LECTURE SERIES
HETEROGENEOUS CATALYSIS

Activation of small molecules
-
Carbon Dioxide

13th January 2017

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Literature

- Handbook of Heterogenous Catalysis, G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp (2. ed.), Vol 5+6., 2008
- Chemical Reviews, 2013, 113, 6621-6658
- Methanol – Chemie und Energierohstoff, F. Asinger, Springer-Verlag, 1985
- Catalytic Activation of Carbon Dioxide, 1988, ACS
- Surf. Science Reports, Surface chemsitry of carbon dioxide, H.-J. Freund, M.W. Roberts, 1996, 225-273
- https://www.umweltbundesamt.de/sites/default/files/medien/378/publikationen/data_on_the_environment_2015.pdf

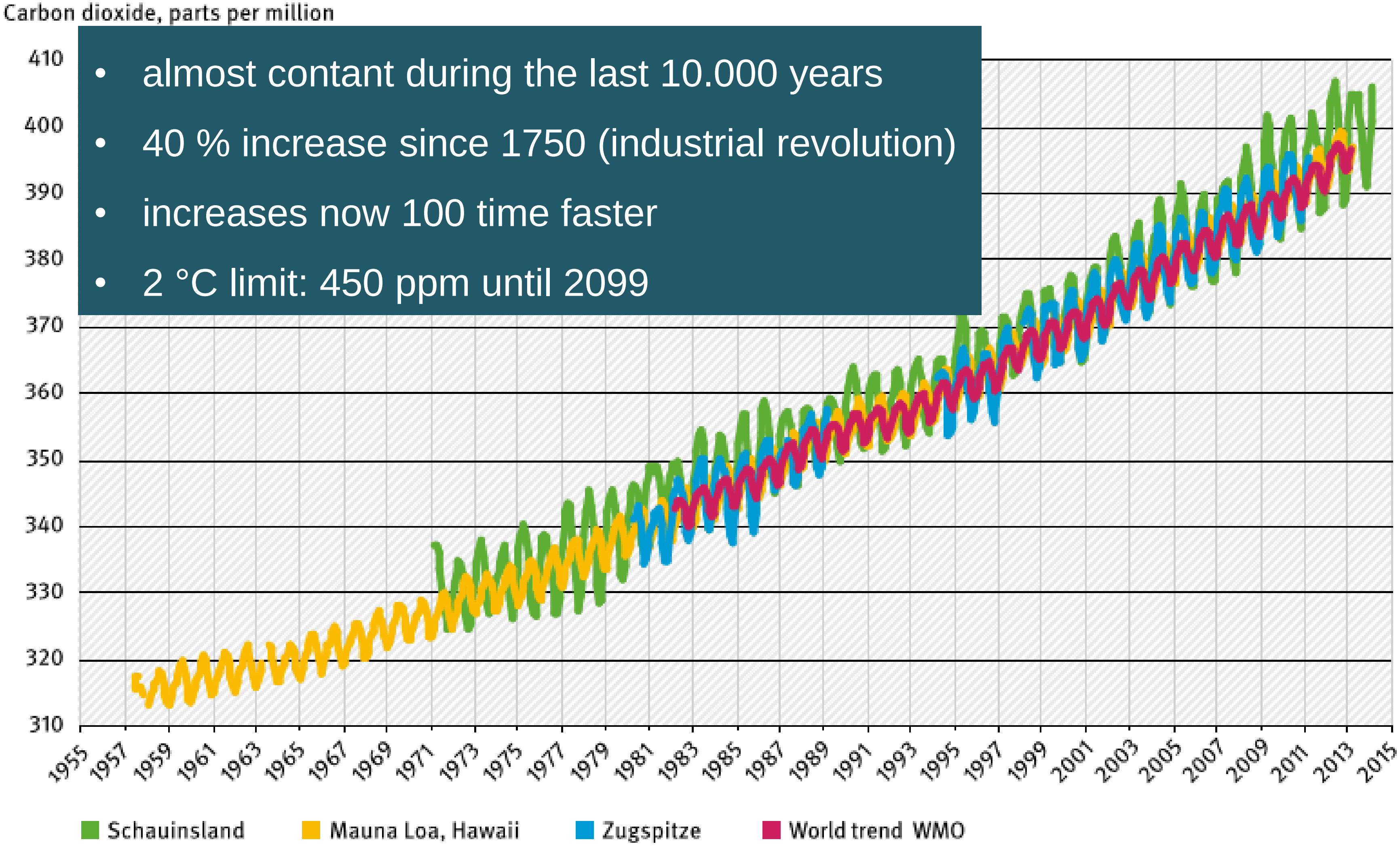
+ references on the slides

Outline

1. Green house gas emissions and CO_2
2. Fundamental aspects of CO_2 activation
3. CO_2 activation on metal oxides
4. CO_2 activation on transition metals
5. Heterogeneous catalysts for CO_2 conversion: product selectivity

