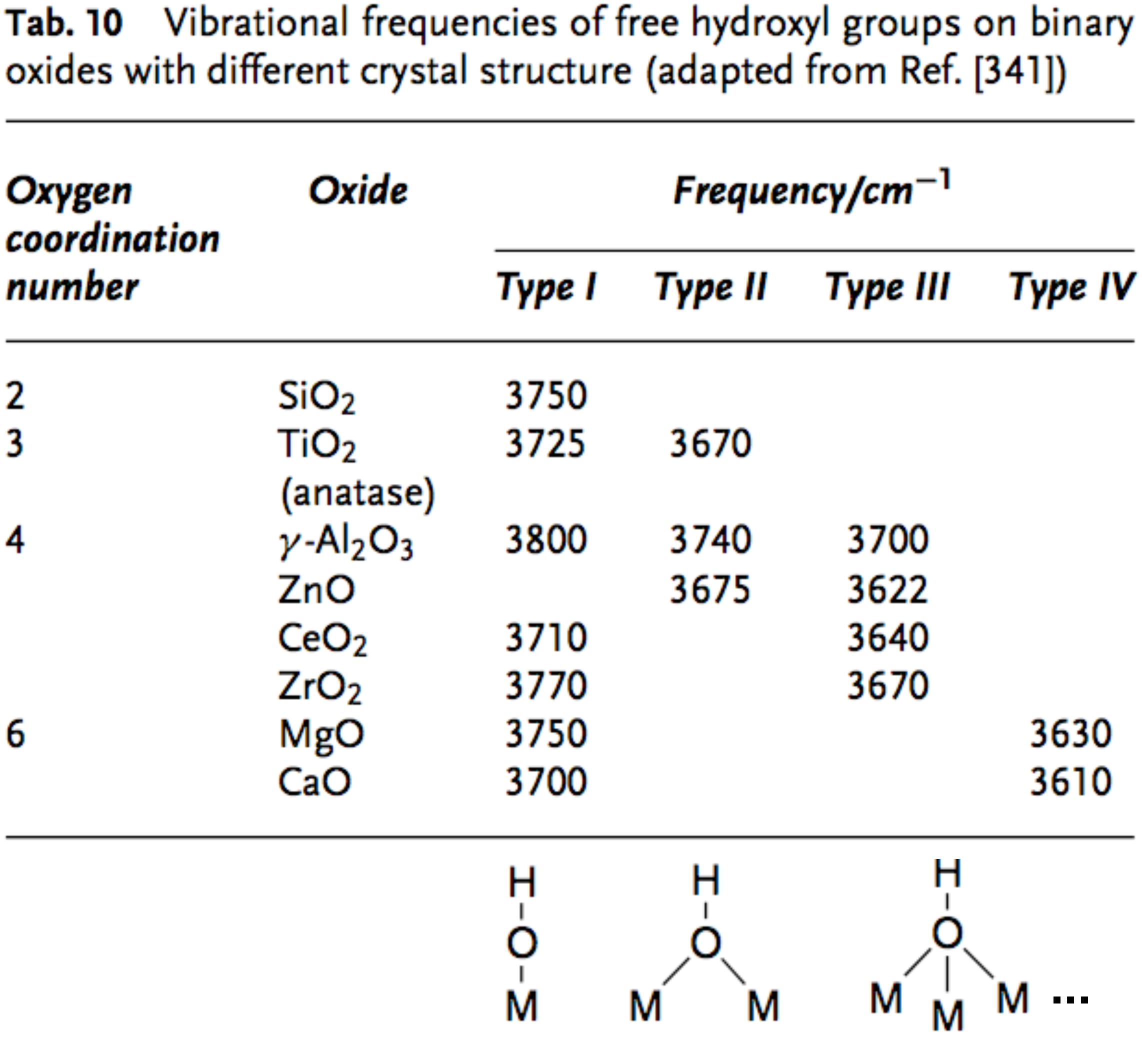
$Na_{53.3}[Al_{53.3}Si_{138.7}O_{384}]$



A. Trunschke, B. Hunger, Topics in Catalysis 19 (2002) 215.

A. Zecchina et al. CHEMICAL SOCIETY REVIEWS, 1996

Positions of isolated OH groups



Tab. 10 Vibrational frequencies of free hydroxyl groups on binary oxides with different crystal structure (adapted from Ref. [341])

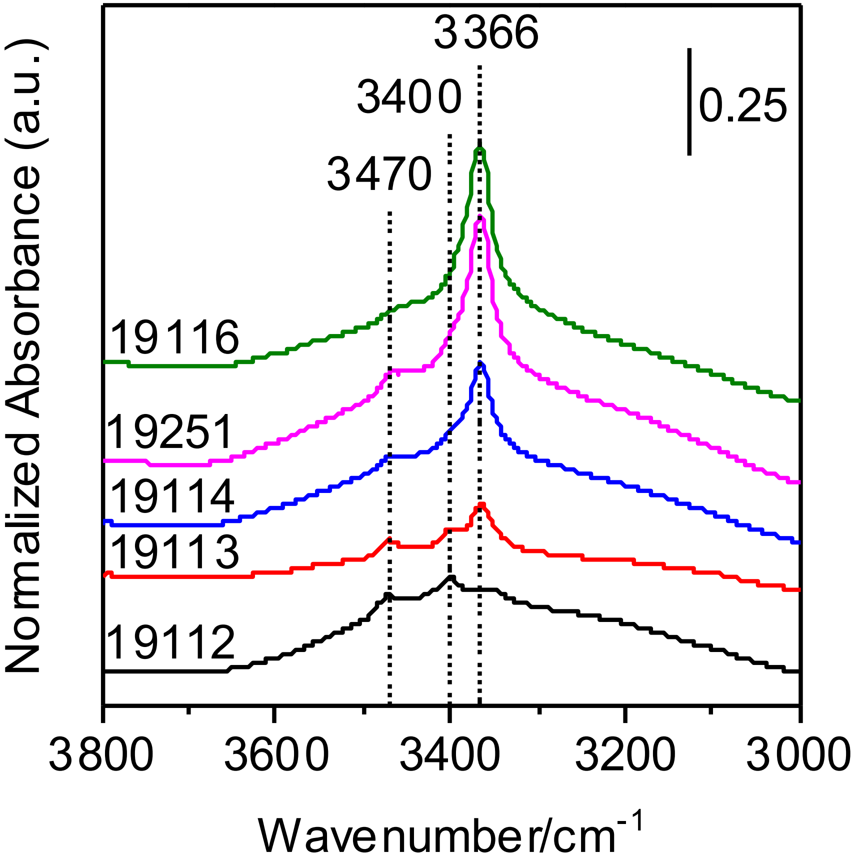
Oxygen coordination number	*Oxide*	*Frequency/cm^{-1}*			
		Type I	*Type II*	*Type III*	*Type IV*
2	SiO_2	3750			
3	TiO_2 (anatase)	3725	3670		
4	γ-Al_2O_3	3800	3740	3700	
	ZnO		3675	3622	
	CeO_2	3710		3640	
	ZrO_2	3770		3670	
6	MgO	3750			3630
	CaO	3700			3610

