Modern Methods in Heterogeneous Catalysis Research

Adsorption of probe molecules

What can we learn about catalysts surfaces by infrared spectroscopy of adsorbed probes?

05 November 2010

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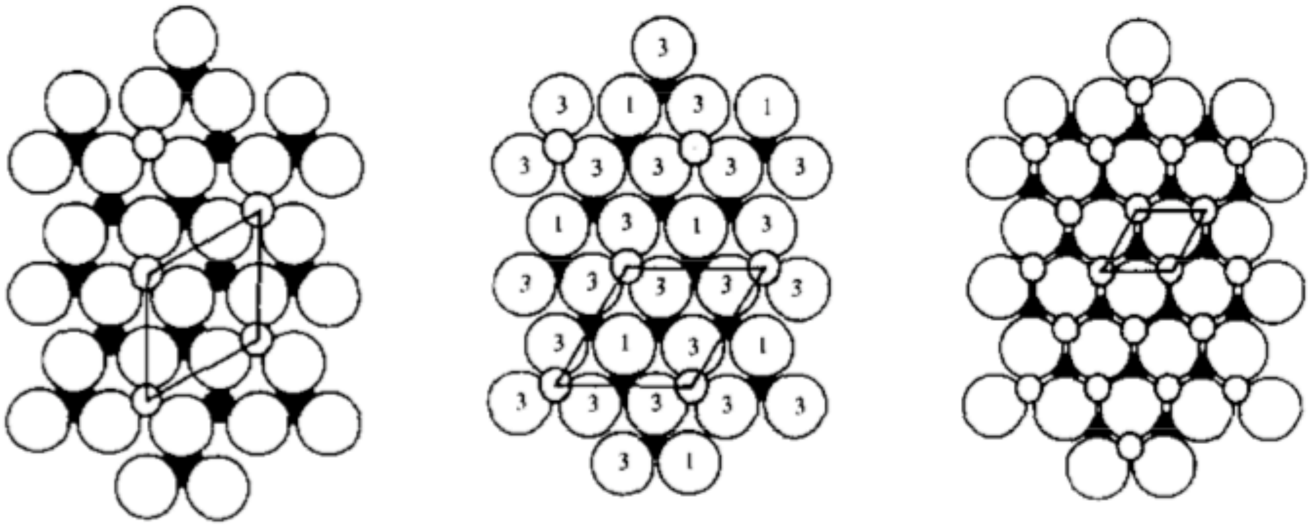
LECTURE SERIES
HETEROGENEOUS CATALYSIS

Outline

1. The catalyst surface
2. Background: Pretreated catalyst
3. Adsorption of small probe molecules (most common)
    1. CO
    2. NO
    3. Ammonia
    4. Pyridine
    5. CO_2
4. Summary

Solid structures and termination



α-Fe_2O_3 Fe_3O_4 FeO

Fig. 1. Schematic top view of an ideal bulk termination of the (111) surface of different iron oxides. One oxygen layer (oxygen anions are indicated by large open circles) and iron cations on both sides of it are shown in each case. Lateral periodicities are indicated by the different two-dimensional unit cells.

A. Barbieri et al. /Surface Science 302 (1994) 259-279.

Solid structures and termination

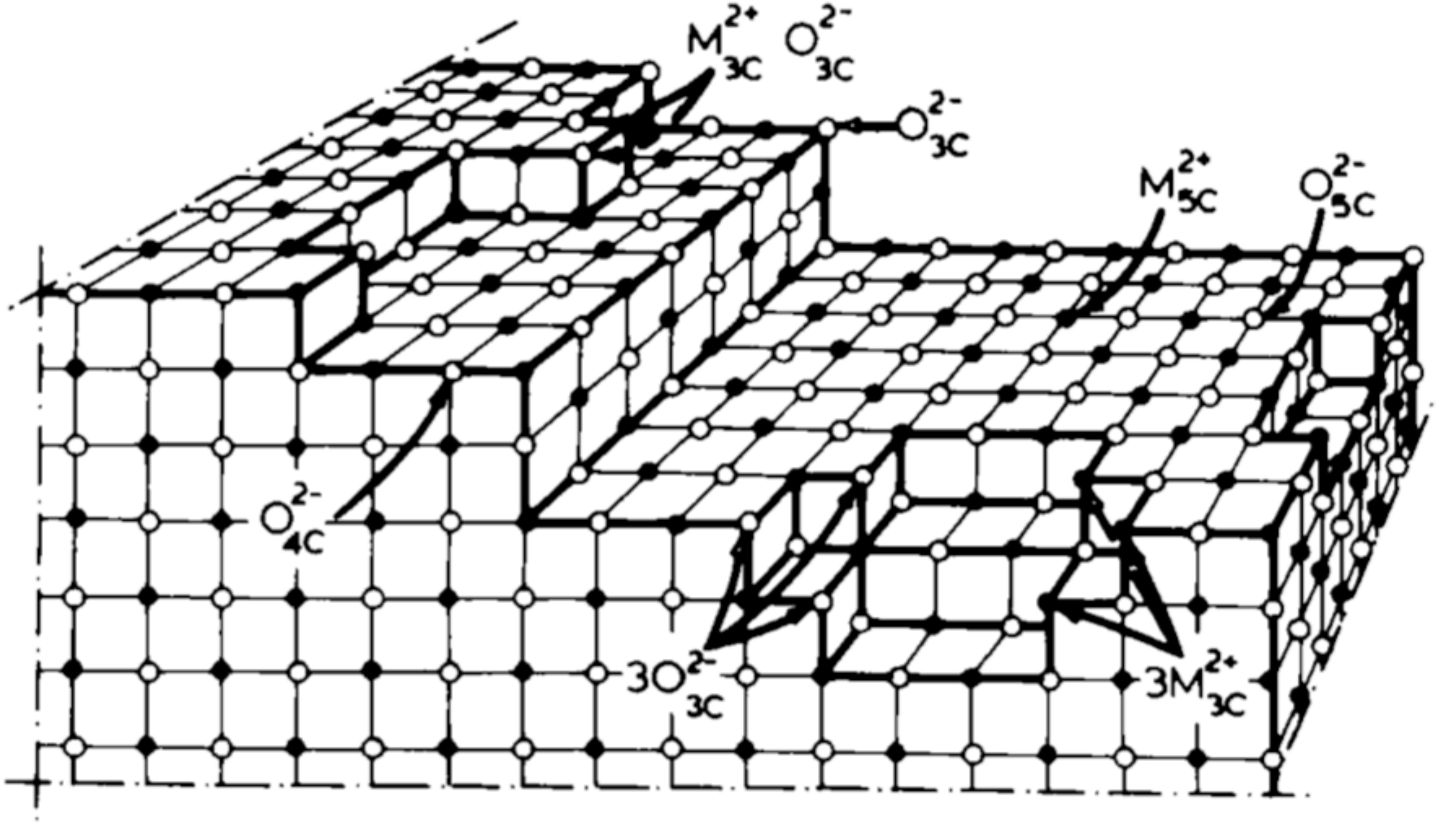


FIG. 1. A model of the surface of alkaline earth oxides, showing families of ions in low coordination.

Zecchina, A. , Coluccia, S. and Morterra, C.(1985) Infrared Sectra of Molecules Adsorbed on Oxide surfaces, Applied Spectroscopy Reviews, 21: 3, 259 — 310

Solid structures and termination

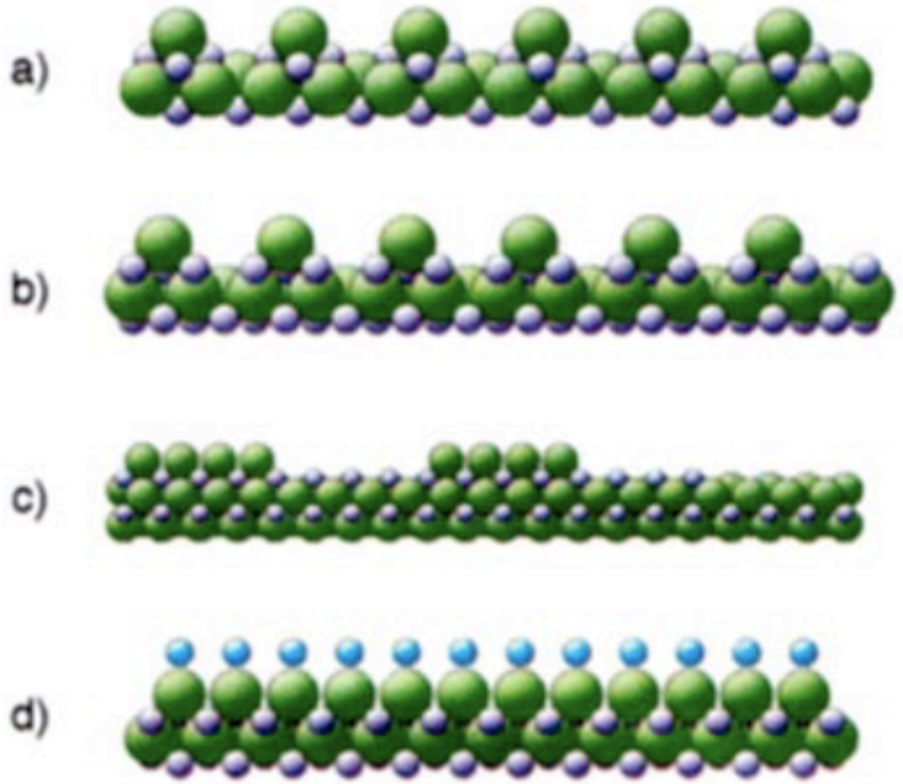
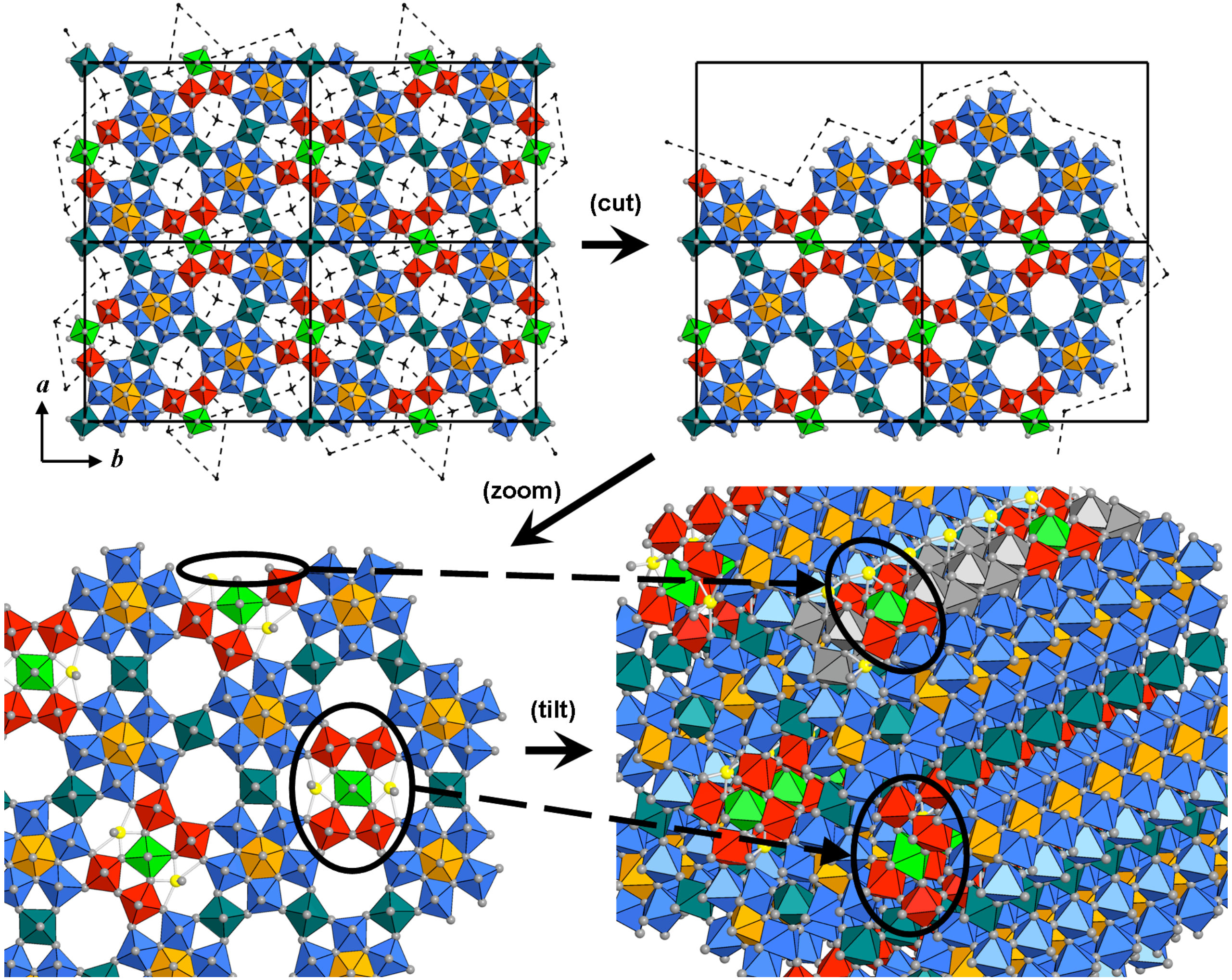


Figure 3. Possibilities for stabilizing polar surfaces: a) Charge reduction by removal of half of the O^{2-} ions. b) octopolar reconstruction. c) domain formation. d) adsorption.

H. Freund, Angew. Chem. Int. Ed. Engl. 36 (1997) 452.

Solid structures and termination



M1 termination, Frank Giergsdies, Wei Zhang, Angew. Chem. Int. Ed. Engl.12 (2010) 6220.

Solid structures and termination

- Most of the materials of interest in heterogeneous catalysis are polycrystalline 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

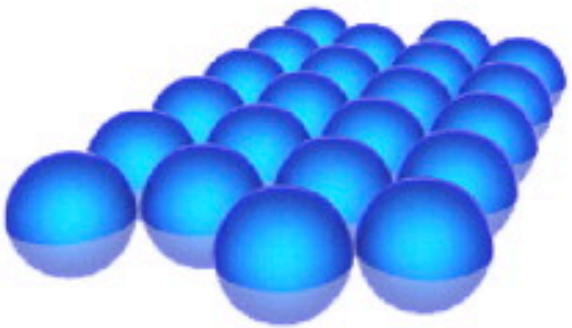
What is an active site?

Microscopic group of atoms, which determines the specific catalytic activity of the surface

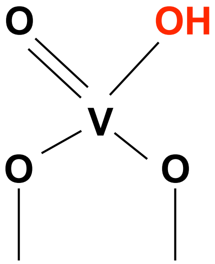
At the active sites, electron transfer between the catalyst surface and the reacting molecule happens that leads to structural rearrangement of the substrate molecule

- The active sites are formed during catalyst activation and forming and undergo 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

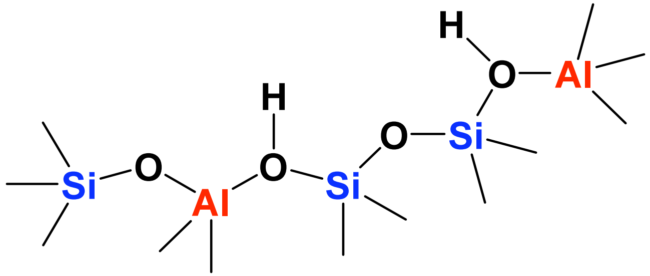
Examples for surface sites



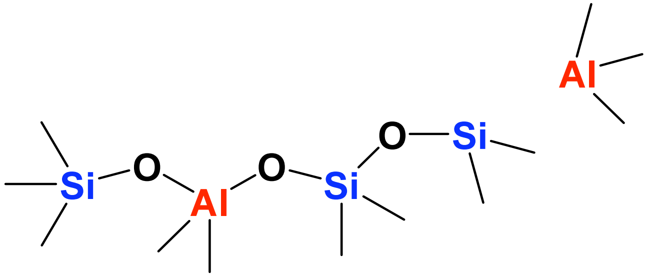
- surface sites of supported metal particles



- electron donating oxygen atoms

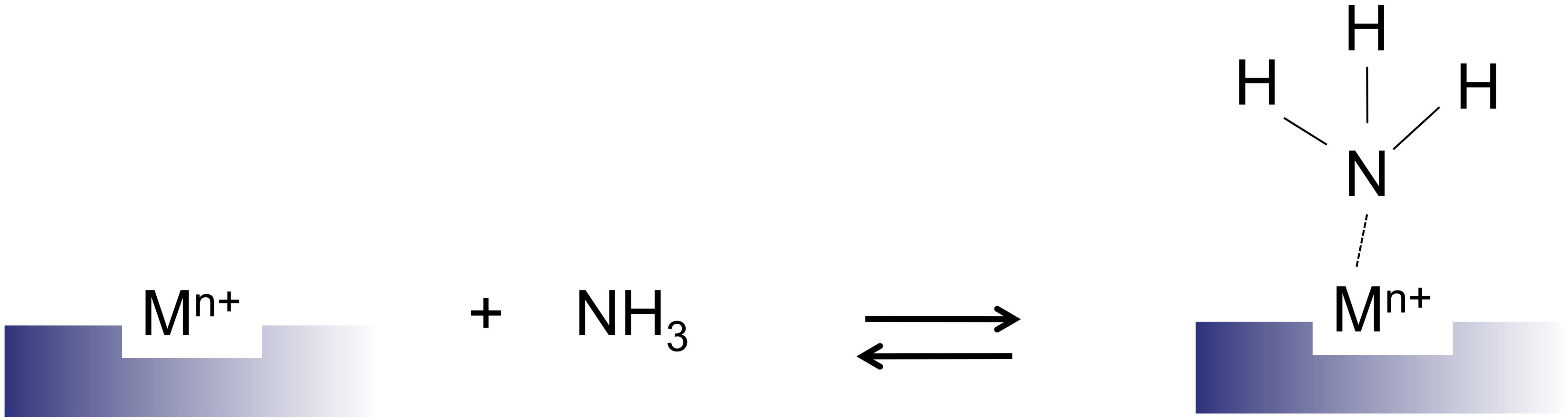


- hydroxyl-hydrate cover



- coordinatively unsaturated metal cations

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, ...