Carbon dioxide concentration (monthly averages)

- almost contant during the last 10.000 years
- 40 % increase since 1750 (industrial revolution)
- increases now 100 time faster
- 2 °C limit: 450 ppm until 2099

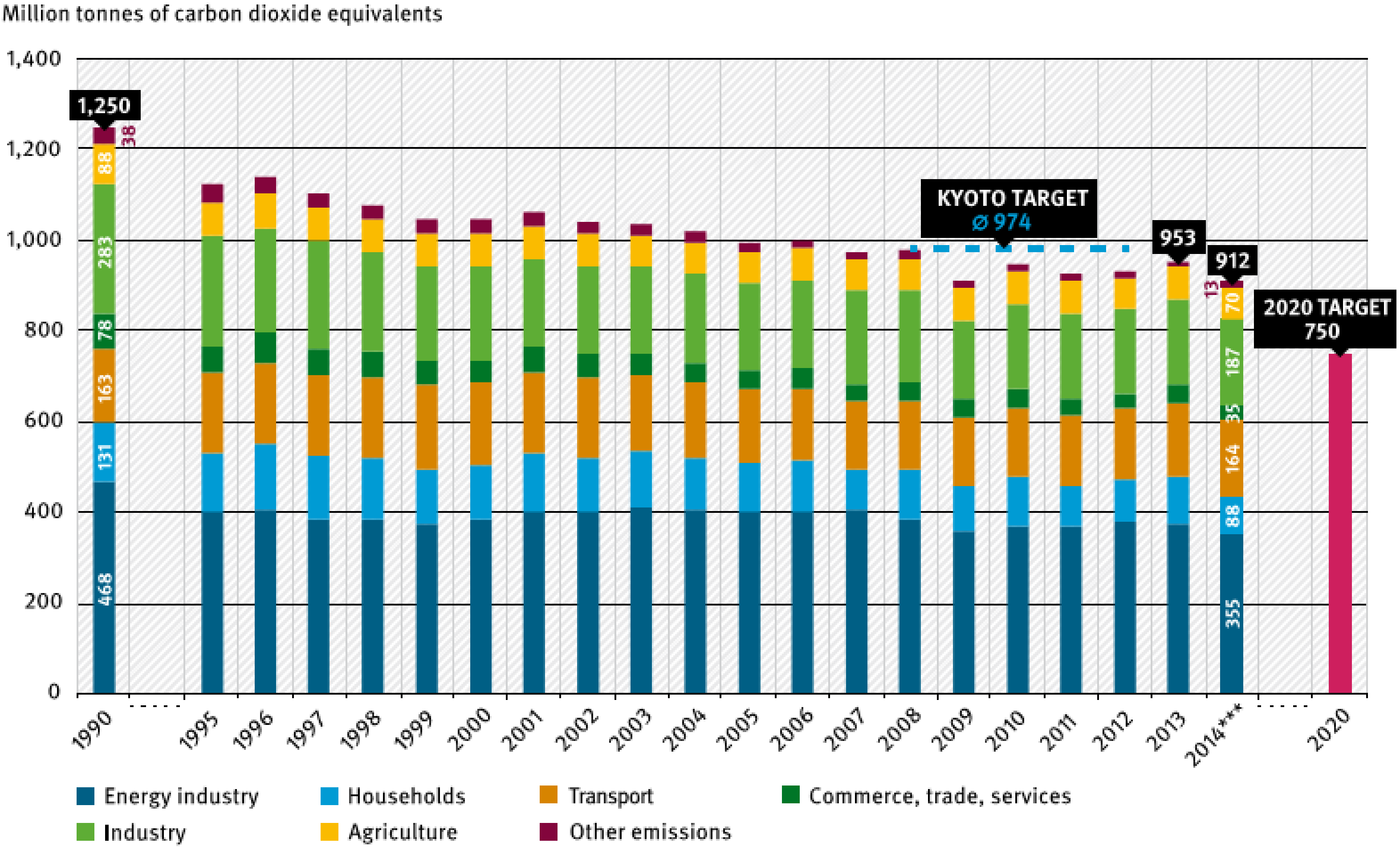


* 1 ppm = 1 part per million = 0,0001 %

Source: Federal Environment Agency (Schauinsland, Zugspitze), World Data Centre for Greenhouse Gases (Mauna Loa, Hawaii), World Meteorological Organization