- ✓ Relation between OH stretching frequency and structure and acidity is not straightforward
- ✓ OH band of MgO, amorphous silica and silica-alumina appear
  at similar position at 3745 ±3 cm^{-1}

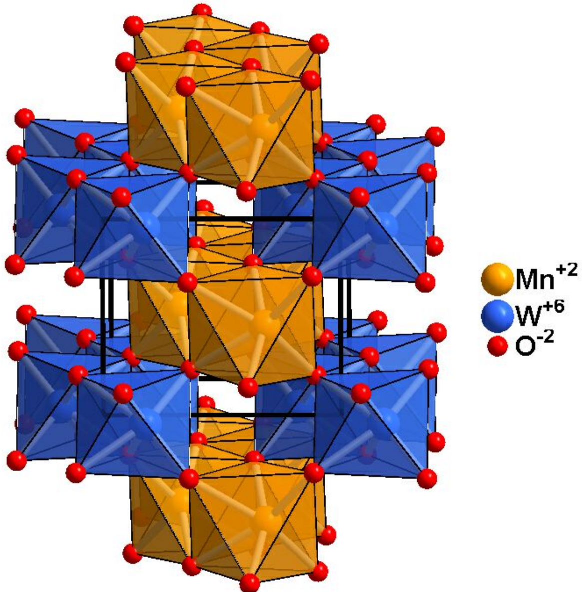
G. Mestl, H. Közinger in Handbook of Heterogeneous Catalysis

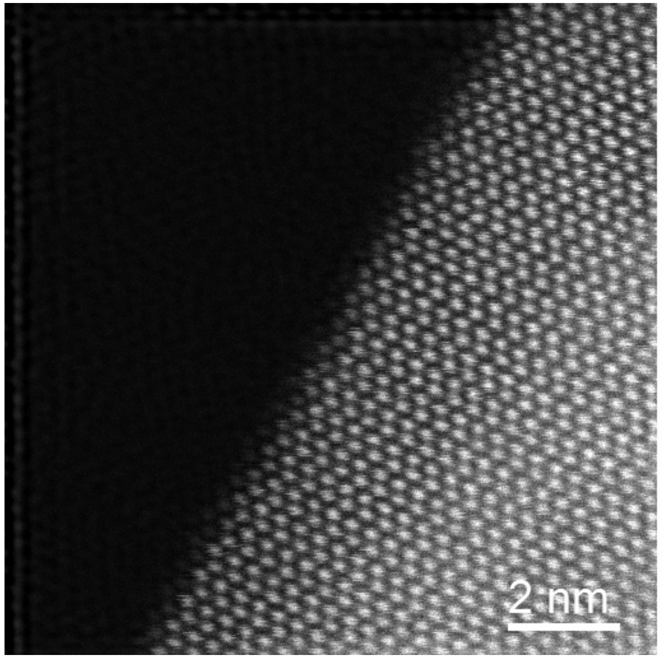
Positions of isolated OH groups

OH groups at the surface of $MnWO_4$



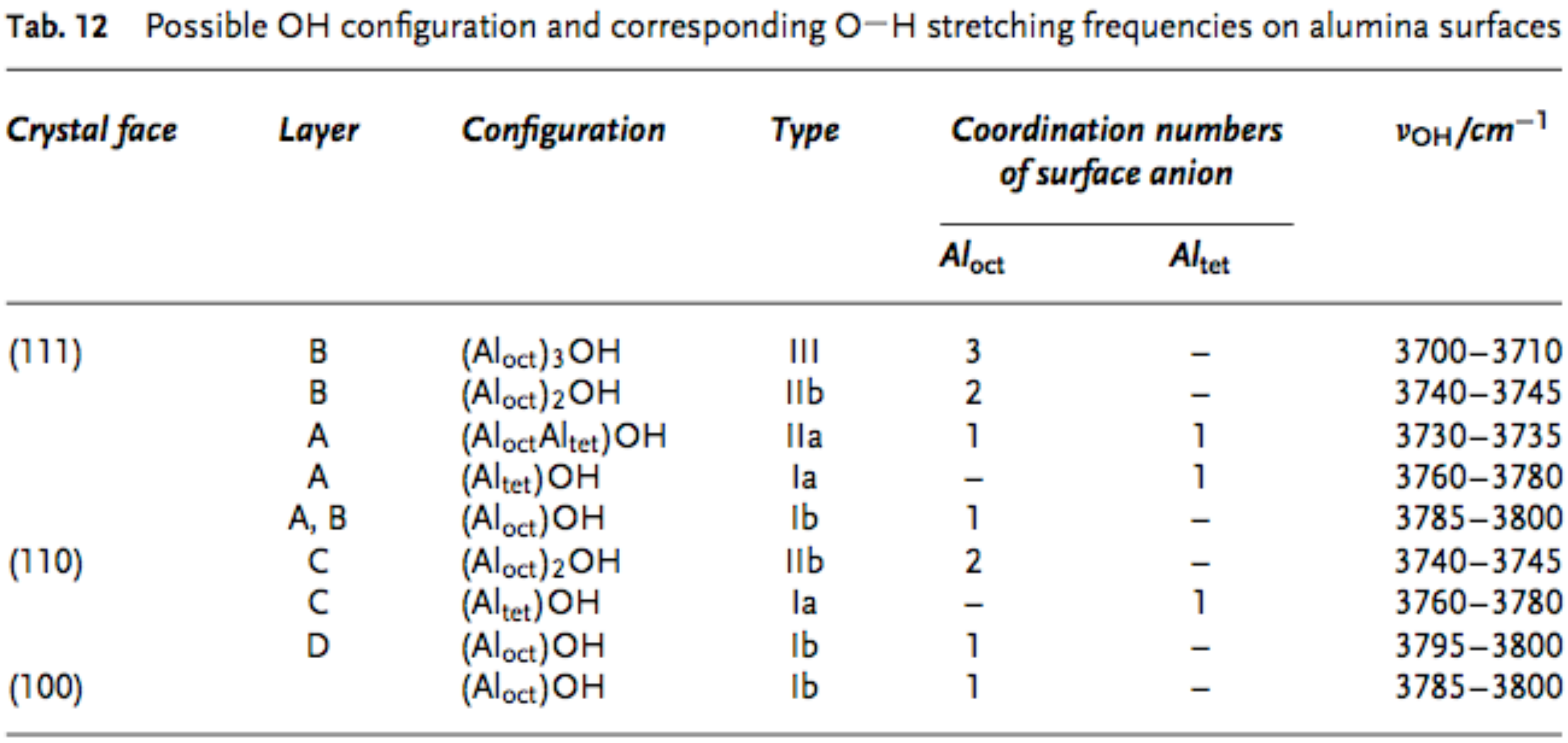
FT-IR after evacuation at 300°C for 1h





Jutta Kröhnert, Xuan Li, Thomas Lunkenbein

Positions of isolated OH groups

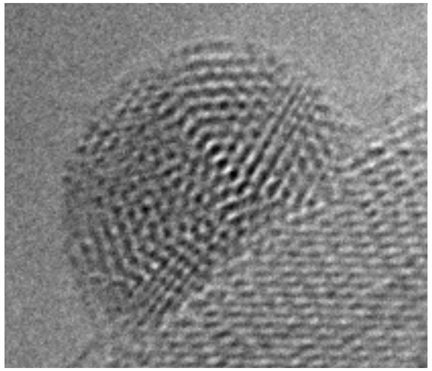


Tab. 12 Possible OH configuration and corresponding O—H stretching frequencies on alumina surfaces