Background: Infrared spectra of oxide surfaces

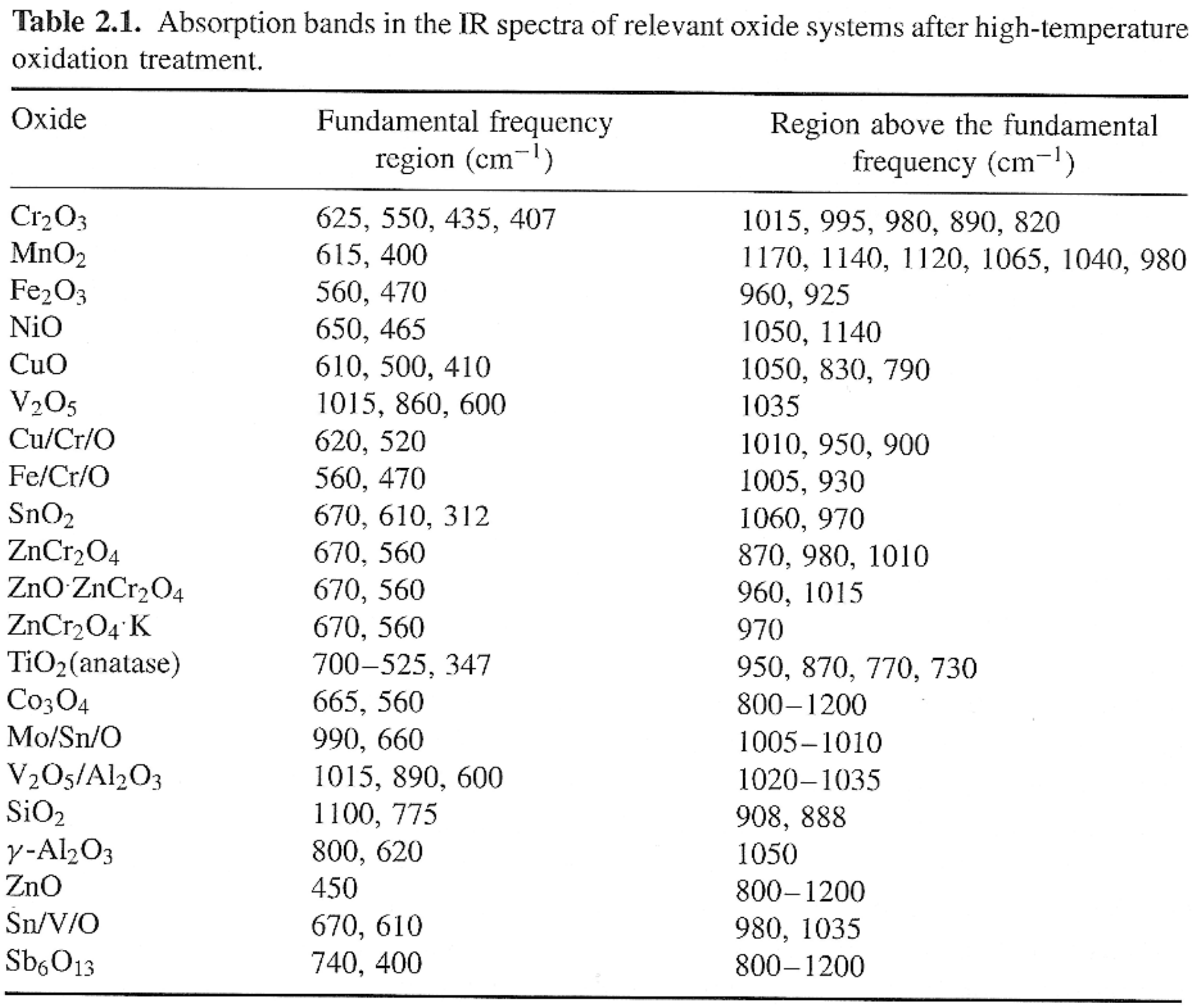


Table 2.1. Absorption bands in the IR spectra of relevant oxide systems after high-temperature oxidation treatment.

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

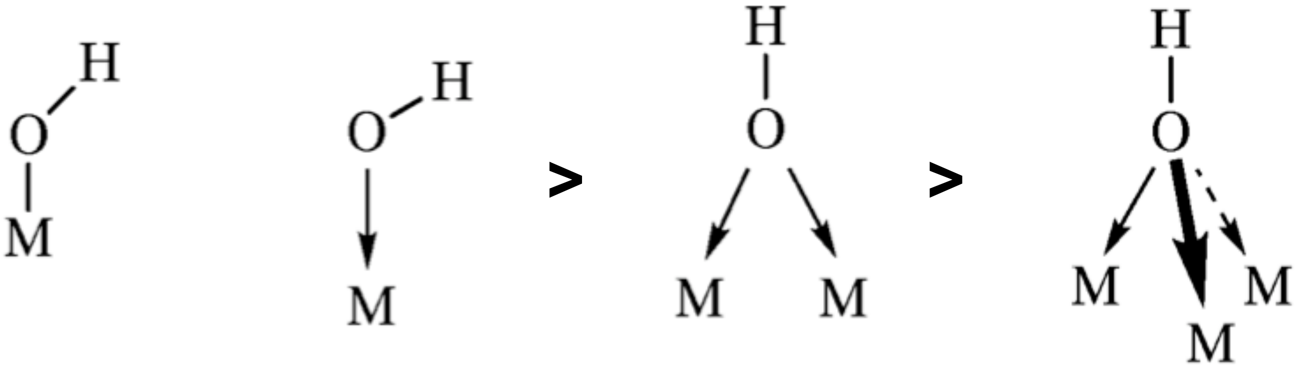
A. Davydov, Molecular Spectroscopy of Oxide Catalyst Surfaces, p. 32

Infrared spectra of oxide surfaces

- 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!

Surface hydroxyl groups

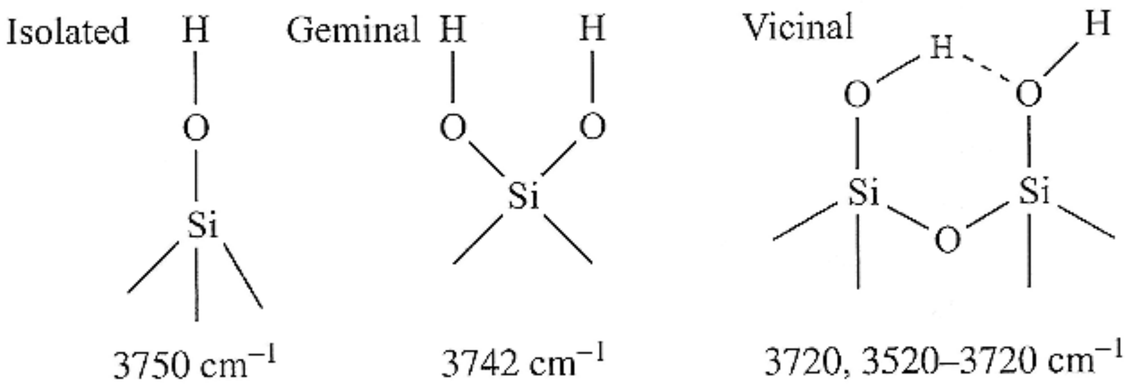
- Isolated hydroxyl groups are responsible for discrete absorption bands in the range 3800-3650 cm^{-1} (if not involved in hydrogen bonding)



- 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!)

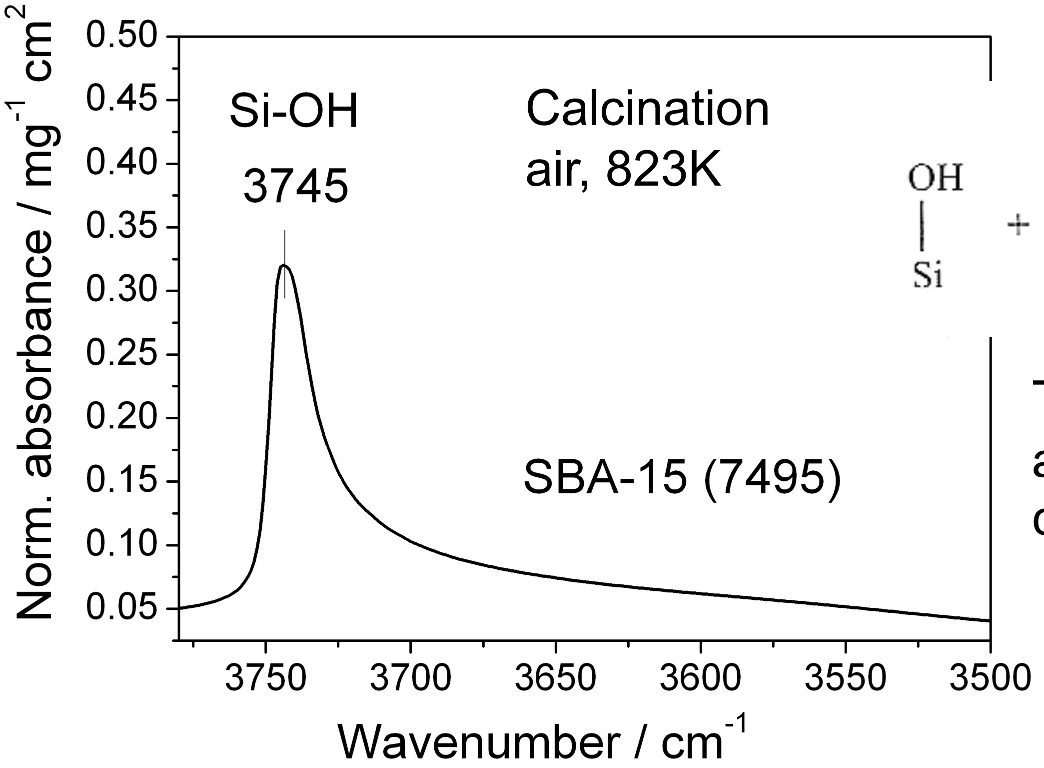


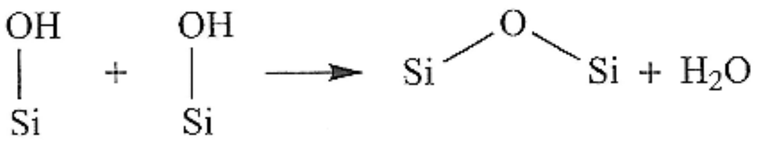
$vOH+\delta OH = 4550\ cm^{-1}$

(no combination band for molecular water in this range,

$H_2O\ v_1+v_2=5100\text{-}5300\ cm^{-1}$)

$\rho = 3 – 5\ OH\ nm^{-2}$



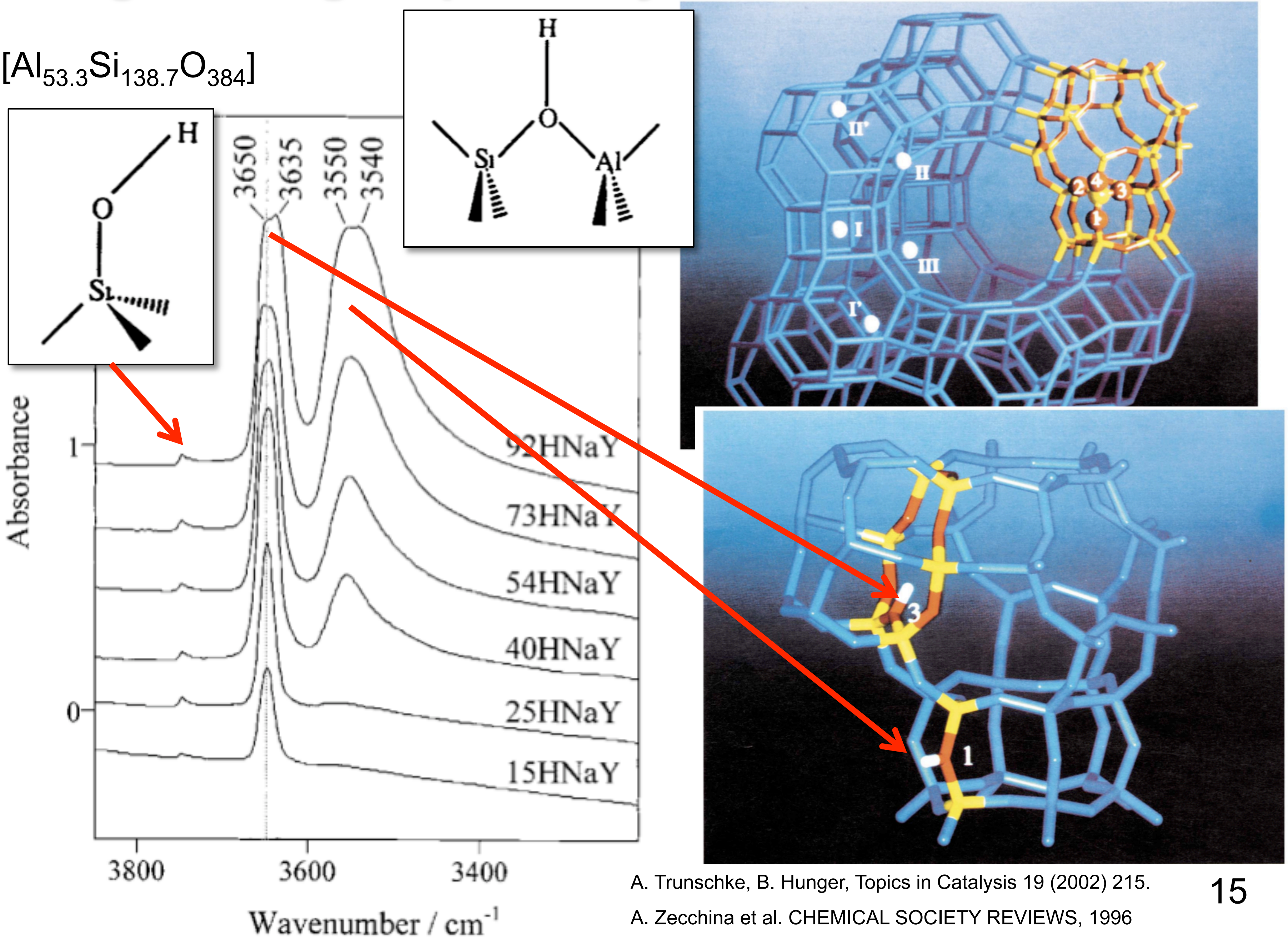


$$\mathrm{Si{-}OH} + \mathrm{Si{-}OH} \longrightarrow \mathrm{Si{-}O{-}Si} + H_2O$$

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

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.