Greenhouse gas emissions in Germany since 1990*

according to sectors of the Climate Action Programme 2020**



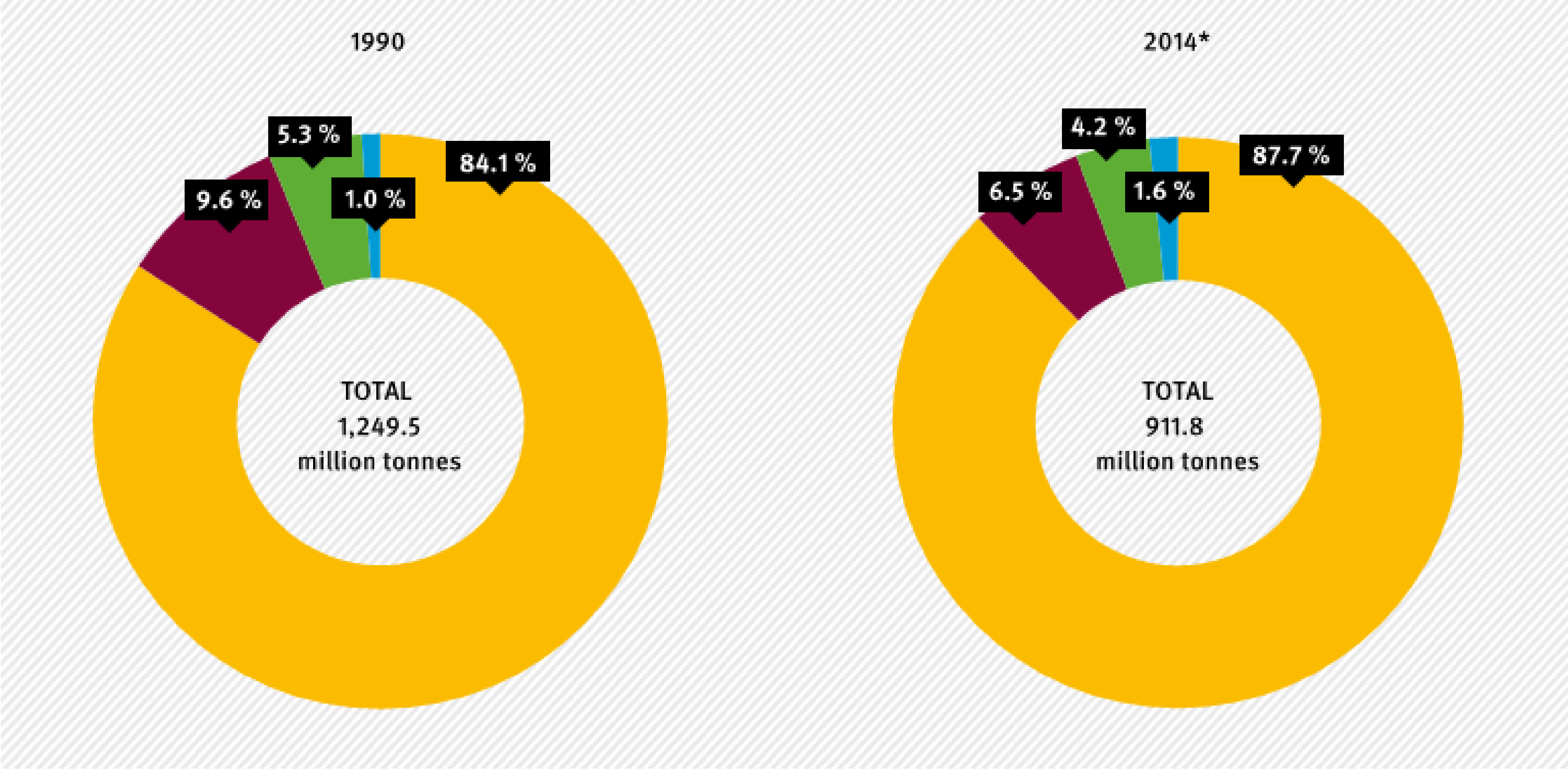
* Without carbon dioxide from LULUCF

** The breakdown of emissions differs from the UN reporting, total emissions are identical

*** Short-term forecast for 2014

Source: Federal Environment Agency 2015, National Greenhouse Gas Inventory 1990 to 2013 and short-term forecast for 2014 (as of 03/2015) and short-term forecast for 2014 (as of 03/2015)