Crystal face	*Layer*	*Configuration*	*Type*	*Coordination numbers of surface anion*		ν_{OH}/cm^{-1}
				Al_{oct}	Al_{tet}	
(111)	B	$(Al_{oct})_3OH$	III	3	–	3700–3710
	B	$(Al_{oct})_2OH$	IIb	2	–	3740–3745
	A	$(Al_{oct}Al_{tet})OH$	IIa	1	1	3730–3735
	A	$(Al_{tet})OH$	Ia	–	1	3760–3780
	A, B	$(Al_{oct})OH$	Ib	1	–	3785–3800
(110)	C	$(Al_{oct})_2OH$	IIb	2	–	3740–3745
	C	$(Al_{tet})OH$	Ia	–	1	3760–3780
	D	$(Al_{oct})OH$	Ib	1	–	3795–3800
(100)		$(Al_{oct})OH$	Ib	1	–	3785–3800

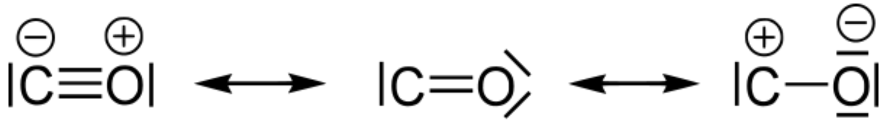
G. Mestl, H. Közinger in Handbook of Heterogeneous Catalysis

Surface sites



Surface sites of supported metal particles

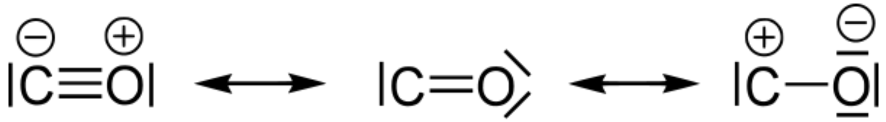
Carbon monoxide - a universal probe



CO can be used to probe

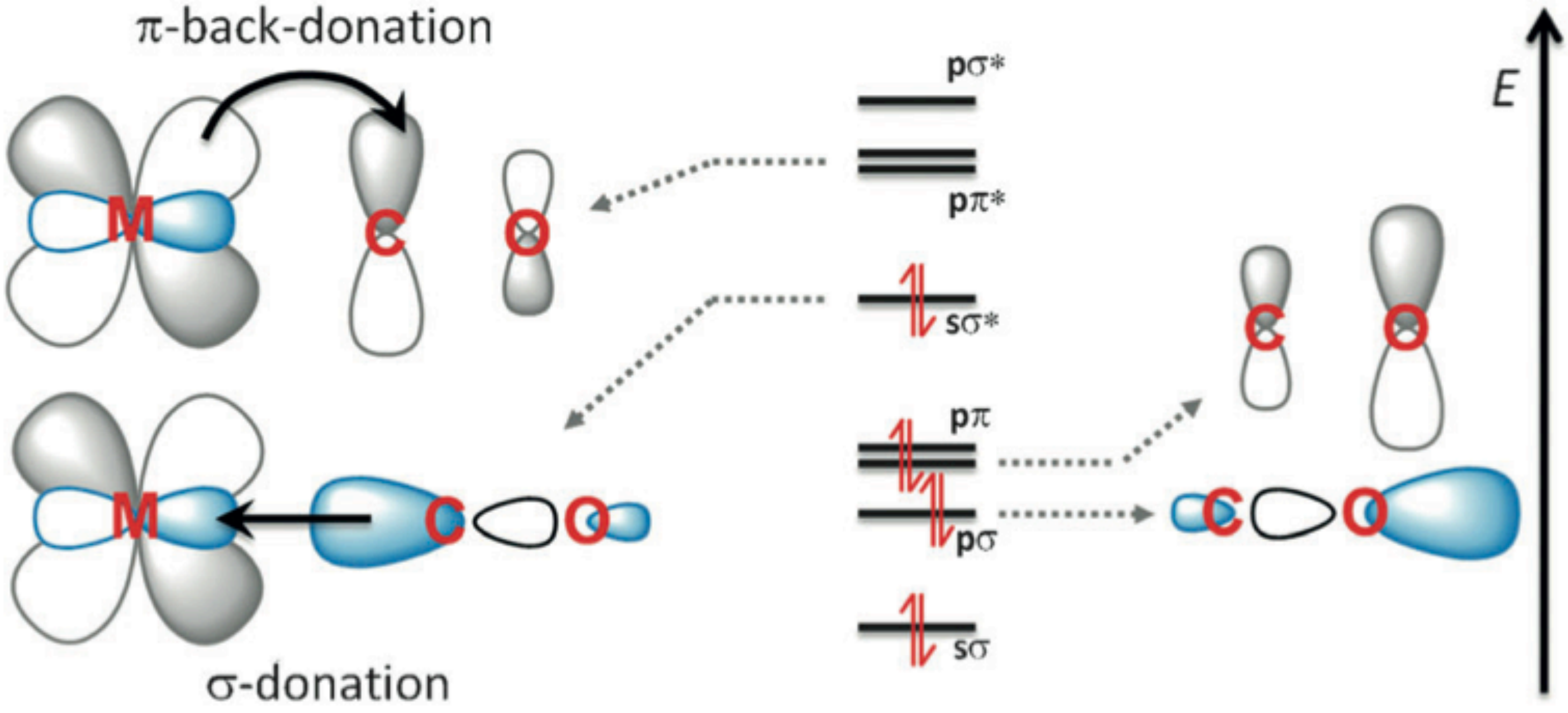
- Particle size, geometric and electronic structure of supported metal particles
- Promoter effects, metal-support interaction
- Oxidation state of coordinatively unsaturated surface cations
- Acid base properties

Carbon monoxide - a universal probe



- Gas phase frequency of CO: 2143 cm^{-1}
- CO can form surface carbonyl complexes with
  - transition metal atoms and
  - transition metal ions
- CO is a weak Lewis base
  - PA = 598 kJ mol^{-1}
  - Adsorption on coordinatively unsaturated surface cations
- Interaction with surface oxygen atoms or ions (formation of carbonate species)
- Interaction / reaction with surface hydroxyl groups (formation of formate complexes)