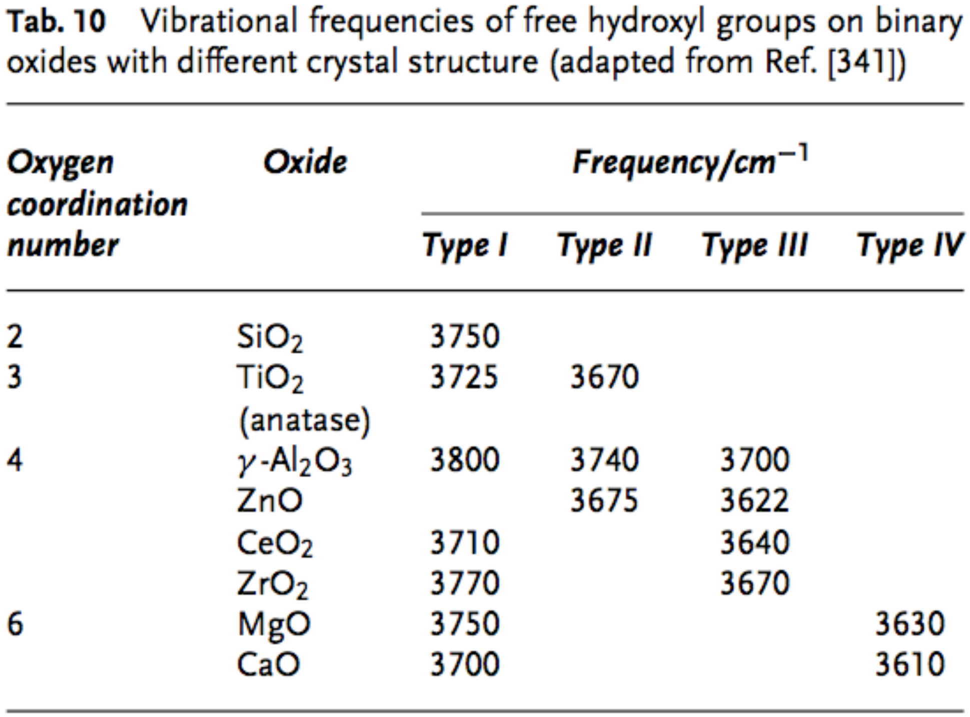
A. Zecchina et al. CHEMICAL SOCIETY REVIEWS, 1996

Positions of isolated OH groups for different oxides

oxide	**TiO_2**	**ZnO**	**MgO**	**Ga_2O_3**	**Fe_2O_3**	**ZrO_2**
OH (cm^{-1})	anatase 3728-15 3676-70 3640 rutile 3735-00 3685-70 3655-50	3680-60 3630-10	3750-30 3630-10	3670	haematite 3720 3700	3770 3670

A. Davydov, Molecular Spectroscopy of Oxide Catalyst Surfaces, p. 59

Positions of isolated OH groups for different oxides



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

- Relations between OH stretching frequency and chemical nature of the metal, structure and acidity are not straightforward
- OH band of MgO, amorphous silica and silica-alumina at 3745 ±3 cm^{-1}

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

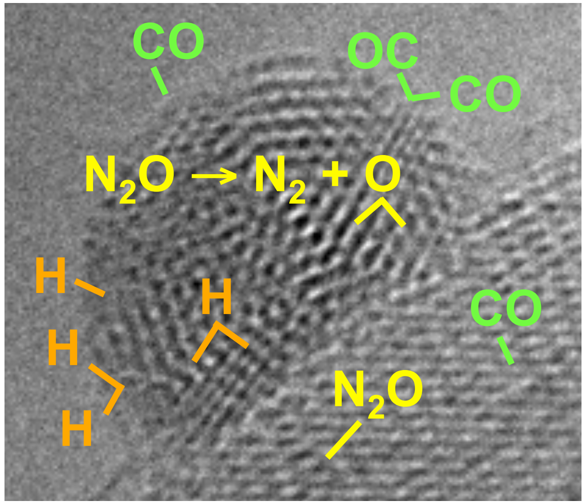
Surface hydroxyl groups

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 peaks
  - 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.

Probing surface sites by adsorption of small molecules



Retrievable information :

- Type of sites
- Number of sites
- Chemical (electronic) surface properties
- „Strength“ 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

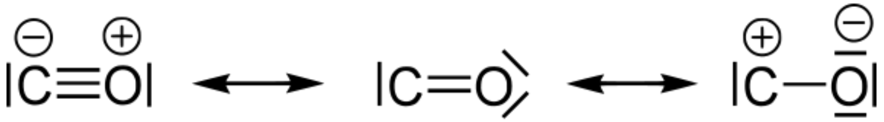
	hard	**soft**
acids	H^+, Li^+, Na^+, K^+ Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Mn^{2+} Sc^{3+}, Ga^{3+}, In^{3+}, La^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+}, As^{3+}, Ge^{3+}, Si^{4+}, Zr^{4+}, Th^{4+}, Ru^{4+}, UO_2^{2+}, $(CH_3)_2Sn^{2+}$, VO^{2+}, MoO^{3+} RCO^+, CO_2, NC^+	Cu^+, Ag^+, Au^+, Tl^+, Hg^+ Pd^{2+}, 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

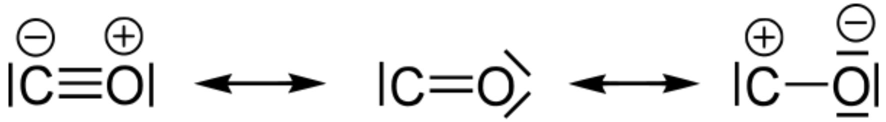
Carbon monoxide - a universal probe



Usage

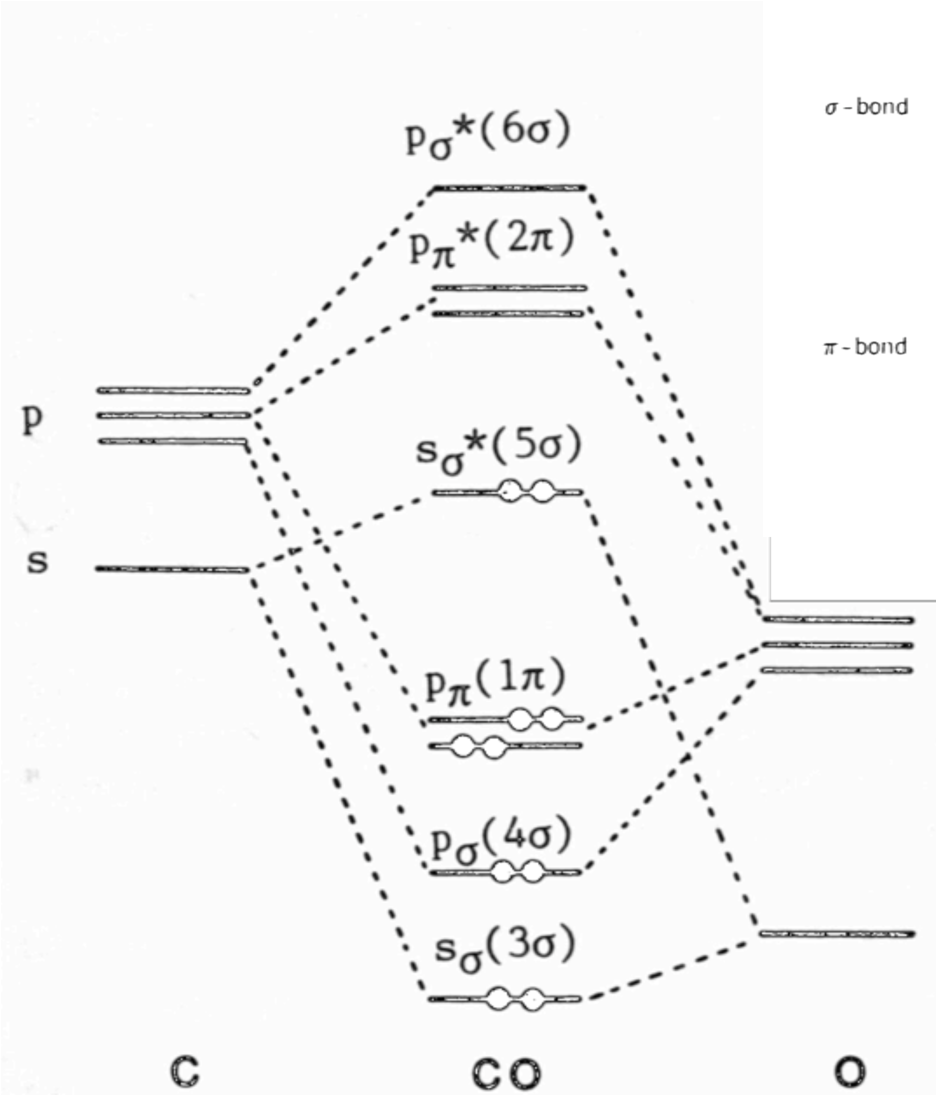
- Particle size, geometric and electronic structure of supported metal particles
- Promoter effects, metal-support interaction
- Oxidation state of coordinatively unsaturated surface cations
- Acid base properties

Carbon monoxide - a universal probe



- CO gas phase frequency 2143 cm^{-1}
- Adsorption at room temperature and 77 K, irreversible and reversible
- 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)
- CO can oxidize supported transition metals

Bonding of CO to transition metals



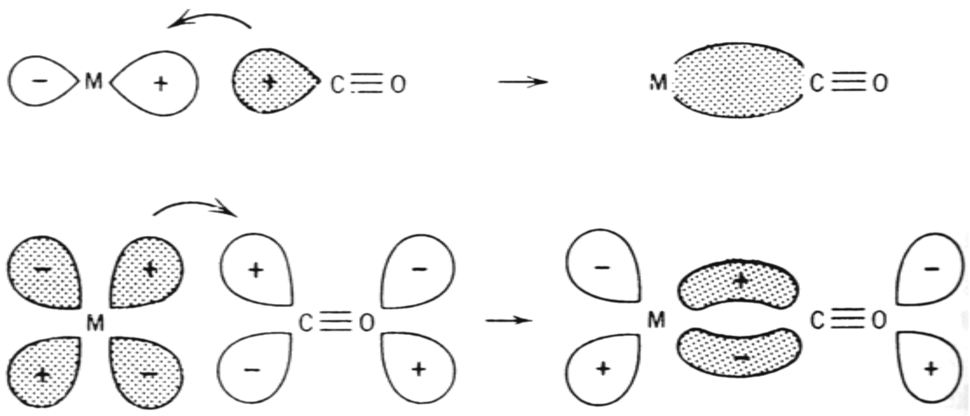
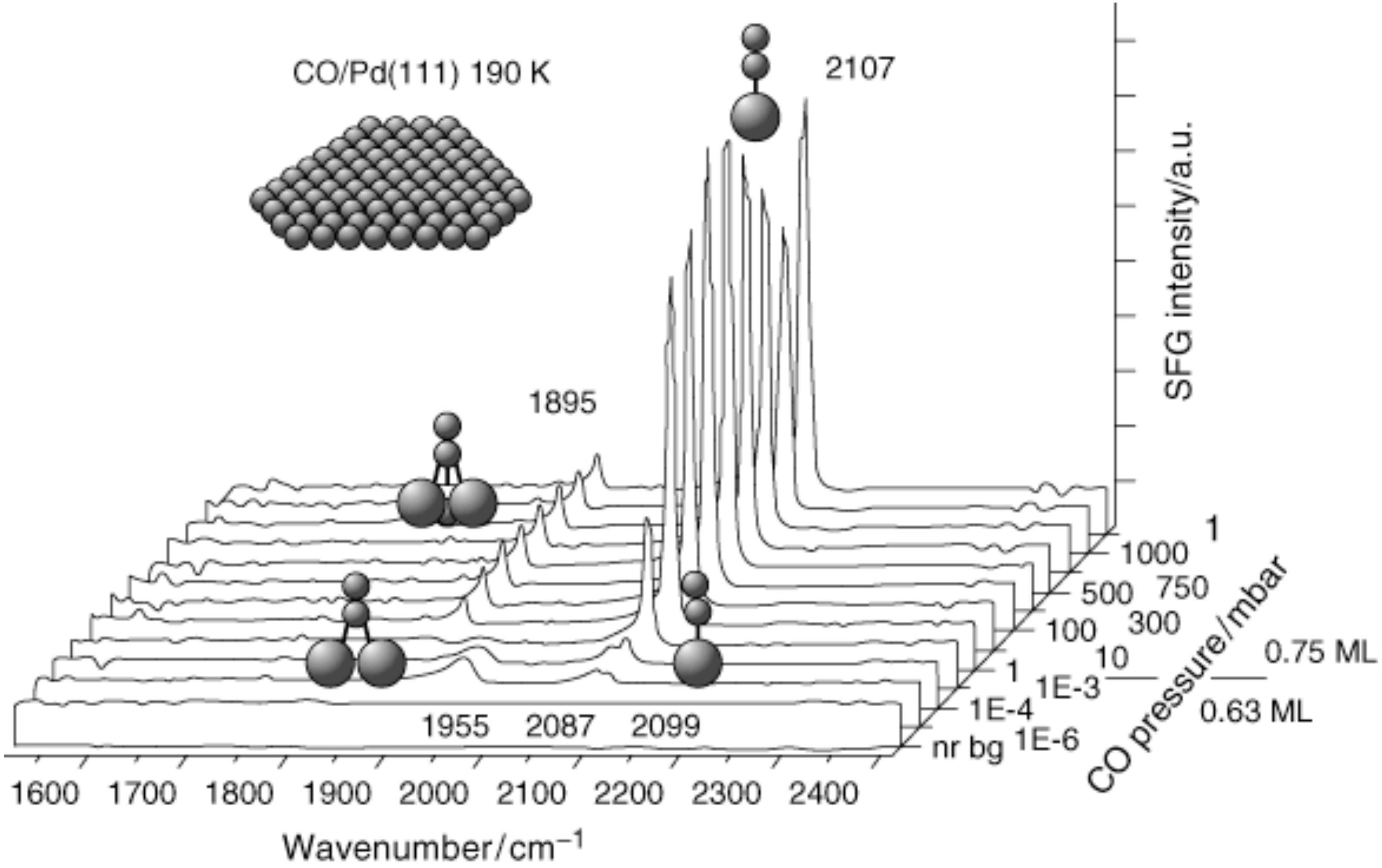


Fig. III-51. The σ- and π-bonding in metal carbonyls.

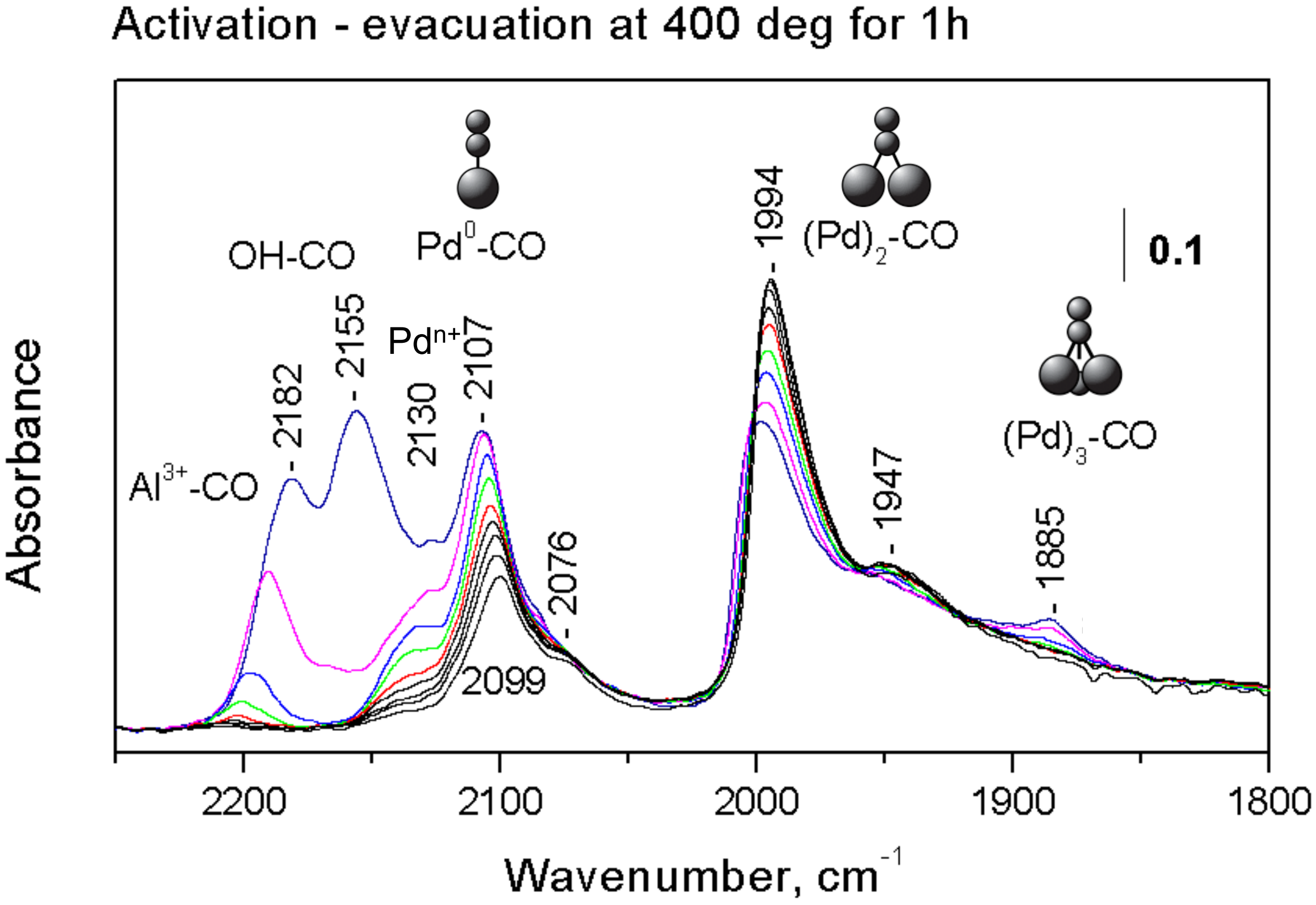
- CO gas phase frequency 2143 cm^{-1}
- Coordination to metals
  - σ-donor bond: ν↑
  - π-acceptor bond: ν↓