Greenhouse gas emissions by gases (in carbon dioxide equivalents)

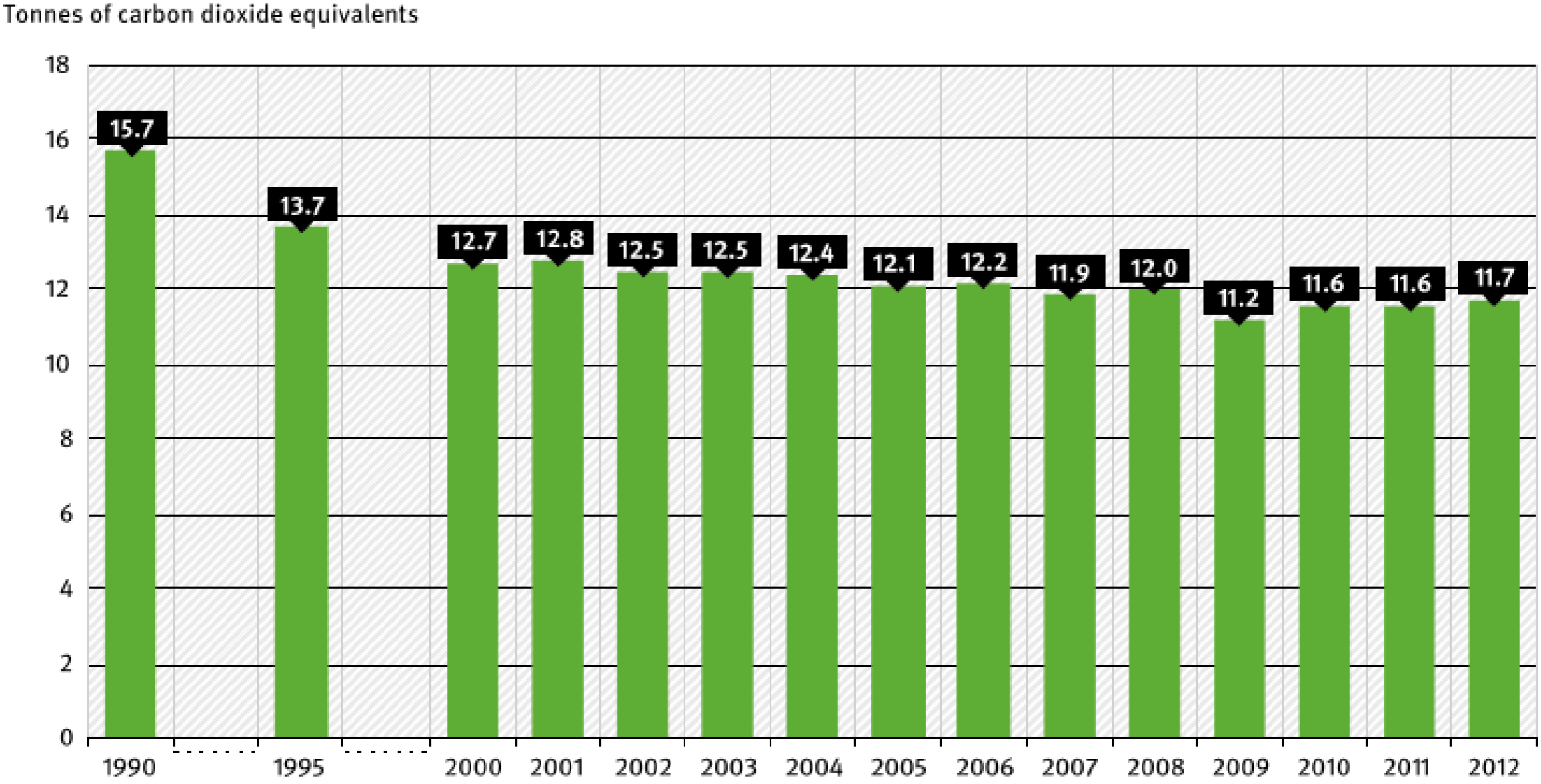


🟨 Carbon dioxide 🟥 Methane 🟩 Nitrous oxide 🟦 "F gases" (HFC, PFC, SF_6, NF_3)