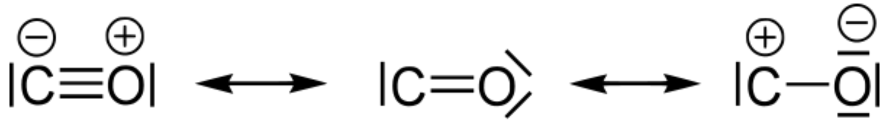
Bonding of CO to transition metals



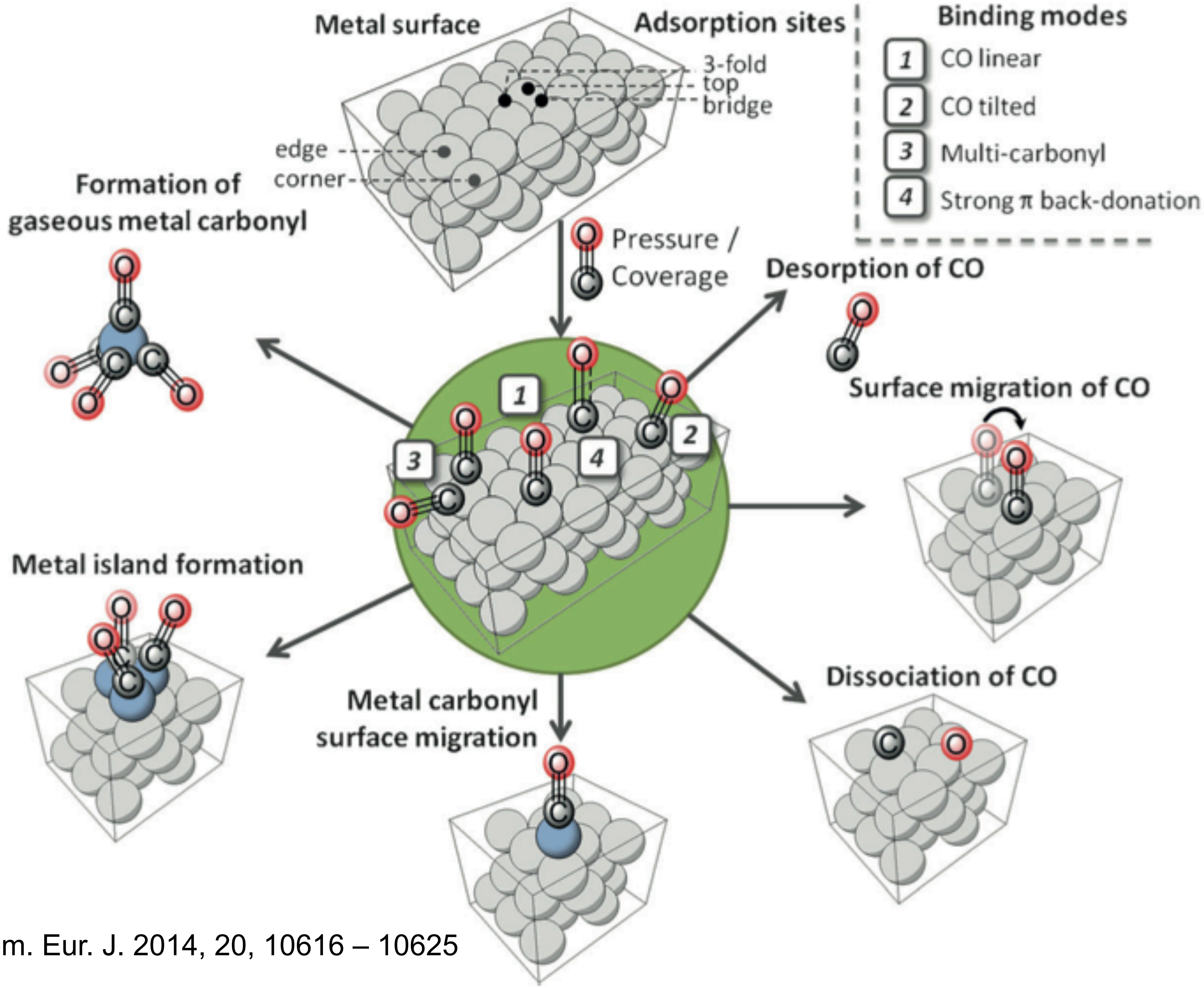
S. Carenco, Chem. Eur. J. 2014, 20, 10616 – 10625

- CO gas phase frequency: 2143 cm^{-1}
- Coordination to metals
    - σ-donor bond – Lewis base *via* HOMO - ν increases
    - π-acceptor bond – Lewis acid *via* LUMO - ν decreases

Bonding of CO to transition metals



$$^{\ominus}|C\equiv O|^{\oplus} \longleftrightarrow |C=O\rangle \longleftrightarrow {}^{\oplus}|C-\overline{\underline{O}}|^{\ominus}$$



S. Carenco, Chem. Eur. J. 2014, 20, 10616 – 10625

CO adsorption on metals

vCO depends on

- Adsorption site
- Surface coverage and presence of co-adsorbed species
  - π-bonding versus resonance interaction between vibrating dipols
  - Measurement of coverage dependency gives information about surface structure
- Metal particle size
  - Pt: vCO increases with increasing particle size
    - Degree of π-bonding is higher with smaller metal coordination number
- Electronic structure of the metal
  - Promoter effects:
    - Ligand (electronic) effect at low coverage
    - Geometric effect – coverage dependency
  - Support effects:
    - Electronic effect may compete with the particle size effect
    - „SMSI“ effect – decrease in adsorption capacity of the metal