CO adsorption sites on metals



H. Freund, Chemisorption, Handbook of Heterogeneous Catalysis

CO adsorption sites on metal particles



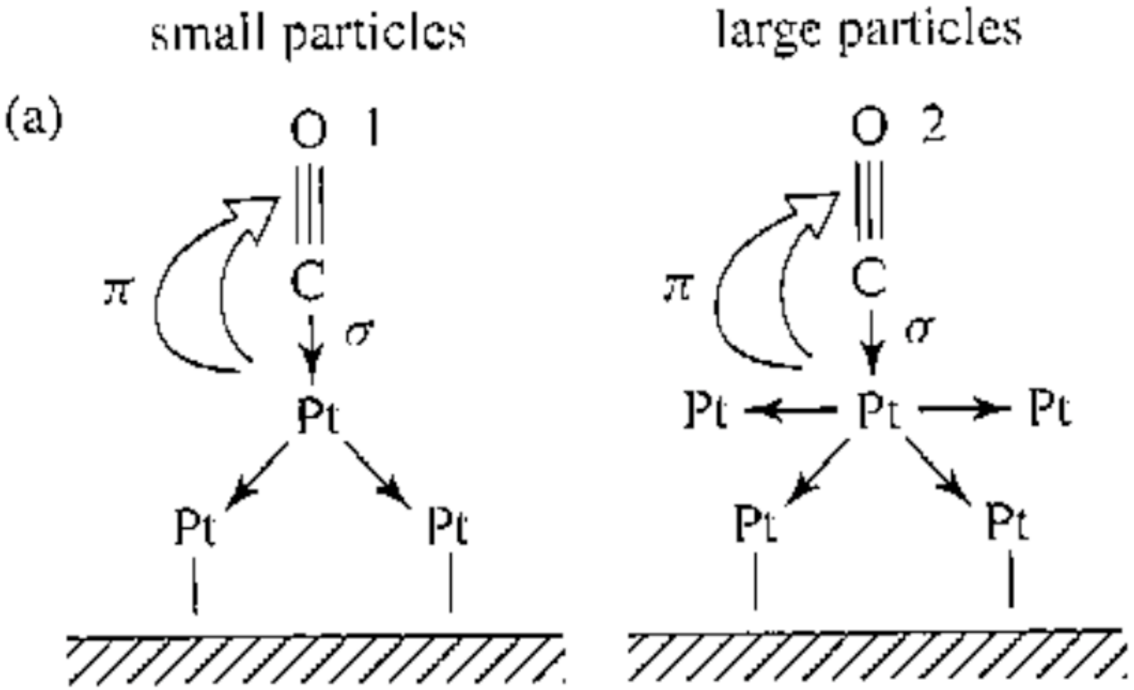
Adsorption of 1 mbar CO on Pd/Al_2O_3 at 77 K and evacuation at 77-124 K

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
    - Degree of π-bonding is higher with smaller metal coordination number

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
        - 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 supported metals

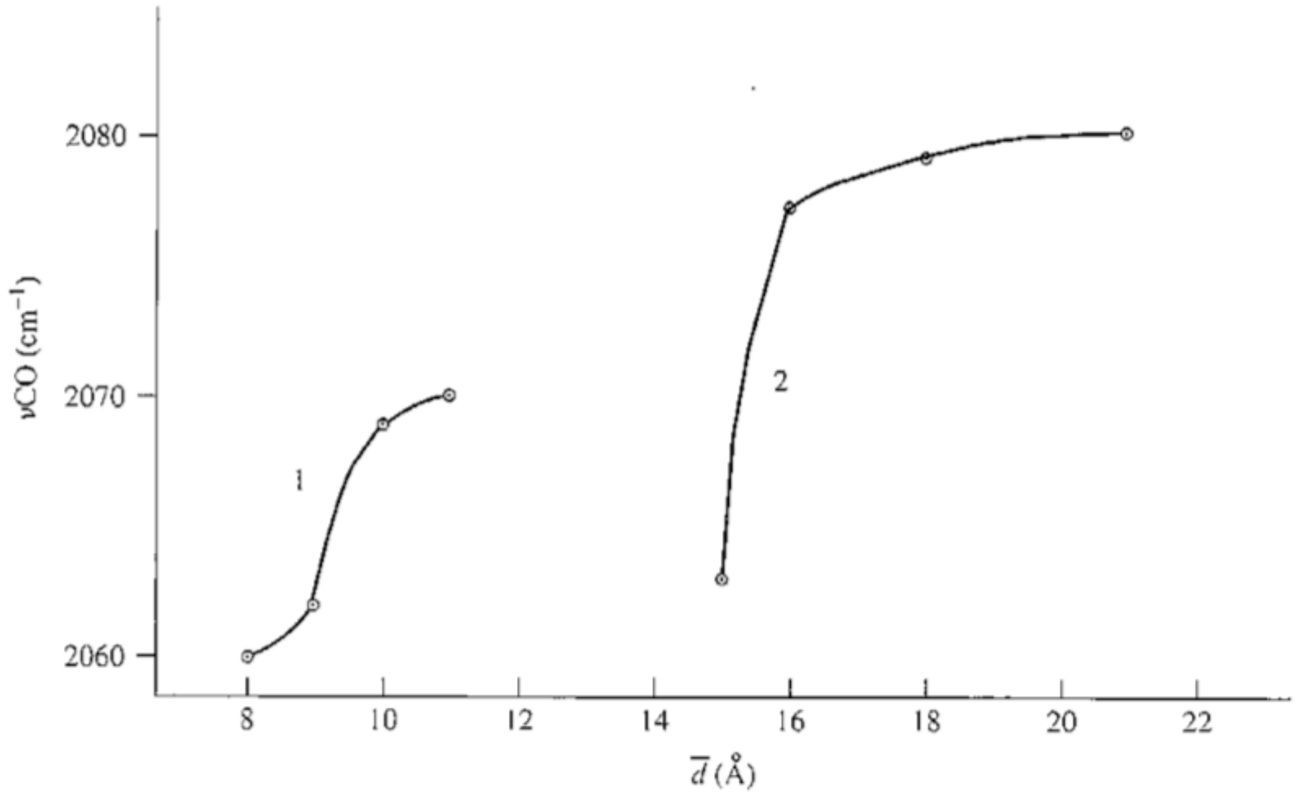
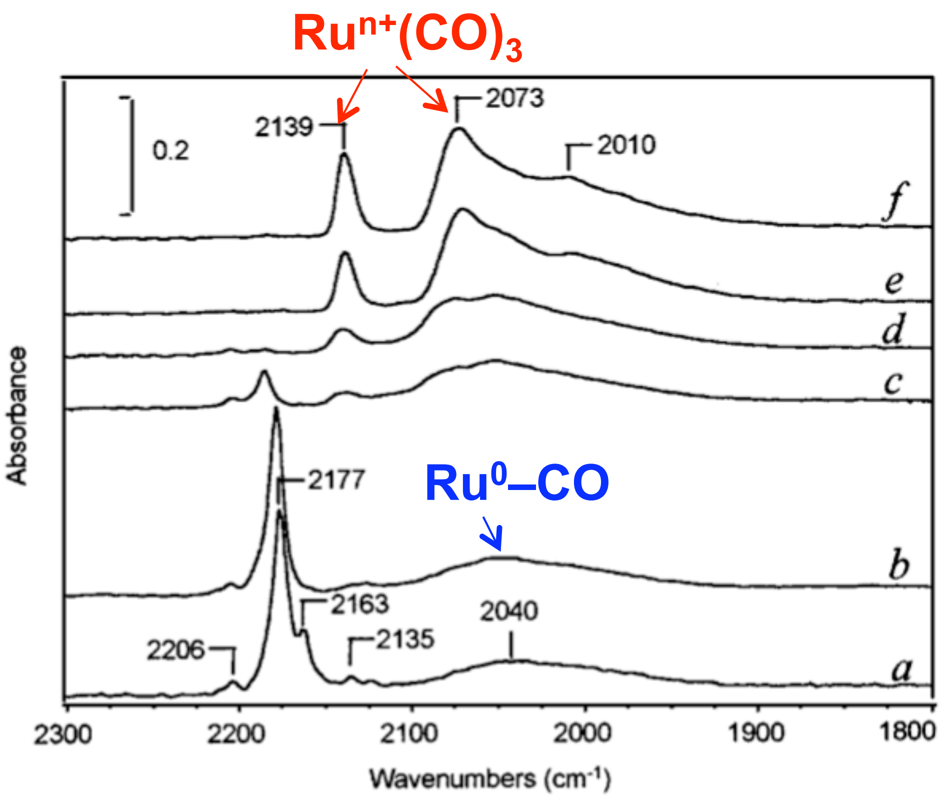


Figure 3.36. Dependence of the stretching vibrations of Pt–CO (at $\theta = 1$) on particle size for different supports: (1) Al_2O_3; (2) SiO_2.

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

CO adsorption on supported metals


$Ru^{n+}(CO)_3$

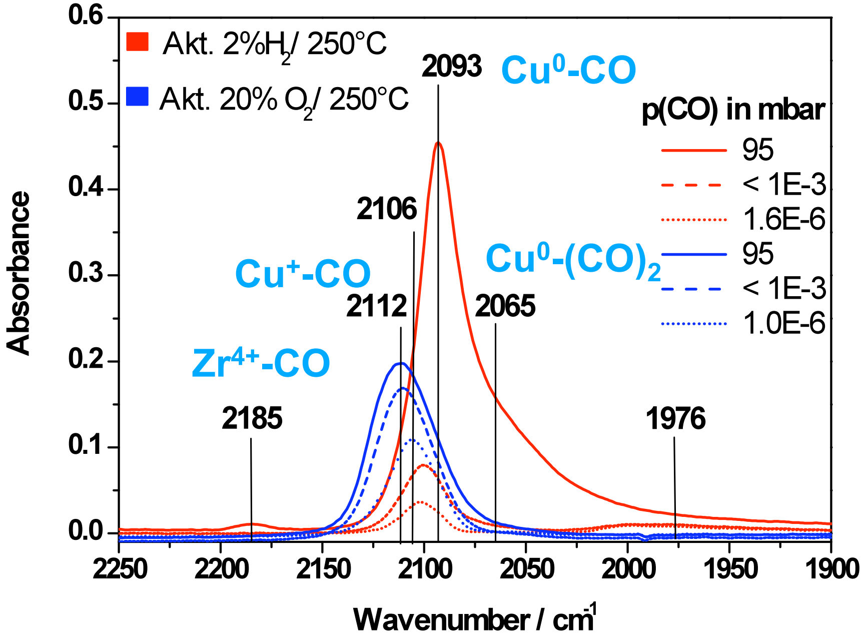
Ru^0–CO

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.).

„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^+

CO adsorption on coordinatively unsaturated (cus) vanadium ions

- Position of the adsorption band of the respective V^{n+}-CO
  - V^{4+}-CO at 2212 – 2180 cm^{-1}
  - V^{3+}-CO at 2197 – 2174 cm^{-1}
  - V^{2+}-CO at about 2150 cm^{-1}
- Stability of the respective adsorption complexes
  - $V^{4+}(3d^1 4s^0)$ - CO - only σ-bond
  - $V^{3+}(3d^2 4s^0)$ - CO – strong σ- and weak π-bond
  - $V^{2+}(3d^3 4s^0)$ - CO – synergism between σ- and π-components

$$V^{2+} > V^{3+} > V^{4+}$$

$$\xleftarrow{\hspace{4cm}}$$

Stability increase

CO adsorption on Lewis acid sites

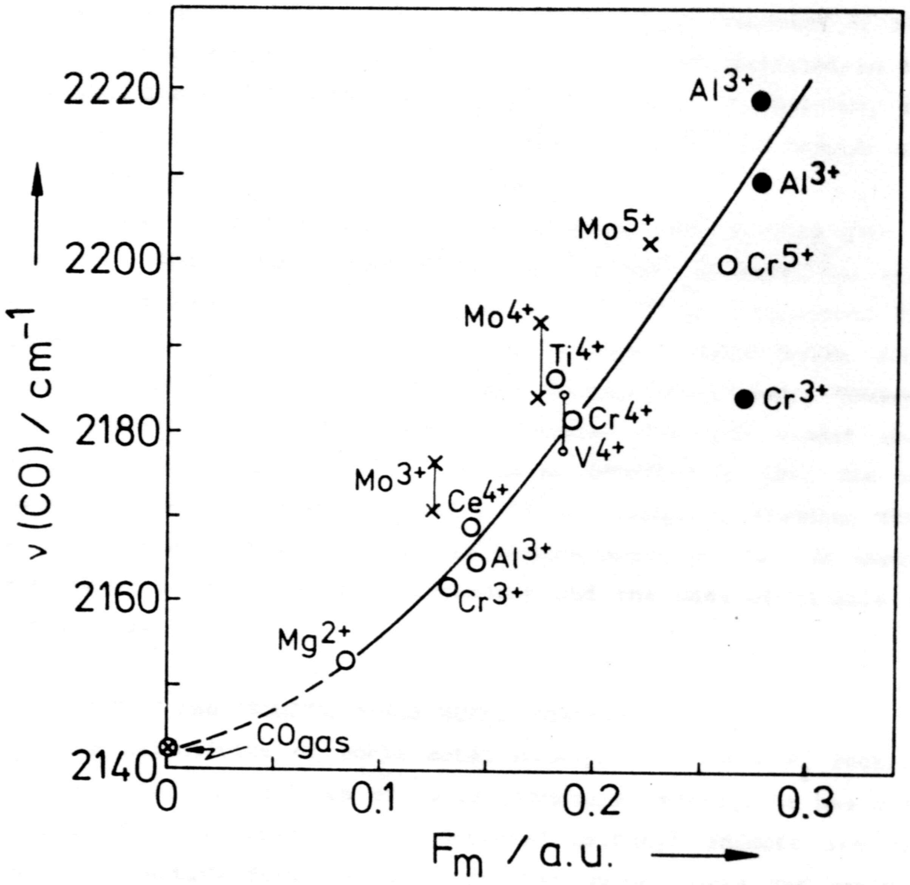


Fig. 5. Correlation of carbonyl stretching frequency of adsorbed CO with modified electric field strength F_m (equ. (v)). ○ :5-coordinate ions; ● :3-coordinate ions; x:5-coordinate Mo^{x+}, supported; o:5-coordinate V, supported.

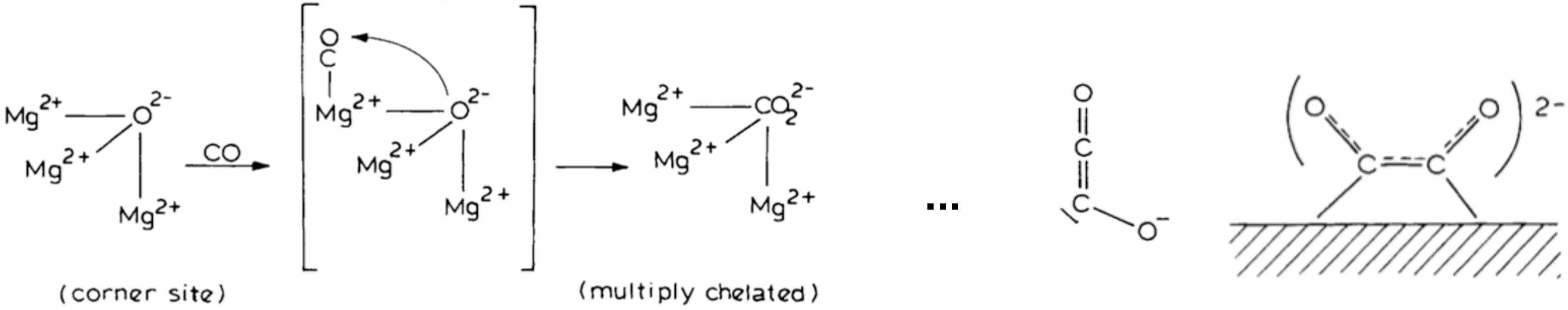
“Modified electric field strength”

$$F_m = Z/N \; * \; R_m^{-2}$$

Z: cation charge
N: coordination number in cus state
R_m: sum of effective ionic radius and van der Waals radius

H. Knözinger, Proc. Int. Symp. Acid-Base Catalysis Sapporo 1988
Eds. K. Tanabe, H. Hattori, T. Yamaguchi, T. Tanaka

CO adsorption on alkaline earth oxides



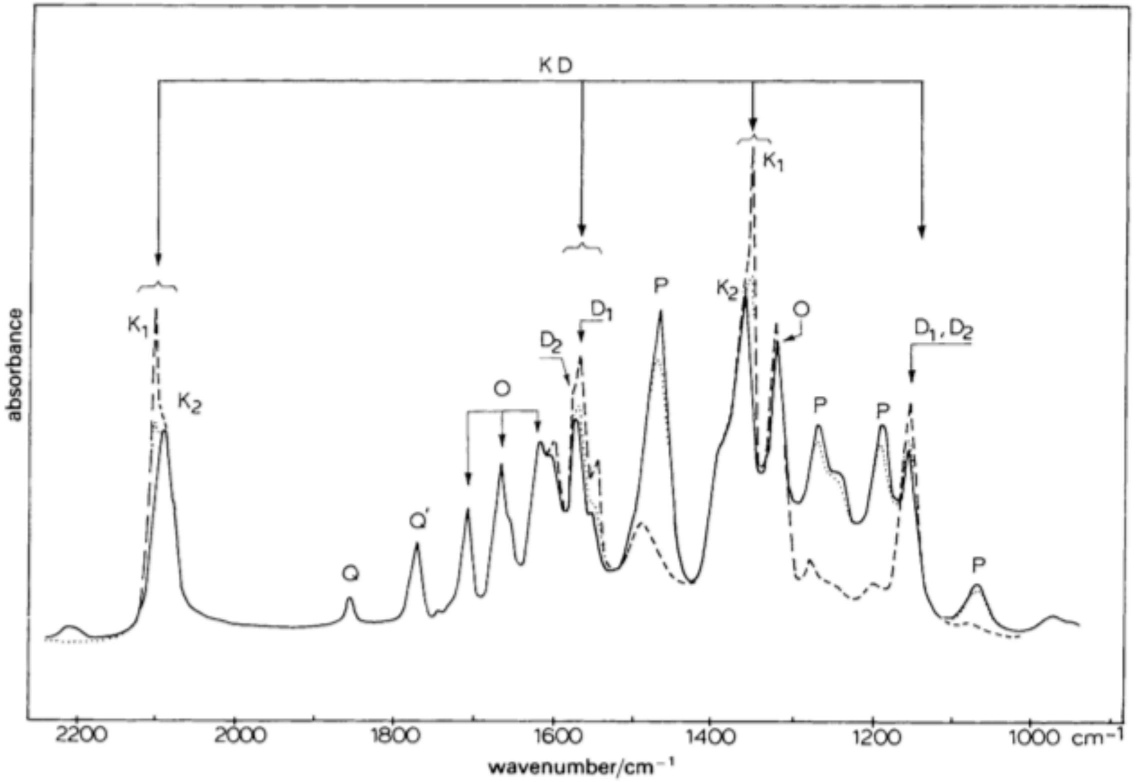


Fig. 1. Interconversion of surface species by progressive decarbonylation: (——) full coverage at room temperature (in the presence of 40 Torr CO), (· · ·) after outgassing 5 min at room temperature, (– – –) after outgassing 30 min at 373 K. Readmission of CO restores the original spectrum (——).

A. Zecchina et al., J. CHEM. SOC. FARADAY TRANS., 1990, 86(4), 703-709

Carbon monoxide - a universal probe

- When substantial d to π* back donation takes place, CO adsorptions are detected below 2100 cm^{-1}
- The surface carbonyl complexes can have linear (2100-1900 cm^{-1}), bridged (below 1900 cm^{-1}), or three coordinated bridged (below 1800 cm^{-1}) structures
- With coordinatively unsaturated ions, poly-carbonyl complexes can be formed

- Frequency shift above the 2143 cm^{-1} is due to primarily σ* to d donation
- The corresponding complexes with surface cations are terminal and C-bonded
- The frequency shift increases with increase in the ratio of charge to the cation radius

- Carbon monoxide molecules σ-bonded to cations adjacent to anion sites of enhanced basicity can undergo nucleophilic attac forming complex surface species (CO_2^{2-}, CO_3^{2-})

NO adsorption

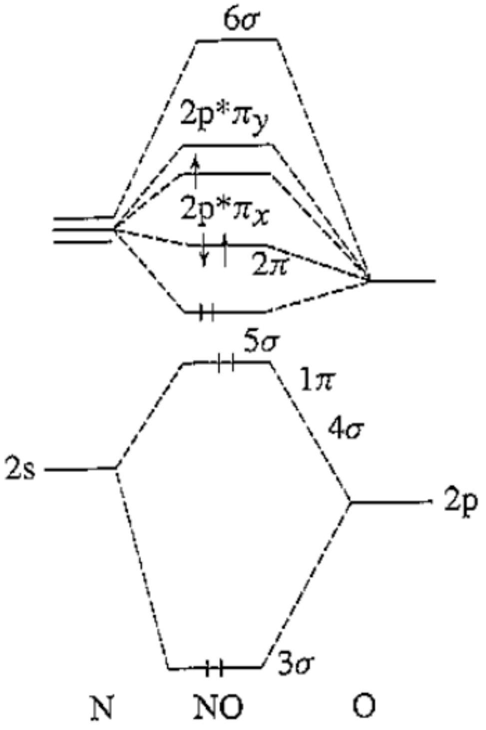


Figure 2.33 Scheme of NO molecular orbitals.

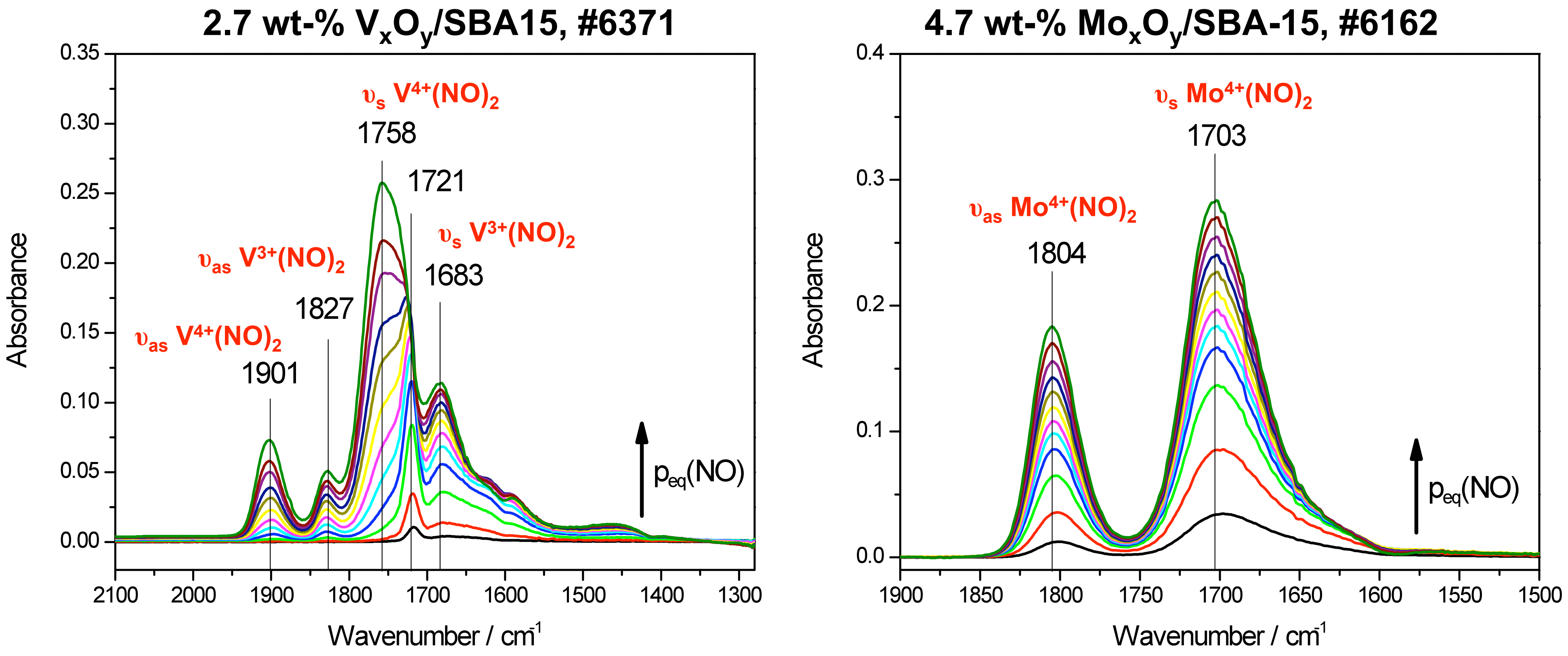
Types of adsorption

- M^{n+} + NO $M^{(n-1)+}$-NO^{+}
- M^{n+} + NO $M^{(n+1)+}$-NO^{-}
- Formation of a coordination bond via the N-atom
- interpretation of spectra more complicated than in case of CO and requires application of complementary methods

compound	frequency (cm^{-1})
$NO^{+}HSO_4^{-}$	2340
NO (gas)	1876
$Li^{+}NO^{-}$	1352

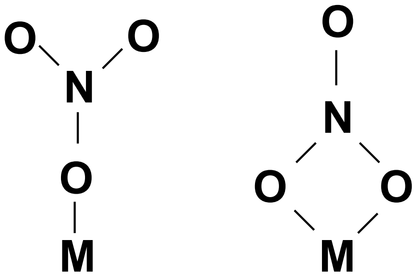
NO stretching vibrations in inorganic model compounds

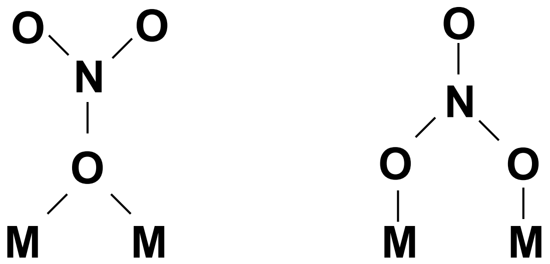
NO adsorption on cus cations



- NO adsorption on reduced V and Mo species leads to formation of dinitrosyl complexes
- Band positions of the NO vibrations characterize the oxidation states of vanadium and molybdenum sites

NO adsorption





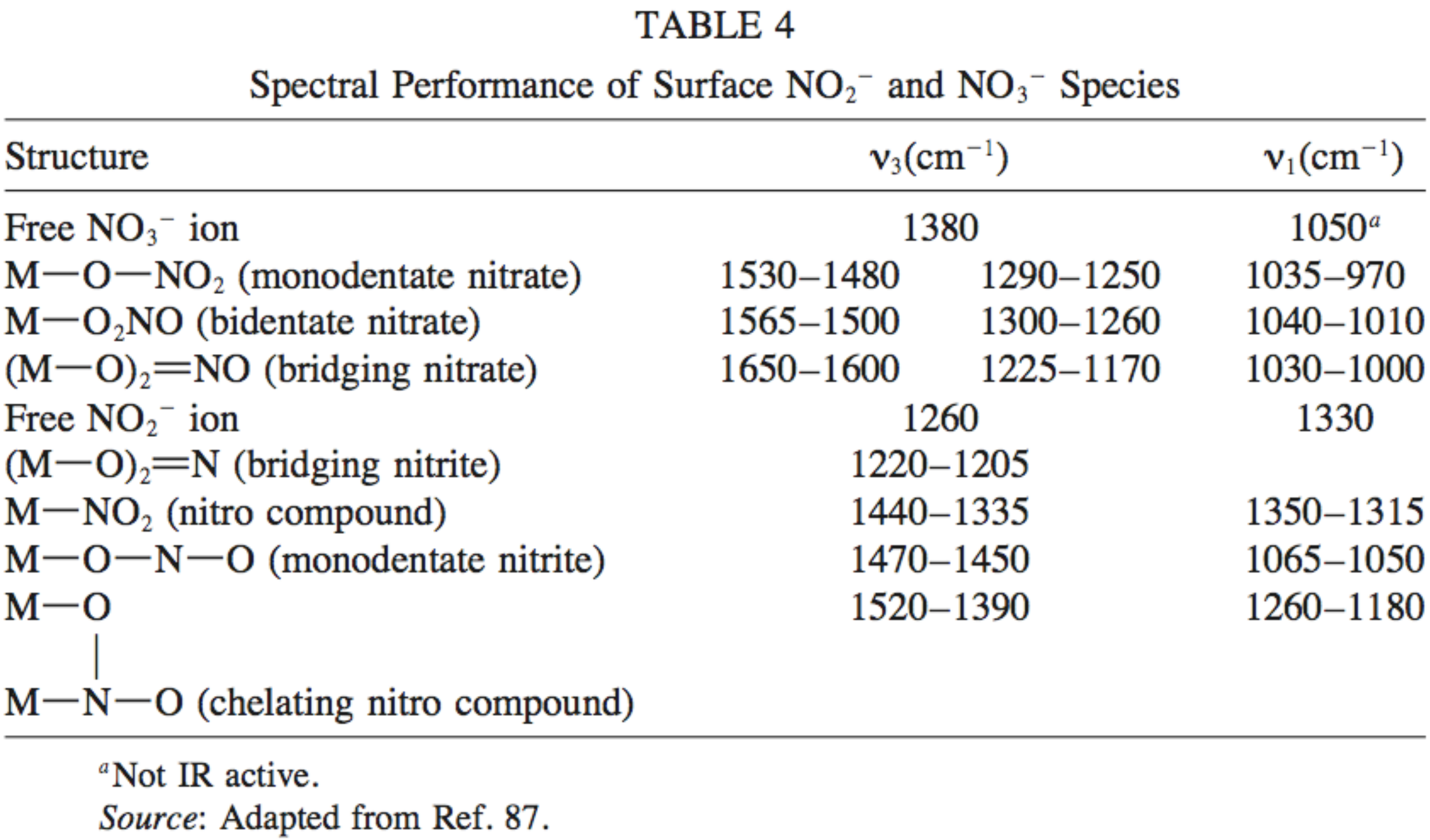


TABLE 4

Spectral Performance of Surface NO_2^- and NO_3^- Species

Structure	$\nu_3(cm^{-1})$		$\nu_1(cm^{-1})$
Free NO_3^- ion	1380		1050[a]
M—O—NO_2 (monodentate nitrate)	1530–1480	1290–1250	1035–970
M—O_2NO (bidentate nitrate)	1565–1500	1300–1260	1040–1010
$(M—O)_2$═NO (bridging nitrate)	1650–1600	1225–1170	1030–1000
Free NO_2^- ion	1260		1330
$(M—O)_2$═N (bridging nitrite)	1220–1205		
M—NO_2 (nitro compound)	1440–1335		1350–1315
M—O—N—O (monodentate nitrite)	1470–1450		1065–1050
M—O | M—N—O (chelating nitro compound)	1520–1390		1260–1180

[a] Not IR active.

Source: Adapted from Ref. 87.

Hadjiivanov, Konstantin I.(2000) „Identification of Neutral and Charged NxOy Surface Species by IR Spectroscopy“, Catalysis Reviews, 42: 1, 71 — 144

Probing surface acidity

- Brønsted acidity:
  - Protonation of the probe
  - Change in the OH frequency by disturbing the OH group with a base
- Lewis acidity – investigation of the complexing ability of the cation