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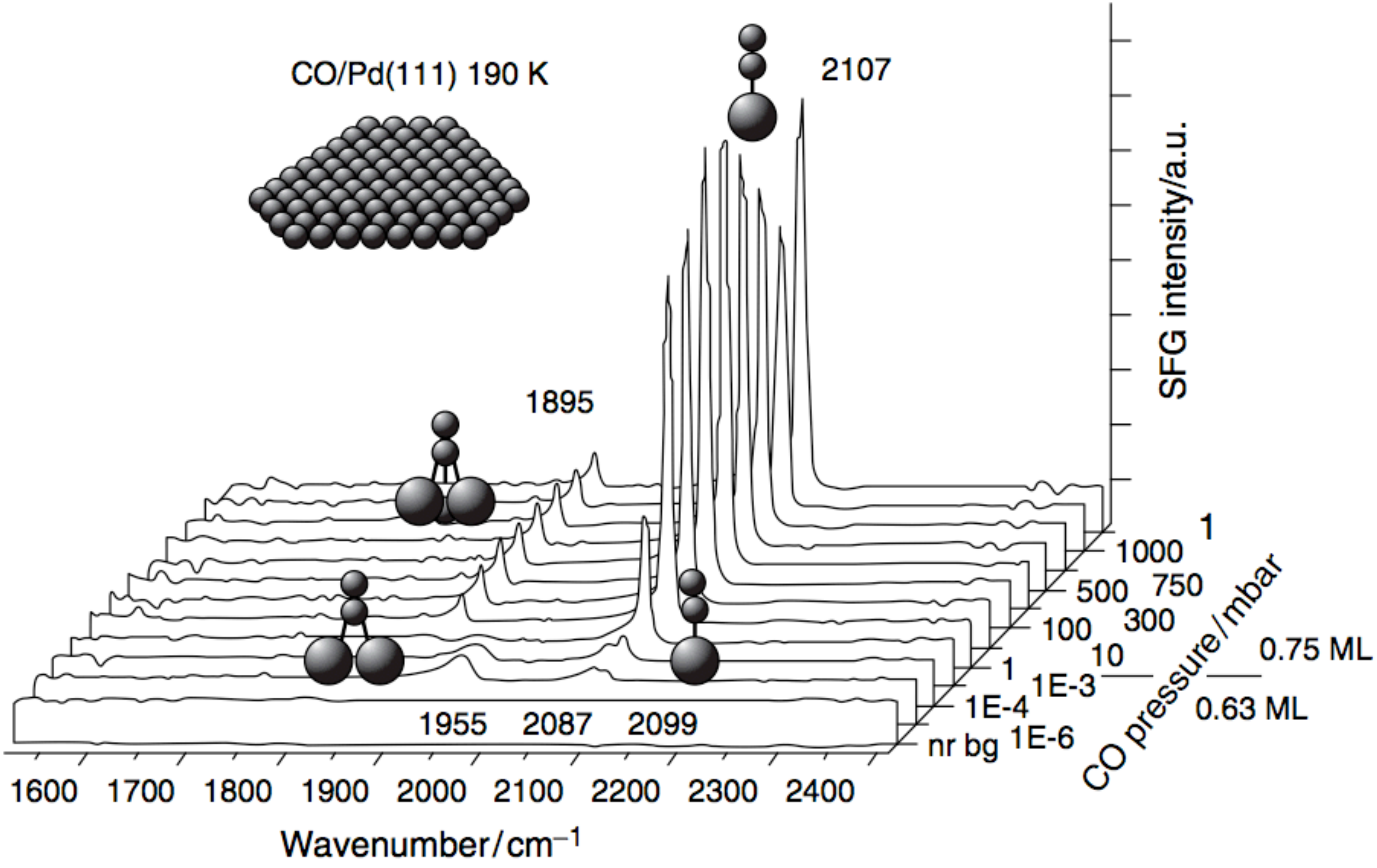
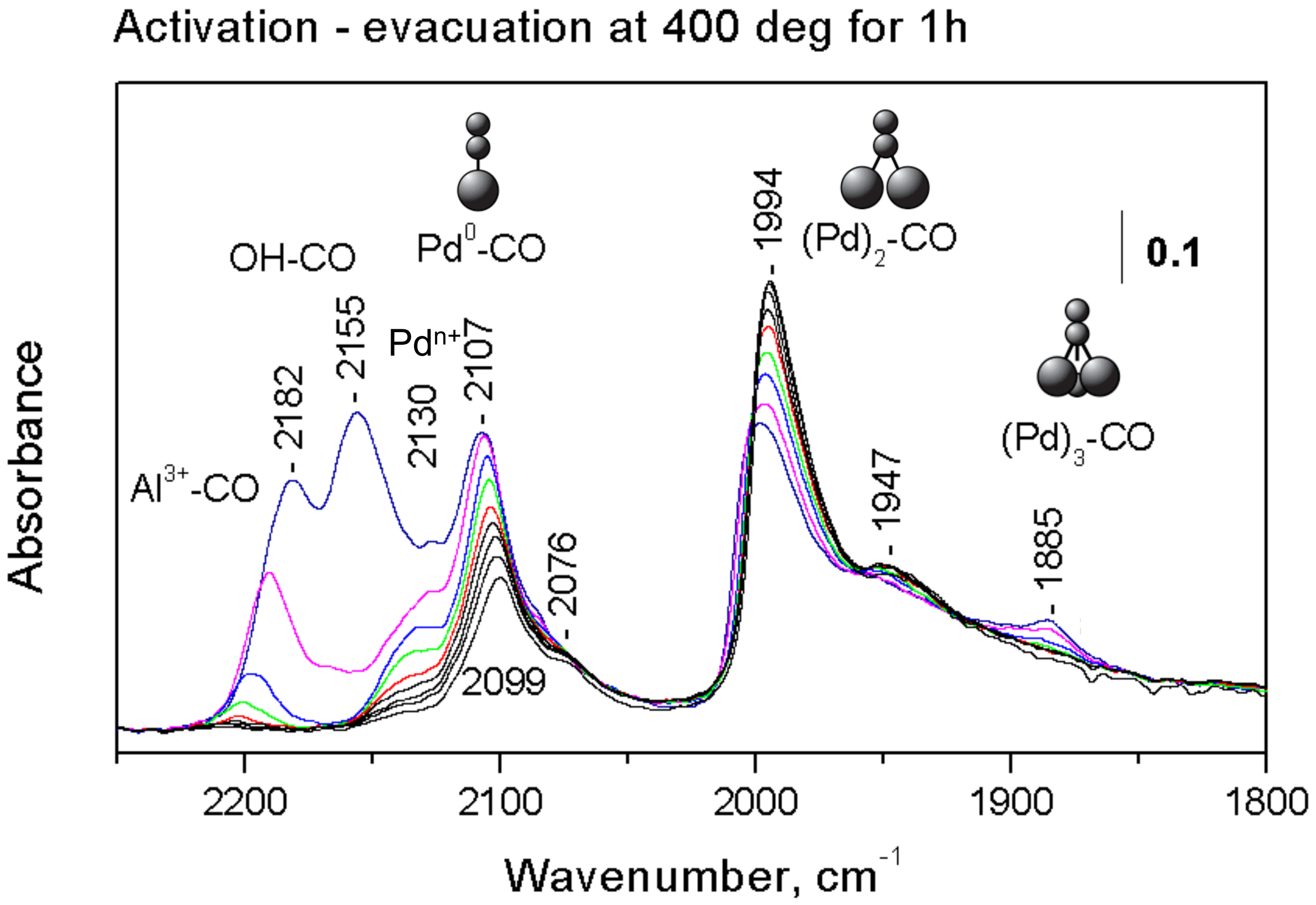
CO adsorption sites on metals



H.-J. Freund, Chapter 5.1.1 – Principles of Chemisorption in *Handbook of Heterogeneous Catalysis*, Wiley-VCH Verlag GmbH & Co. KGaA, 2008.