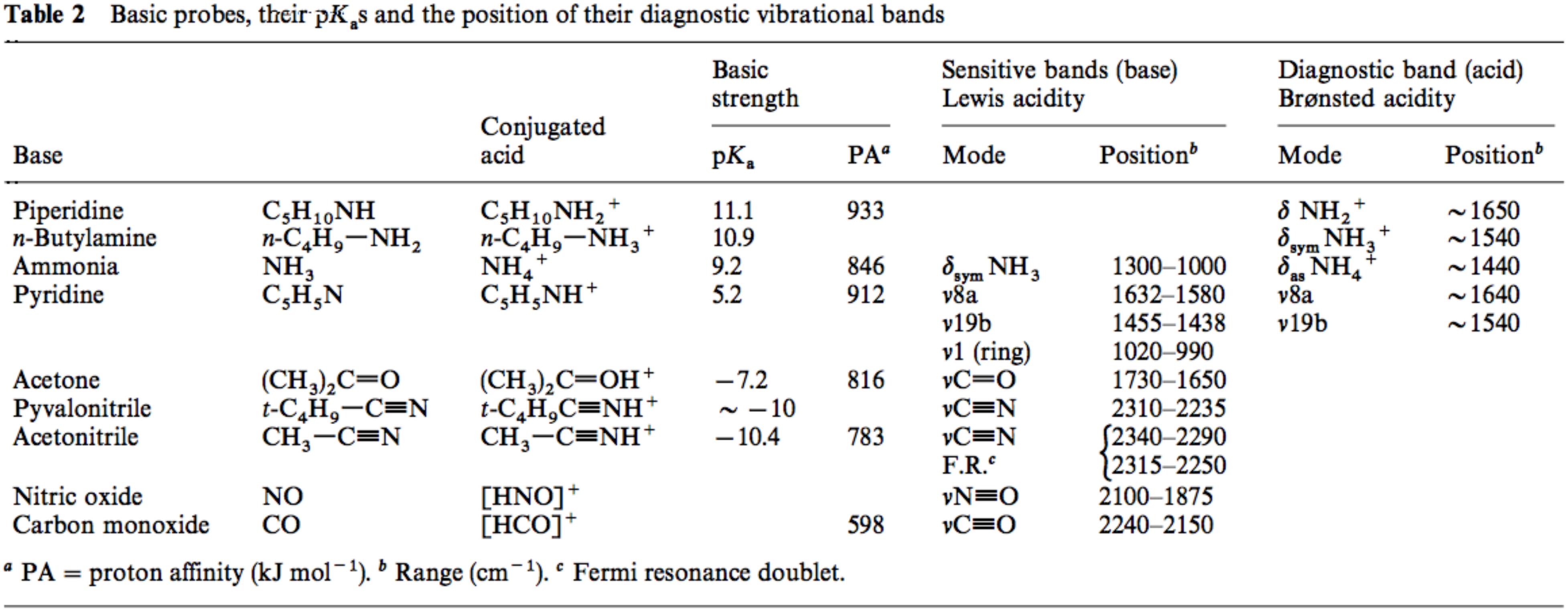


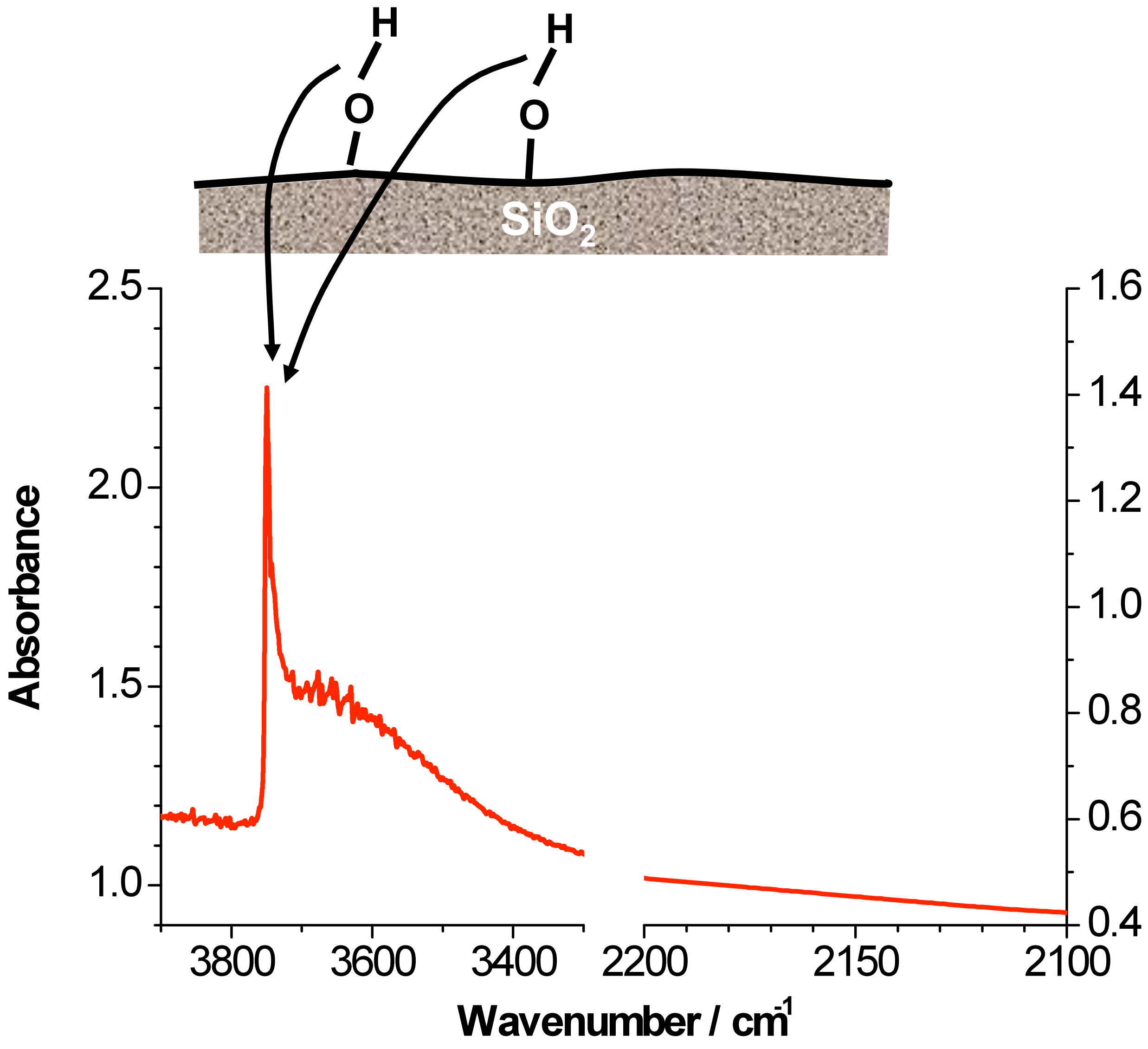
Table 2 Basic probes, their pK_as and the position of their diagnostic vibrational bands

			Basic strength		Sensitive bands (base) Lewis acidity		Diagnostic band (acid) Brønsted acidity	
Base		Conjugated acid	pK_a	PA[a]	Mode	Position[b]	Mode	Position[b]
Piperidine	$C_5H_{10}NH$	$C_5H_{10}NH_2^+$	11.1	933			δ NH_2^+	~1650
n-Butylamine	n-C_4H_9—NH_2	n-C_4H_9—NH_3^+	10.9				δ_{sym} NH_3^+	~1540
Ammonia	NH_3	NH_4^+	9.2	846	δ_{sym} NH_3	1300–1000	δ_{as} NH_4^+	~1440
Pyridine	C_5H_5N	$C_5H_5NH^+$	5.2	912	ν8a	1632–1580	ν8a	~1640
					ν19b	1455–1438	ν19b	~1540
					ν1 (ring)	1020–990		
Acetone	$(CH_3)_2C{=}O$	$(CH_3)_2C{=}OH^+$	−7.2	816	νC=O	1730–1650		
Pyvalonitrile	t-C_4H_9—$C{\equiv}N$	t-$C_4H_9C{\equiv}NH^+$	~ −10		νC≡N	2310–2235		
Acetonitrile	CH_3—$C{\equiv}N$	CH_3—$C{\equiv}NH^+$	−10.4	783	νC≡N	2340–2290		
					F.R.[c]	2315–2250		
Nitric oxide	NO	$[HNO]^+$			νN≡O	2100–1875		
Carbon monoxide	CO	$[HCO]^+$		598	νC≡O	2240–2150		

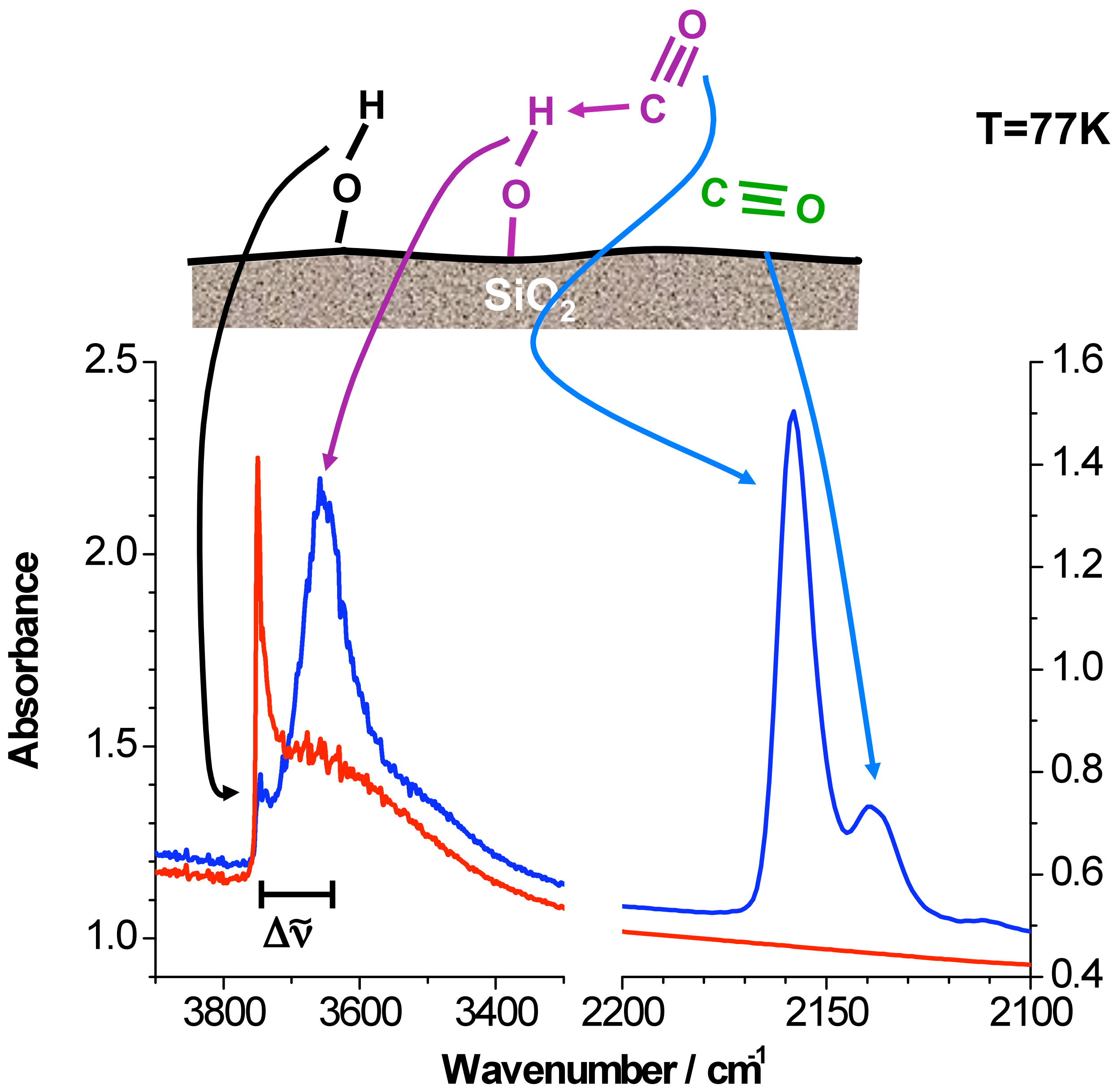
[a] PA = proton affinity (kJ mol^{-1}). [b] Range (cm^{-1}). [c] Fermi resonance doublet.

G. Busca, PCCP 1 (1999) 723.

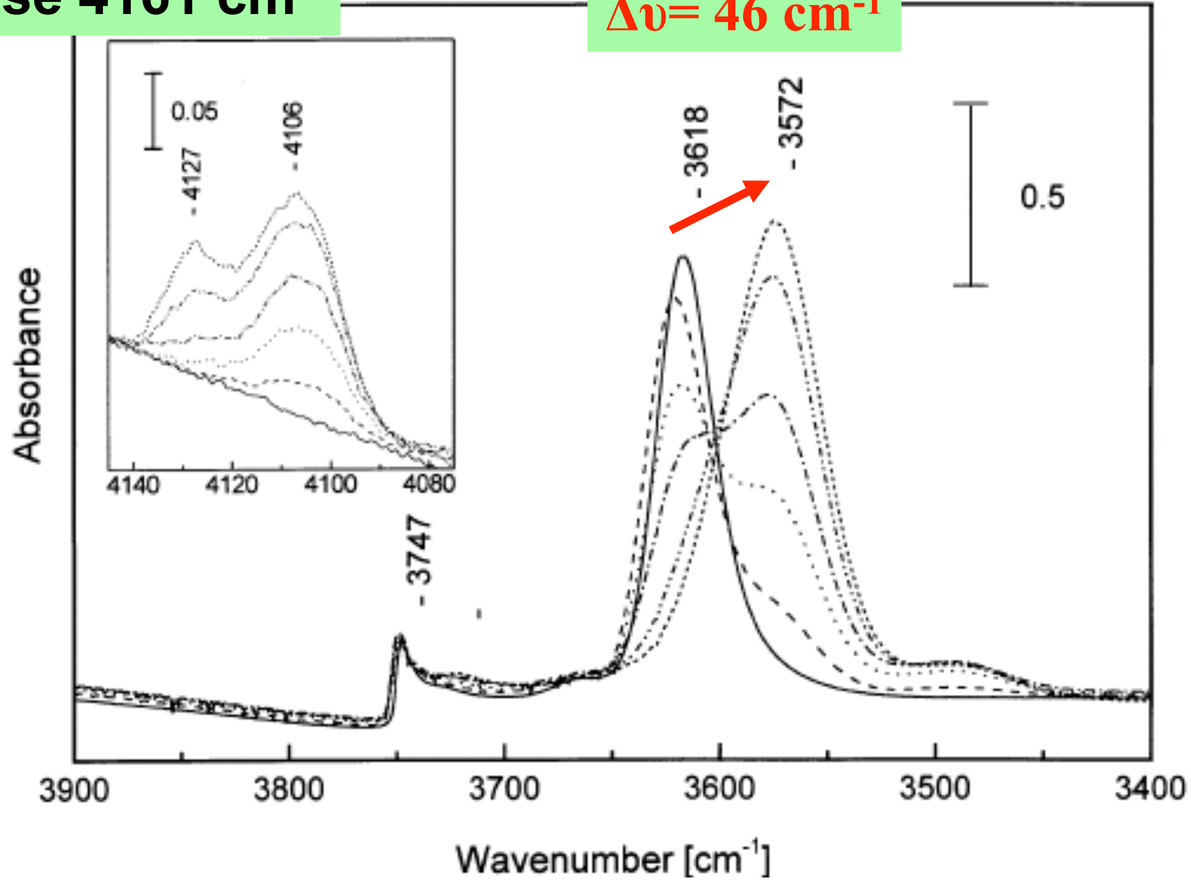
Interaction of CO with protons



Interaction of CO with protons



Adsorption of hydrogen



H_2 Gas Phase 4161 cm^{-1}

Δυ= 46 cm^{-1}

Figure 1. (a) Low-temperature adsorption of hydrogen: Infrared spectra of the OH and HH region (inset) of [Al]-HZSM-5 at 85 K: (——) vacuum, (- - -) 5.0 hPa H_2, (· · ·) 20 hPa H_2, (-·-) 50 hPa H_2, (-·-··) 200 hPa H_2, (- - - -) 500 hPa H_2. (b) Corresponding difference spectra after subtraction of the background spectrum of the zeolite.

Sigl et al. Catal. Lett. 45 (1997) 27-33.

Comparison of CO, N_2, H_2, and D_2 adsorption

Summary of experimental infrared frequency shifts for adsorption of CO, N_2, H_2 and D_2 on [Al]-, [Ga]- and [Fe]-HZSM-5

	IR-frequency/acidic hydroxyl groups (cm^{-1})					IR-frequency shift/probe molecules (cm^{-1})			
	$\nu_{initial}$	$\Delta\nu_{+CO}$	$\Delta\nu_{+N_2}$	$\Delta\nu_{+H_2}$	$\Delta\nu_{+D_2}$	$\Delta\nu$(C–O)	$\Delta\nu$(N–N)	$\Delta\nu$(H–H)	$\Delta\nu$(D–D)
[Al]-HZSM-5	3618	−313 [a]	−109 [b]	−45	−52	+32 [a]	+2 [b]	−55	−40
[Ga]-HZSM-5	3622	−291 [a]		−35	−41	+29 [a]		−50	−37
[Fe]-HZSM-5	3637	−289		−37	−44			−50	−33

- The ΔvOH values for H_2, N_2, and CO probe molecules correlate with their respective PA values

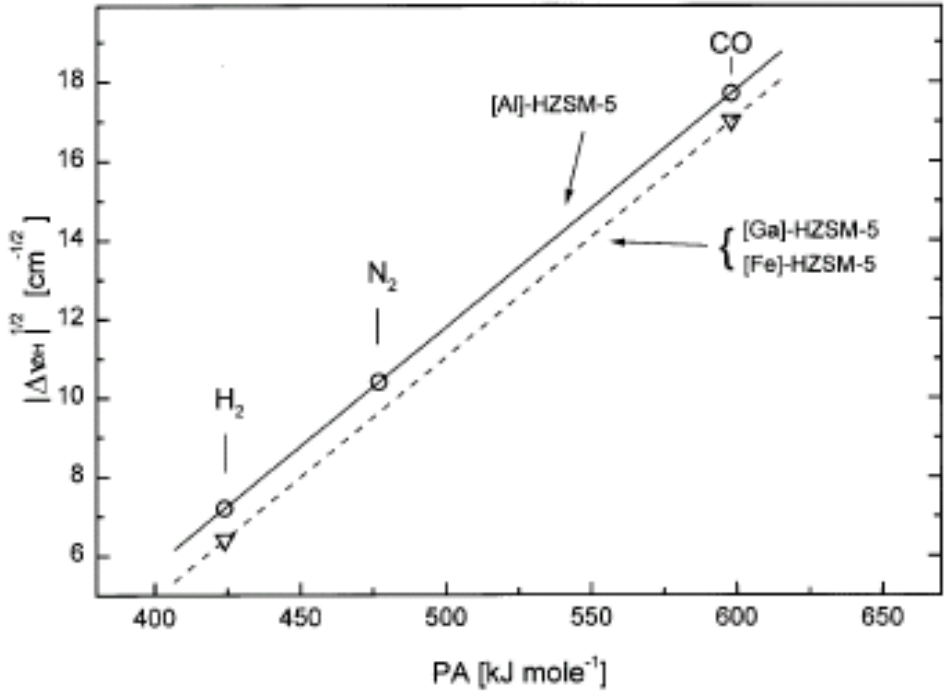


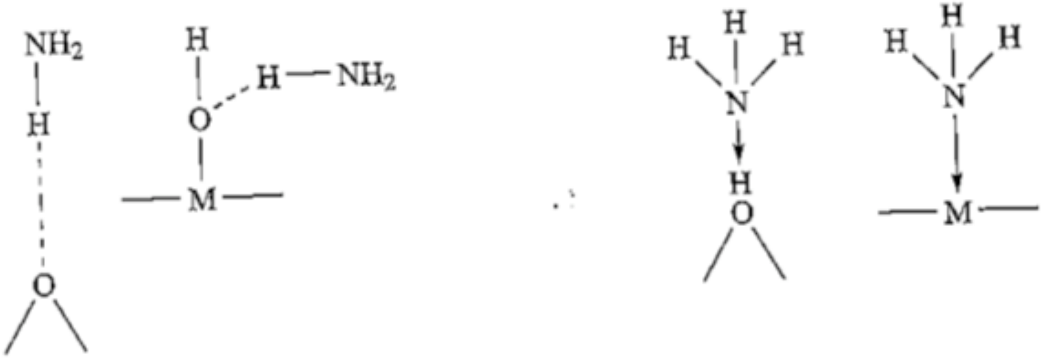
Figure 4. Correlation of $|\Delta\nu_{OH}|^{1/2}$ and the proton affinities PA of H_2, N_2 and CO.

Sigl et al. Catal. Lett. 45 (1997) 27-33.

Adsorption of ammonia

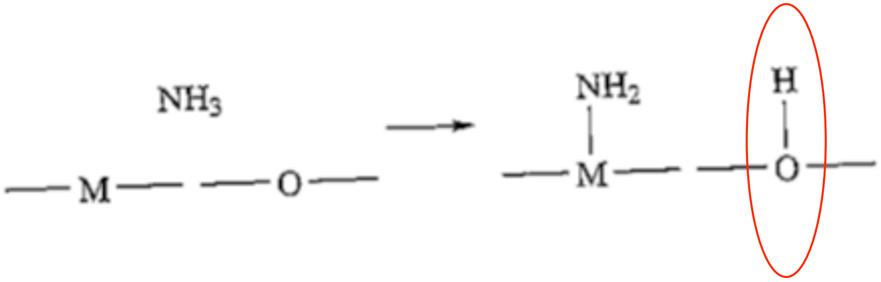
free ammonia: v_4 (δ_{as}) = 1400 cm^{-1}

protonation to NH_4^+: v_4 (δ_{as}) = 1440 cm^{-1}



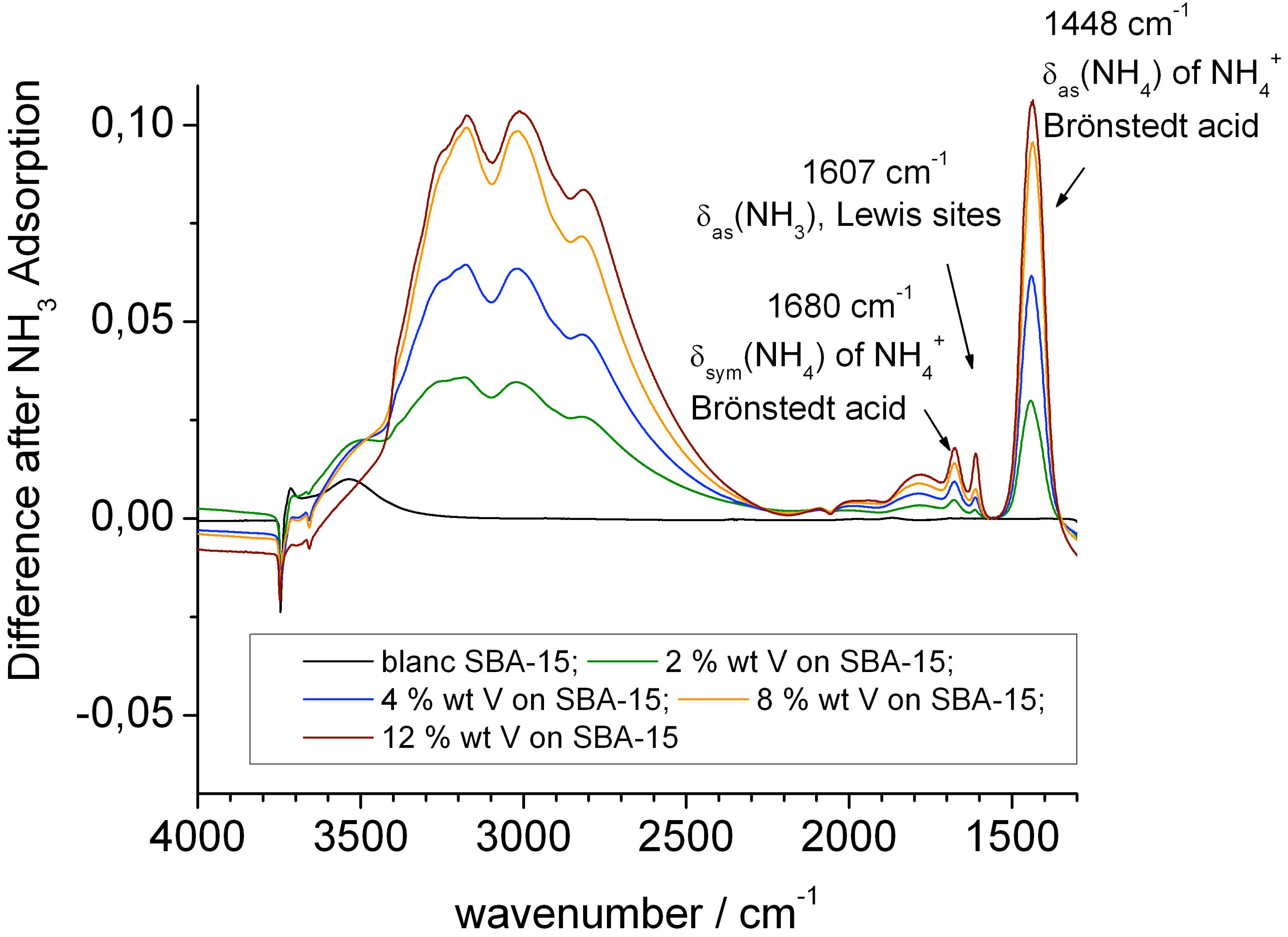
Lewis acid sites: NH_3: v_2 (δ_s) = 1300-1000 cm^{-1}

δ NH_2 = 1490-1630 cm^{-1}



A. Davydov, Molecular Spectroscopy of Oxide Catalyst Surfaces, p. 80

Adsorption of ammonia



Adsorption of ammonia

BUDNEVA *et al.*: *ACID CENTERS*

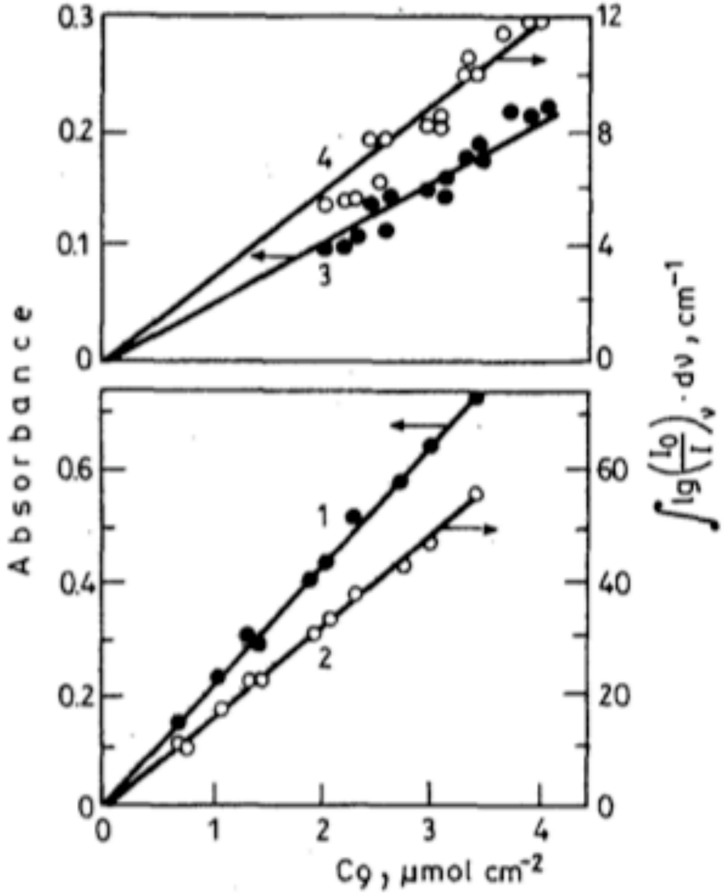


Fig. 2. Variations of absorption and integral absorption bands at 1430 cm^{-1} (1-2) and 1250 cm^{-1} (3-4) against concentration of adsorbed NH_3 on 10 wt.% V_2O_5/Al_2O_3

ammonium ions:

$\varepsilon_{1430} = 2.15 \times 10^5$ cm^2/mol

coordinated ammonia:

$\varepsilon_{1610} = 5.9 \times 10^5$ cm^2/mol

Budneva et al., React. Kinet. Catal. Lett. 34(1987) 63-67.

TPD of ammonia on Y-type zeolites (FAU)

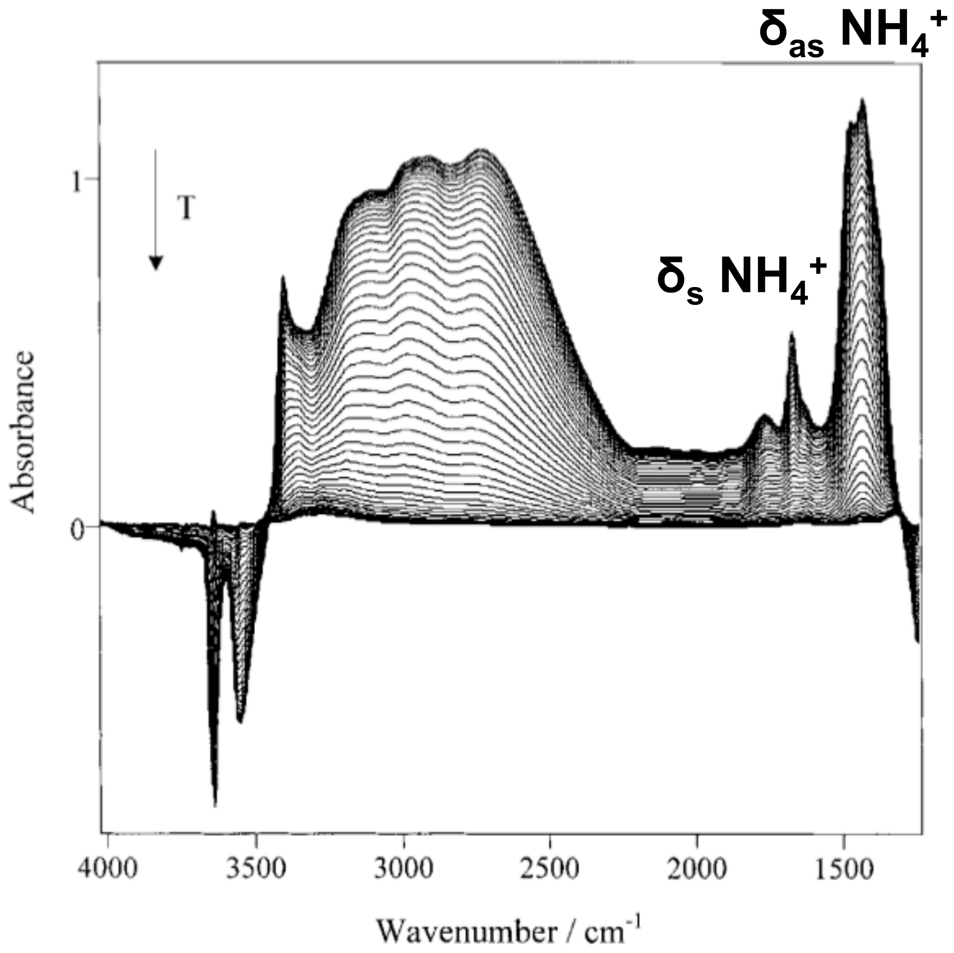


Figure 10. Spectra of 73HNaY during TPD of ammonia ($\Delta T = 5$ K).

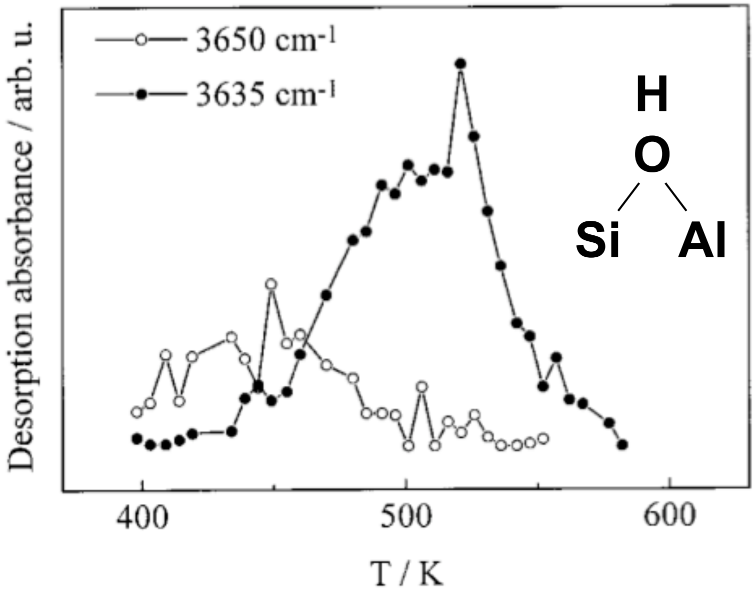
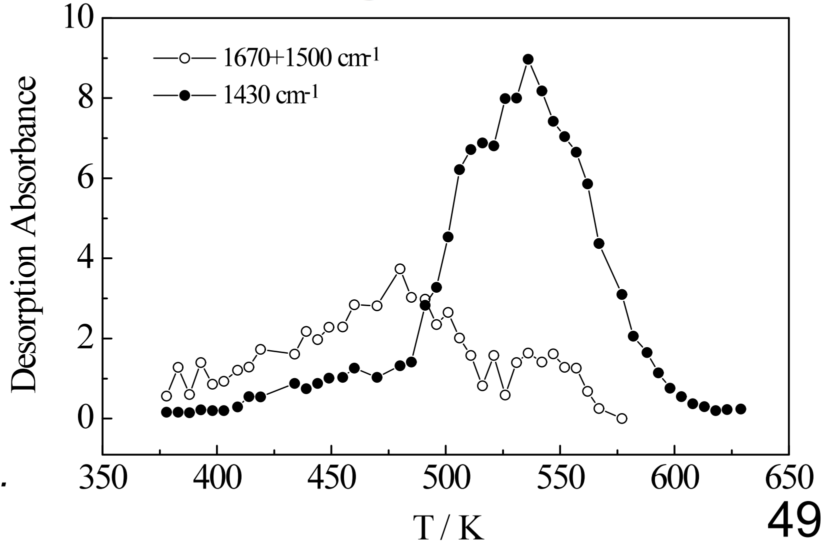
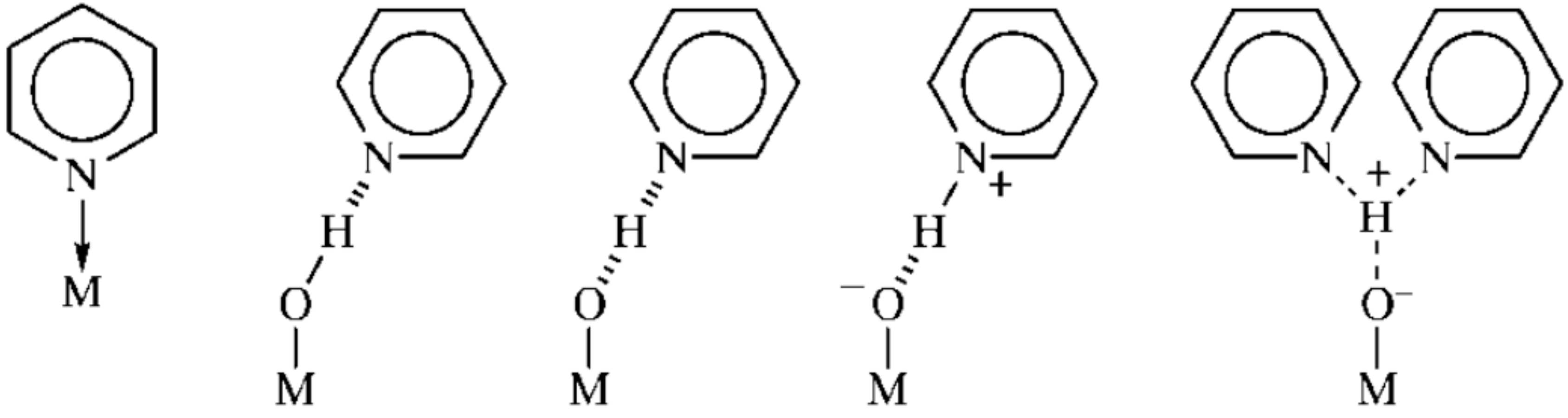


Figure 14. Desorption absorbances of the sub-bands in the region of OH stretching modes on 73HNaY.