CO adsorption sites on supported metal particles



Activation - evacuation at 400 deg for 1h

Adsorption of 1 mbar CO on Pd/Al_2O_3 at 77 K and evacuation at 77-124 K

Jutta Kröhnert

CO adsorption on metals

vCO depends on

- Adsorption site
- Surface coverage and presence of co-adsorbed species
  - π-bonding versus resonance interaction between vibrating dipols
  - Measurement of coverage dependency gives information about surface structure
- Metal particle size
  - Pt: vCO increases with increasing particle size
    - Degree of π-bonding is higher with smaller metal coordination number
- Electronic structure of the metal
  - Promoter effects:
    - Ligand (electronic) effect at low coverage
    - Geometric effect – coverage dependency
  - Support effects:
    - Electronic effect may compete with the particle size effect
    - „SMSI“ effect – decrease in adsorption capacity of the metal

CO adsorption on metals

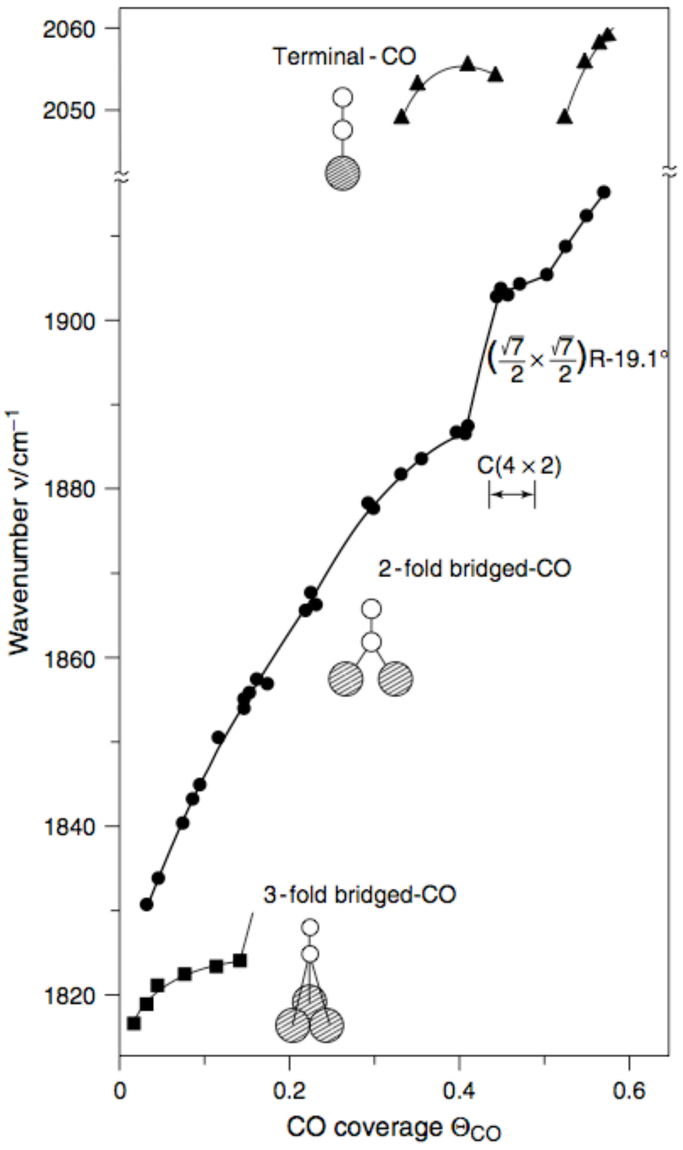


Fig. 23 Stretching frequency of CO adsorbed on Ni(111) as a function of CO coverage. The surface was dosed at 90 K and subsequently annealed to 240 K [145].

- Change of adsorbate site upon increase of coverage
- Shift caused by the coupling of the dynamic dipoles which depends on intermolecular distance
- Structural assignment based on vibrational data must be viewed with caution

H.-J. Freund, Chapter 5.1.1 – Principles of Chemisorption in *Handbook of Heterogeneous Catalysis*, Wiley-VCH Verlag GmbH & Co. KGaA, 2008.

CO adsorption on metals

vCO depends on

- Adsorption site
- Surface coverage and presence of co-adsorbed species
  - π-bonding versus resonance interaction between vibrating dipols
  - Measurement of coverage dependency gives information about surface structure
- Metal particle size
  - Pt: vCO increases with increasing particle size
    - Degree of π-bonding is higher with smaller metal coordination number
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    - Geometric effect – coverage dependency
  - Support effects:
    - Electronic effect may compete with the particle size effect
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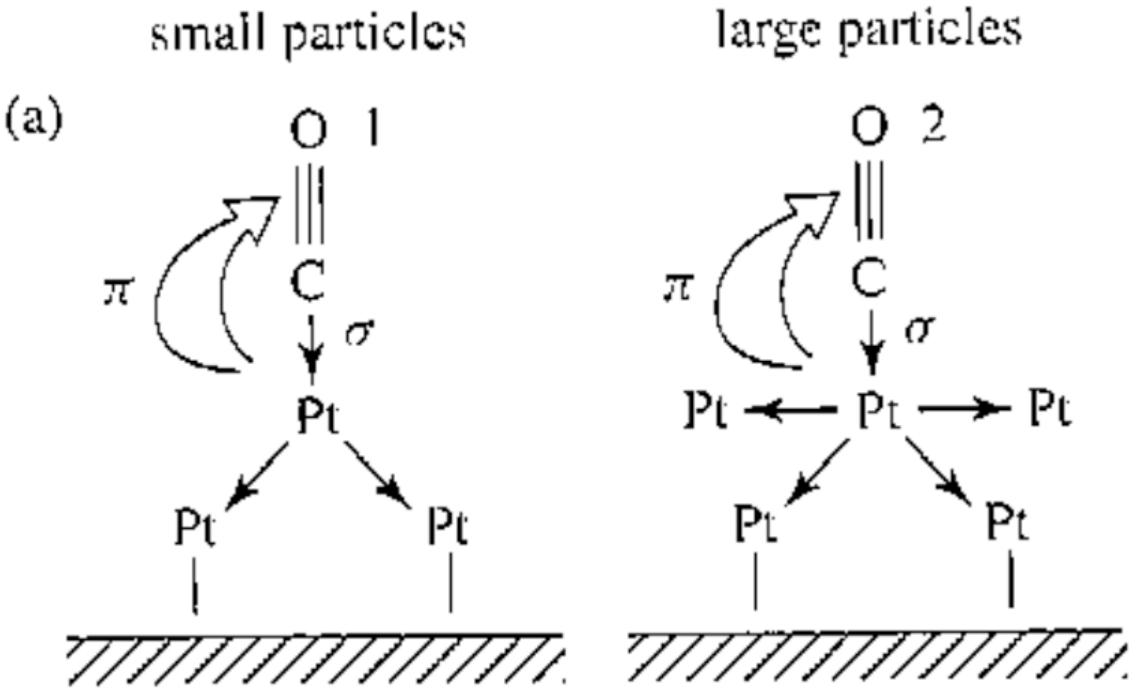
CO adsorption on supported metals



A. Davydov, Molecular Spectroscopy of Oxide Catalyst Surfaces, p. 245

CO adsorption on supported metals

vCO depends on

- Surface coverage and presence of co-adsorbed species
  - π-bonding versus resonance interaction between vibrating dipols
  - Measurement of coverage dependency gives information about surface structure
- Metal particle size
  - Pt: vCO increases with increasing particle size
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  - Promoter effects:
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    - Electronic effect may compete with the particle size effect
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CO adsorption on supported metals

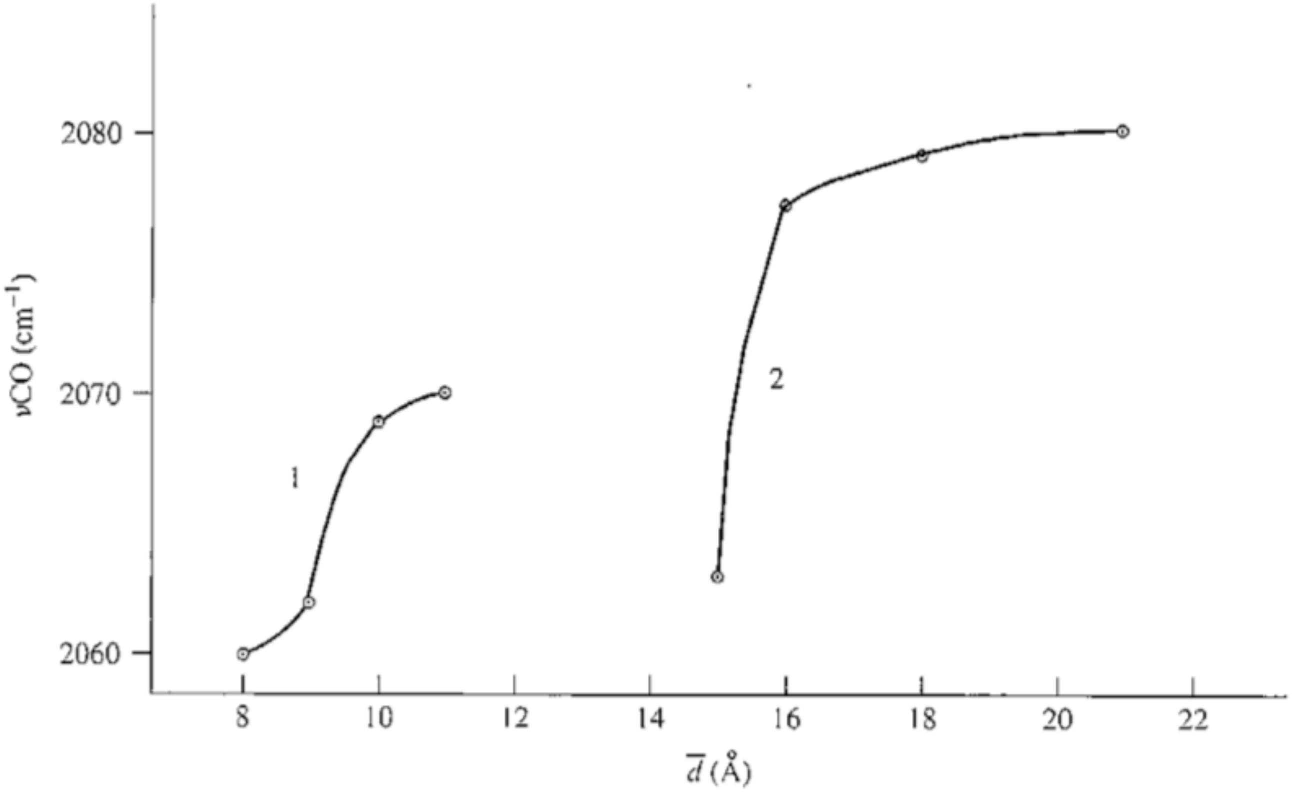


Figure 3.36. Dependence of the stretching vibrations of Pt−CO (at $\theta = 1$) on particle size for different supports: (1) Al_2O_3; (2) SiO_2.

A. Davydov, Molecular Spectroscopy of Oxide Catalyst Surfaces, p. 244

Corrosive adsorption

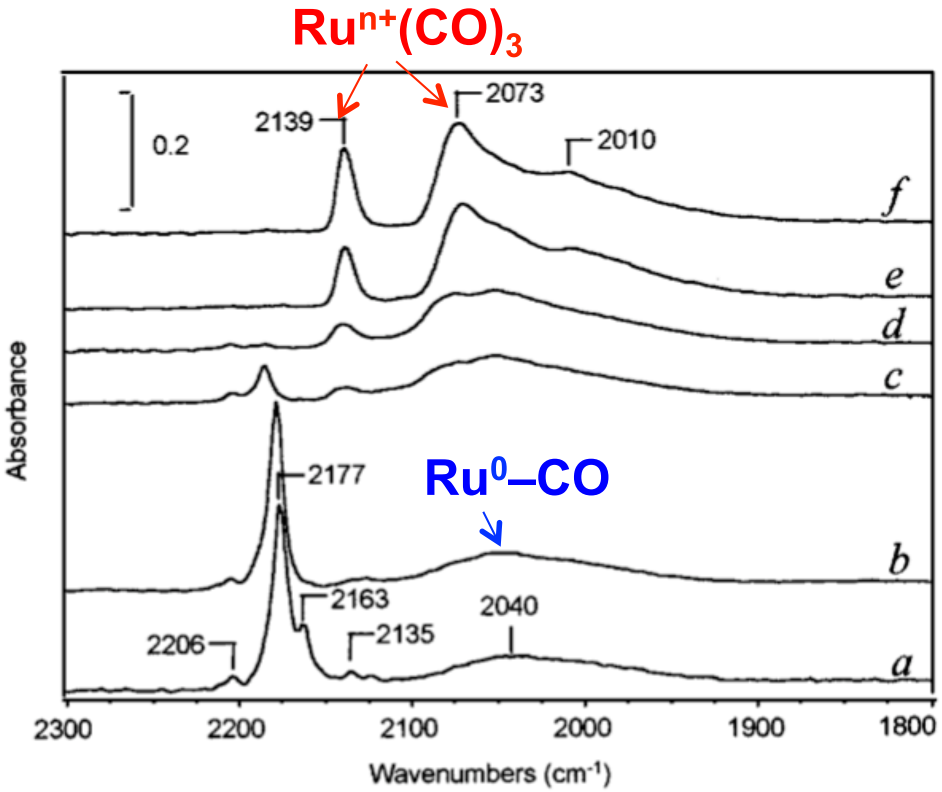
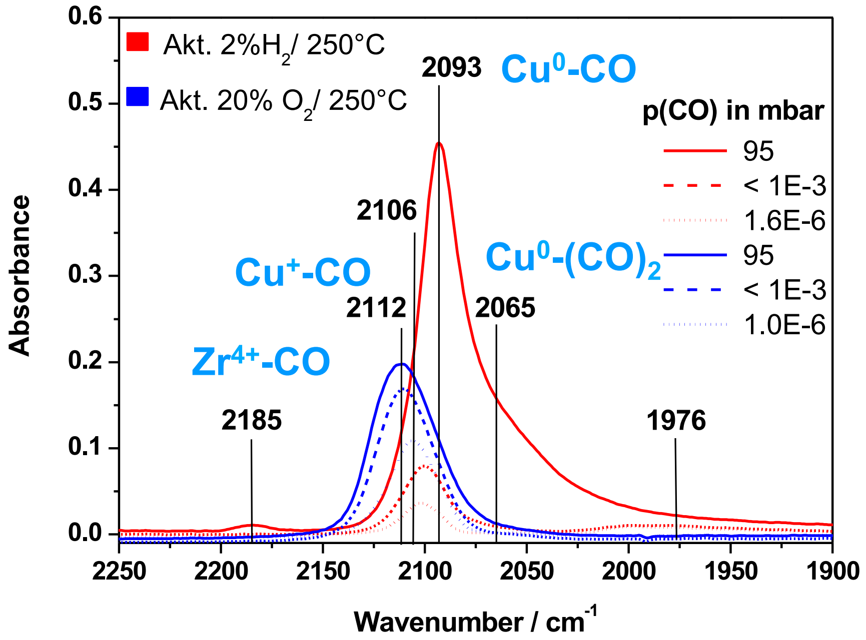