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

Adsorption of pyridine



I II III IV V

Scheme I Adsorption modes of a base (*e.g.* pyridine) on the surface Lewis (I) and Brønsted sites (*e.g.* terminal) on a solid oxide surface.

G. Busca, PCCP 1 (1999) 723.

Adsorption of pyridine

1545 cm^{-1} Bønsted acid sites

1455 cm^{-1}: Lewis acid sites

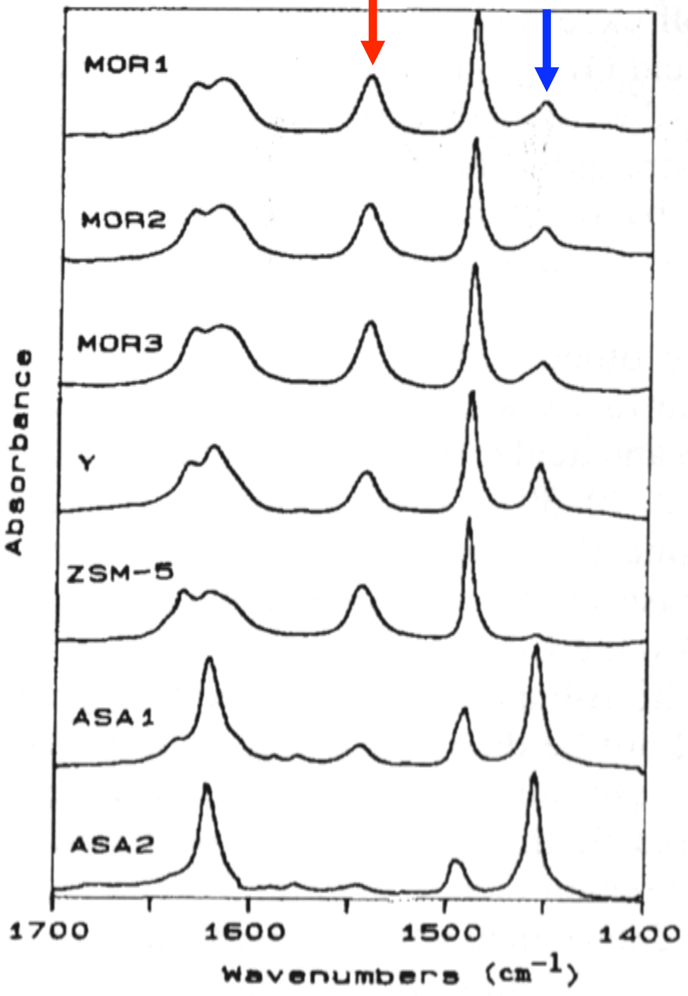


FIG. 2. Difference spectra obtained during addition of pyridine, before saturation occurred.

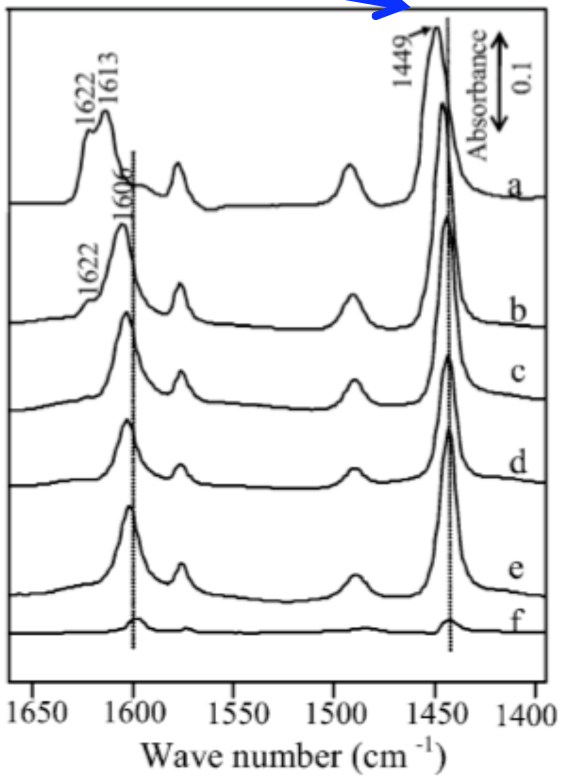
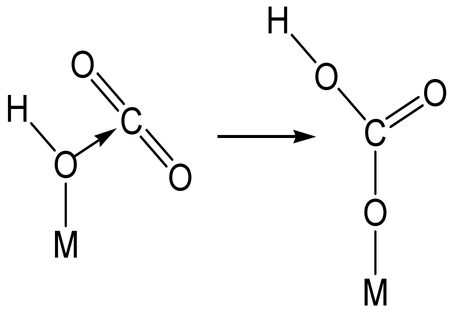


Fig. 4. Acid properties: pyridine adsorption on Al_2O_3 (a), the calcined hydrotalcites with Mg/Al molar ratios of 0.6 (b), 1.4 (c), 2.2 (d), and 3.0 (e), and MgO (f). Spectra were measured after adsorption and evacuation at 40 °C.

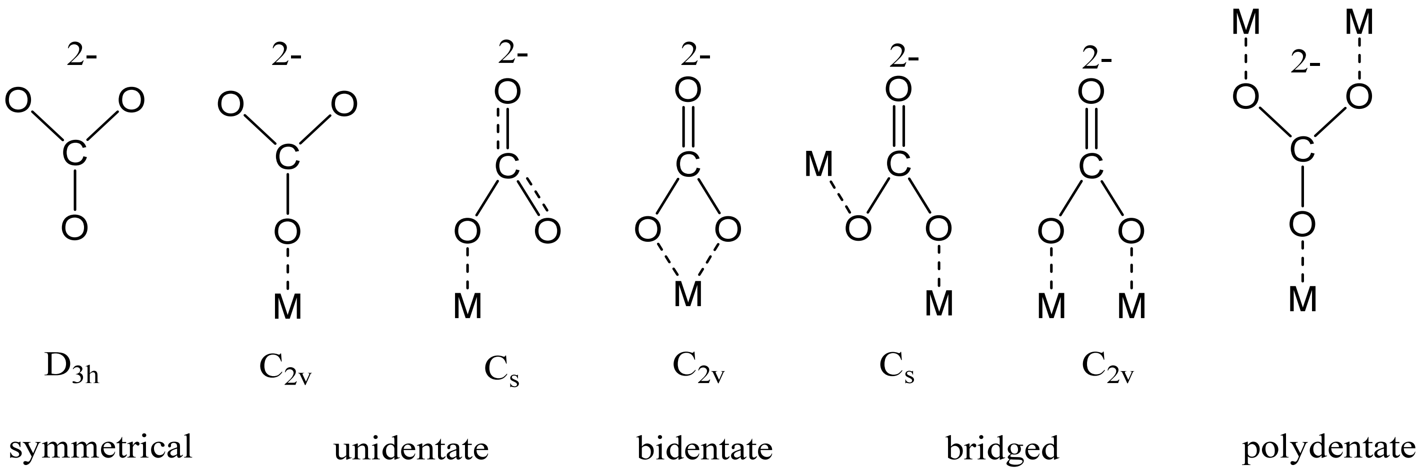
H.A. Prescott et al. / Journal of Catalysis 234 (2005) 119.

CO_2 as probe for basic sites

Formation of bicarbonates by reaction of CO_2 with basic OH groups



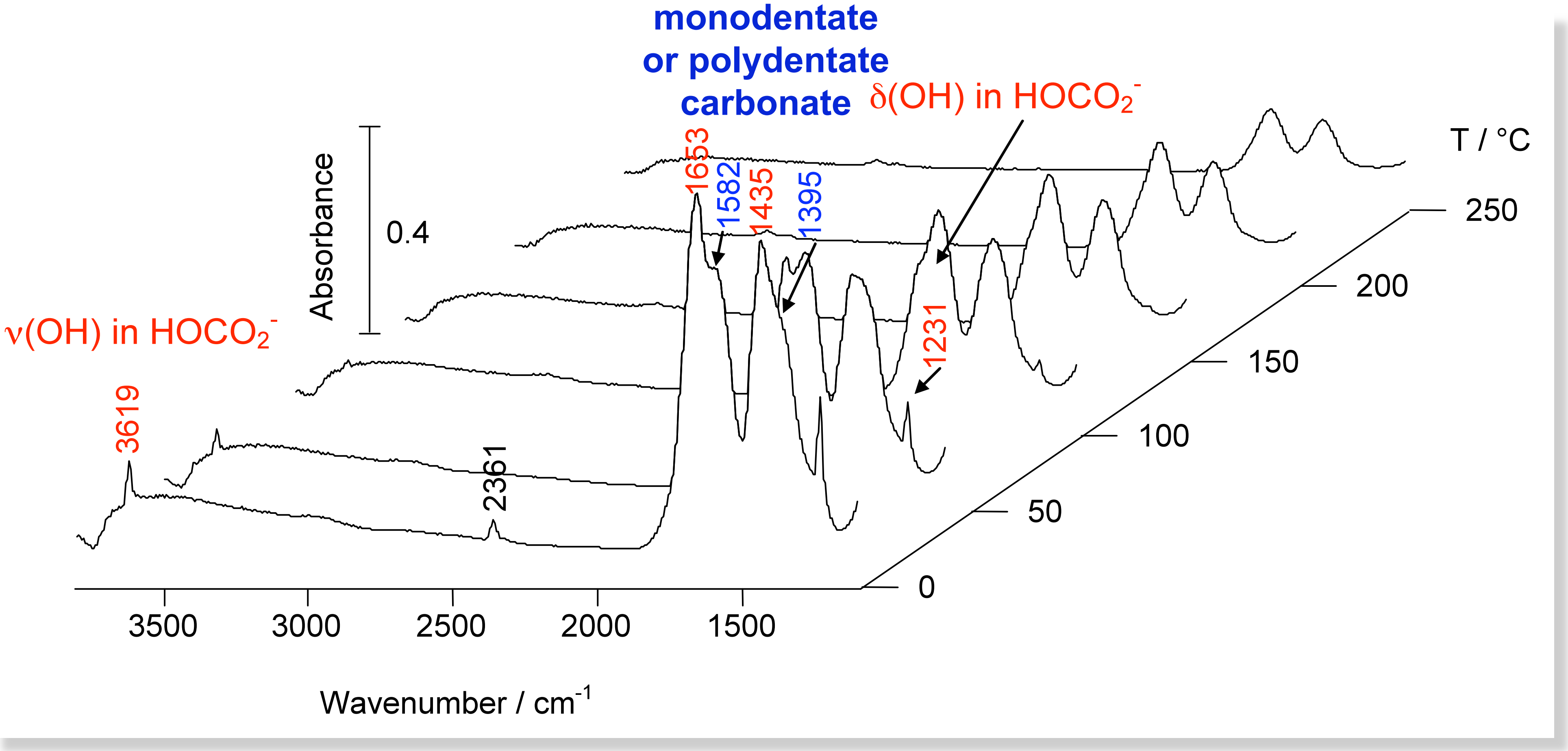
Free carbonate and surface carbonates formed by CO_2 adsorption



Other probes: e.g., SO_2, pyrrole, $CHCl_3$, CH_3CN, $B(OCH_3)_3$

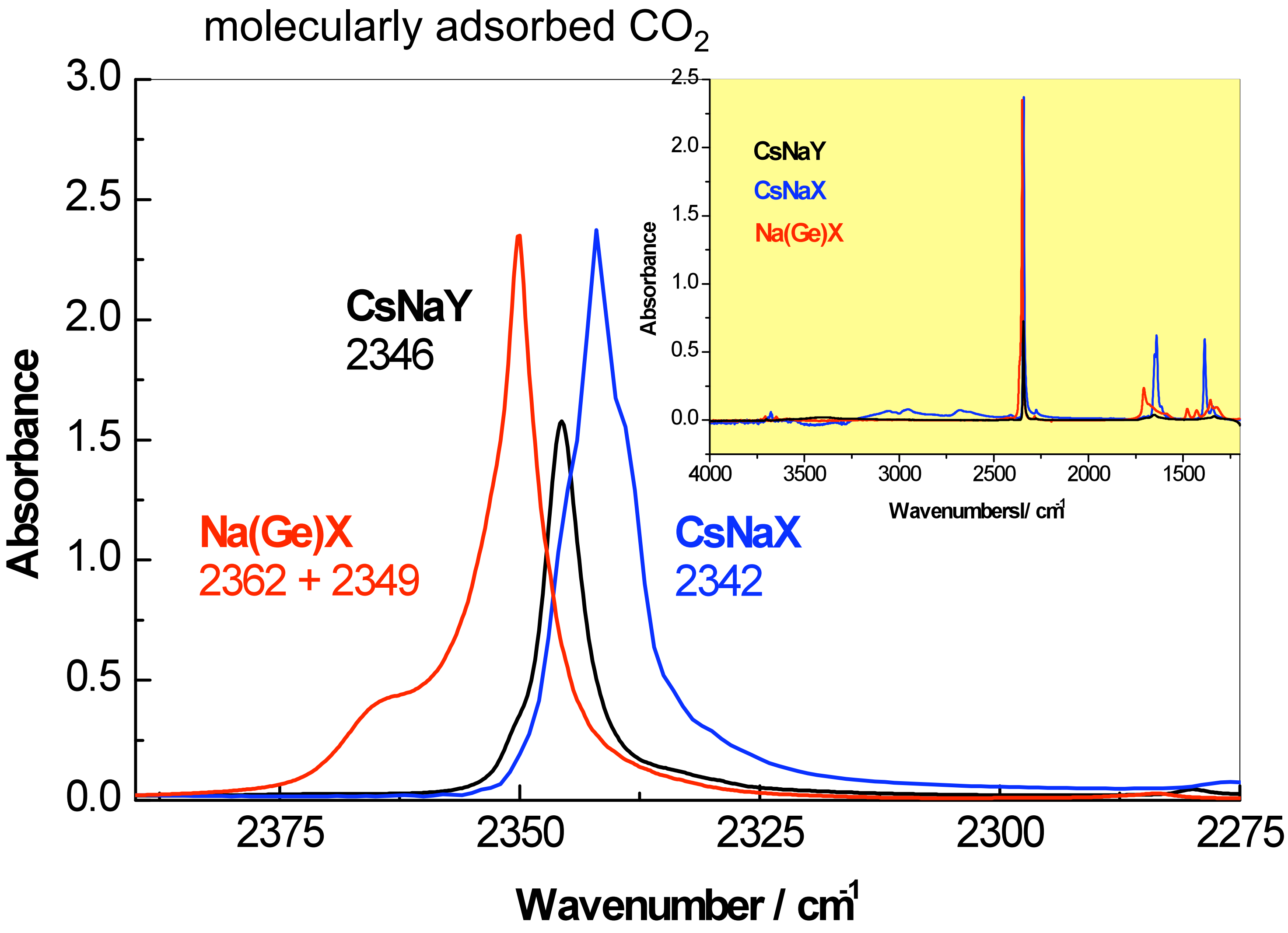
J.C. Lavalley, Catal. Today 27 (1996) 377.

CO_2 TPD



Adsorption and temperature-programmed desorption of CO_2 on MgO-Al_2O_3 (Mg/Al=0.6)

CO_2 as probe for Lewis acid sites



molecularly adsorbed CO_2

Summary

- FTIRS of adsorbed probe molecules is a standard method for characterization of
  - Electronic and geometric structures of supported metal particles
  - Coordinatively unsaturated surface sites
  - Acid-base properties
- The method gives information about the catalyst precursor that generally differs from the active state of the catalyst
- Proper in-situ pre-treatment or activation is necessary
- Comparative analysis of catalysts can explain trends
- Temperature-programmed desorption or isotope exchange experiments often required to underlay interpretation

Further reading

1. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Sixth Edition, Part A, John Wiley & Sons, Hoboken, New Jersey, 2009.
2. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Sixth Edition, Part B, John Wiley & Sons, Hoboken, New Jersey, 2009.
3. A. Davydov, Molecular Spectroscopy of Oxide Catalyst Surfaces, John Wiley & Sons, Chinchester, England, 2003.
4. J.L.G. Fierro, Spectroscopic Characterization of Heterogeneous Catalysts, Elsevier, Amsterdam, 1990.

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