FIG. 6. IR spectra of CO adsorbed on RuT-1 sample reduced at 523 K. Adsorption of 1 Torr at 100 K (a), and time/temperature evolution of the spectra during the increase of temperature up to ambient temperature (b–d); heating the sample in CO atmosphere for 5 min at 373 K (e) and 423 K (f) (b–f spectra taken at r.t.).

CO can undergo „corrosive“ adsorption due to oxidation of the metal by CO dissociation

FTIR Study of CO Interaction with Ru/TiO_2 Catalysts, K. Hadjiivanov *et al.*, JOURNAL OF CATALYSIS 176, 415–425 (1998)

Stability of adsorbed CO



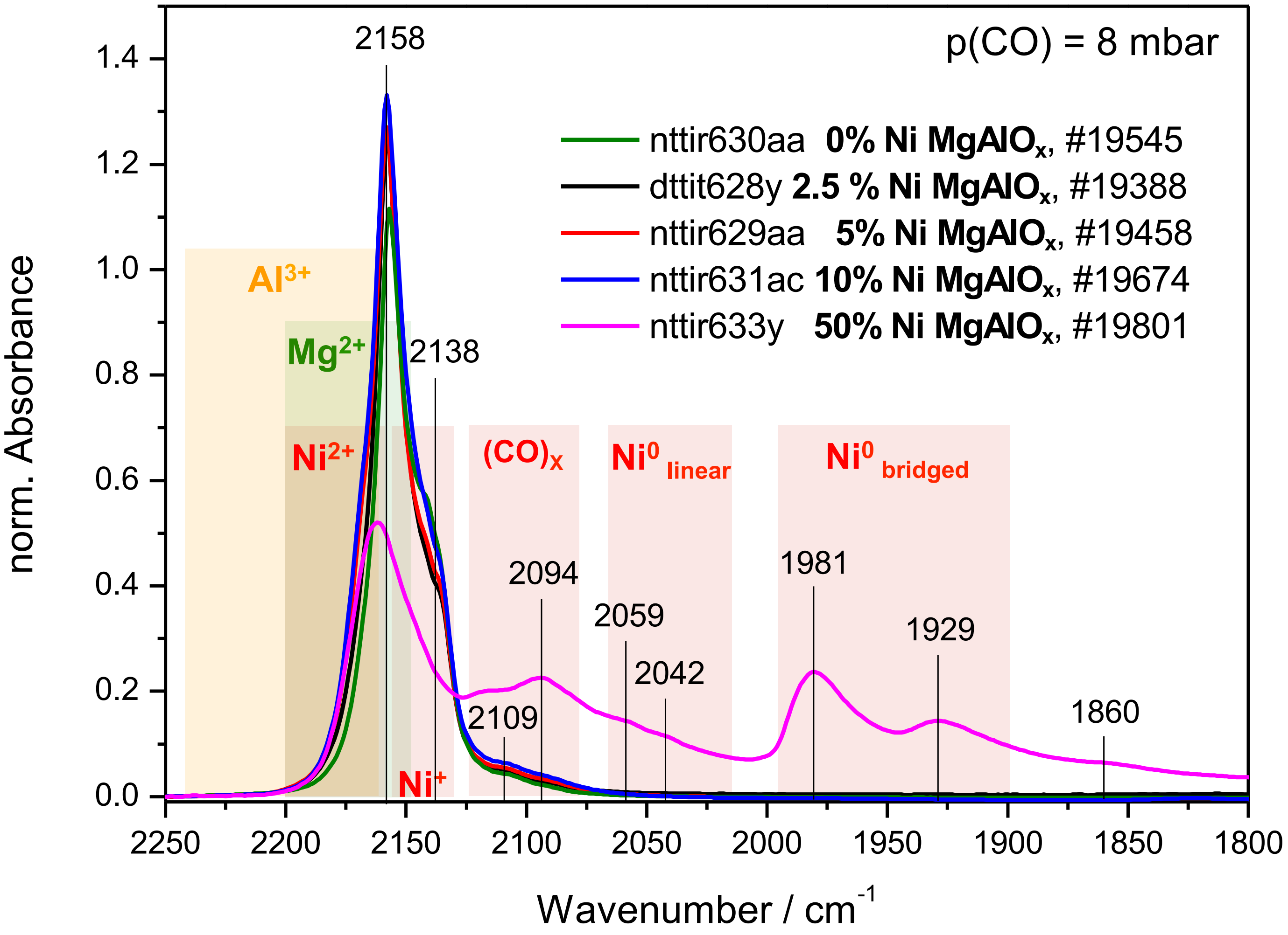
- Overlapping spectral range of 2110-2080 for Cu^+-CO and Cu^0-CO
- The stability of the species is a criterion for discrimination: Cu^0-(CO) complexes are easily decomposed during evacuation
- Cu^{2+} cannot be probed by CO at room temperature

Difference FTIR spectra of CO adsorbed at RT on Cu/ZrO_2
Desorption of CO through evacuation after sample reduction and oxidation

- The remaining small band (red) after evacuation indicates a fraction of oxidized Cu even in the “reduced” Cu/ZrO_2 sample
- After oxidation the carbonyl band is shifted to higher wavenumbers and is more stable, indicating a higher fraction of Cu^+

Probing metal and ion sites on Ni catalysts by CO

CO adsorption at 77K



Jutta Kröhnert, Katharina Mette