*short-term forecast, preliminary figures

Source: Federal Environment Agency 2015, National Greenhouse Gas Inventory 1990 - 2013 (as of 27/01/2015), short-term forecast (as of 03/2015)

Per capita emissions



Source: Federal Ministry for the Environment, Nature Conservation, Building and Nuclear Safety (eds.) 2014
Climate protection in figures, p. 22

CO_2 Emissions – A Global Issue

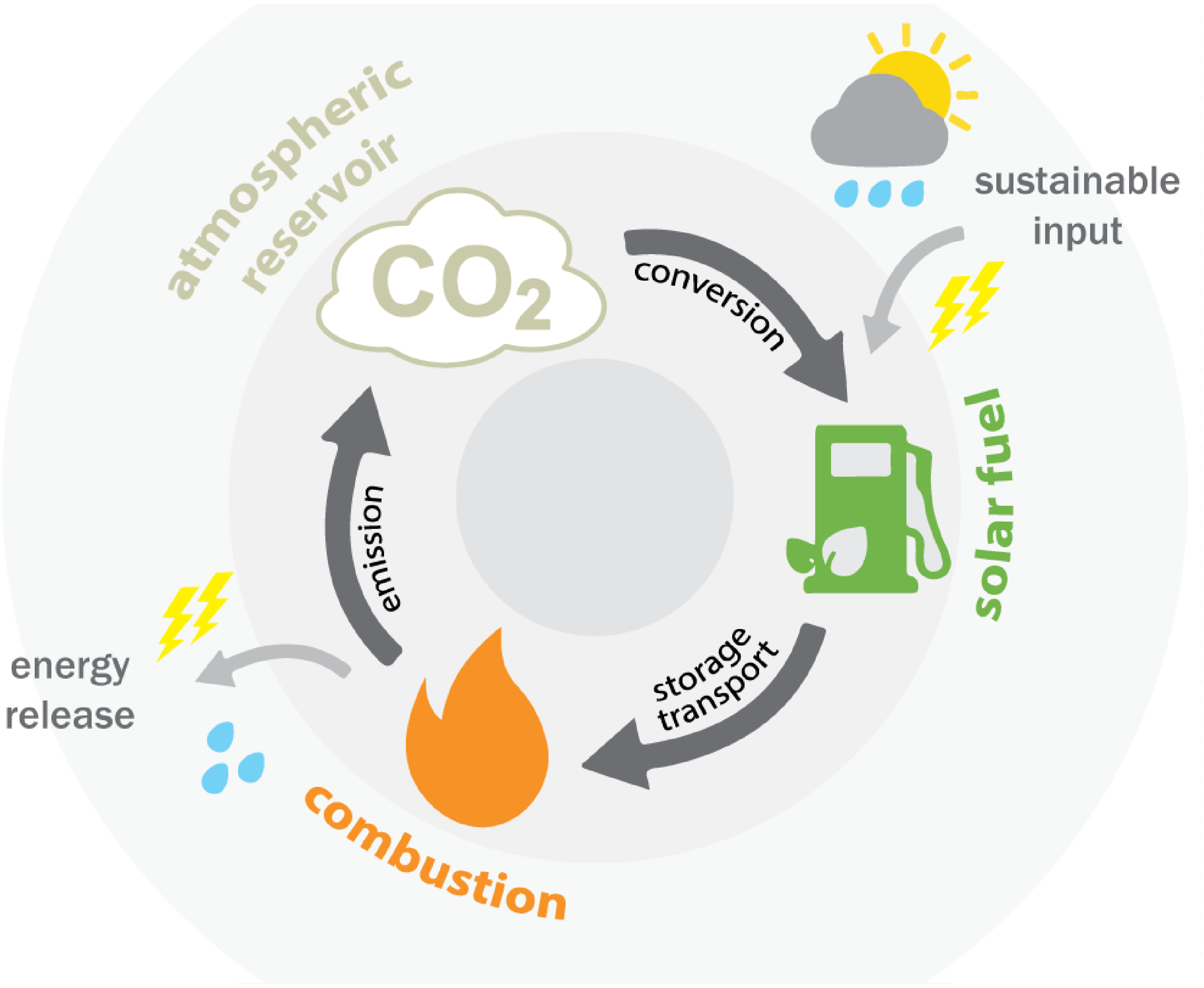
UCLA – beagreencommuter.com

~ 10 t/a in Europe

~ 7 t/a CH_3OH

70.000 km/a by car

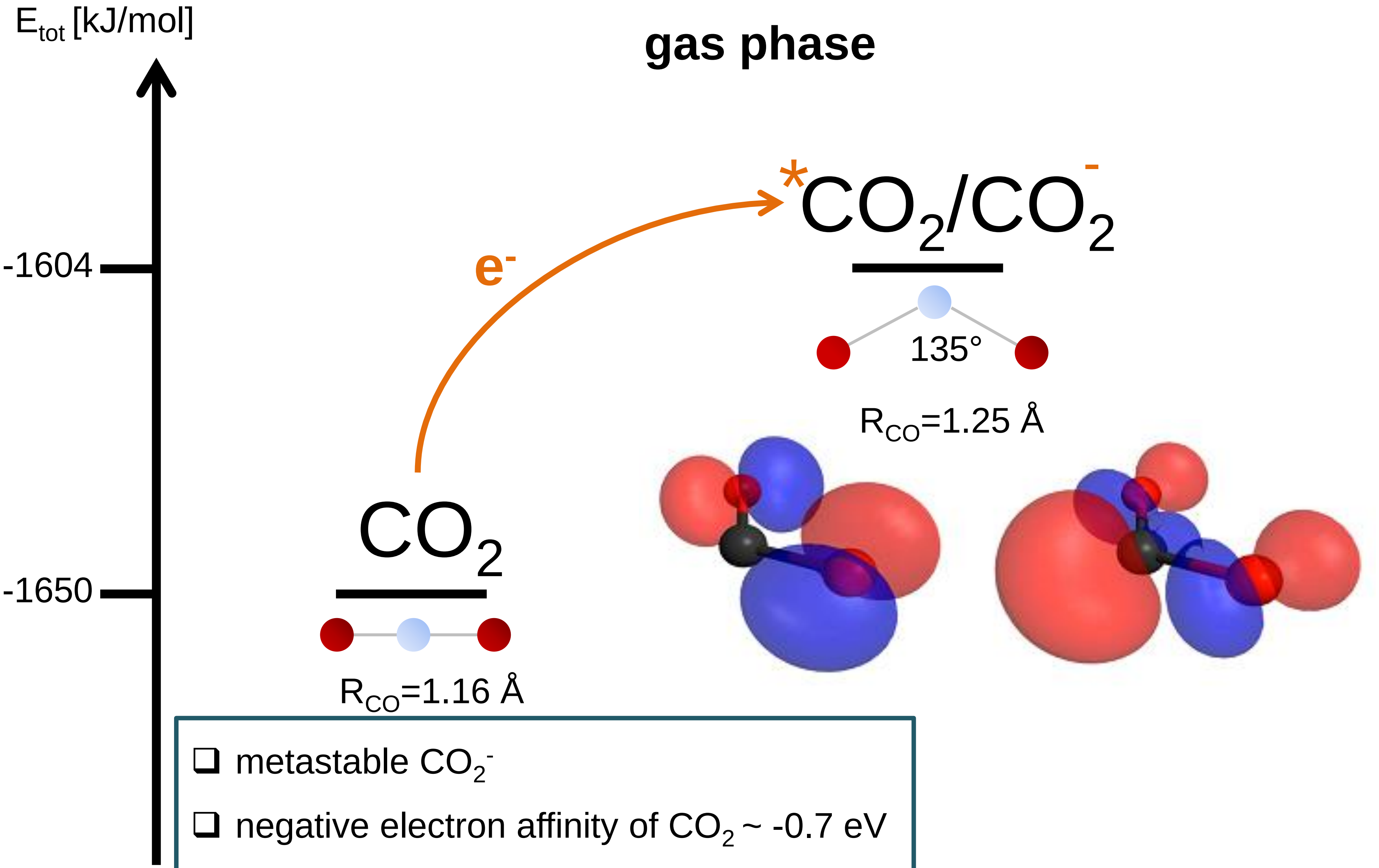
Carbon Capture and Usage - A Sustainable Energy Concept



©Dutch Institute for Fundamental Energy Research - DIFFER

CO_2 activation

gas phase



- ☐ metastable CO_2^-
- ☐ negative electron affinity of CO_2 ~ -0.7 eV
- ☐ lifetime of 60-90 µs

CO_2 activation: How was this measured?

Principal: Collision ionization technique

- alkali atom beam
- Energy determined by TOF
- Calibration with known values

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projectile energy

finite positive energy

EA target M: here CO_2

Cs

$$\mathrm{E.A.(M)} = \mathrm{I.P.(P)} + E^0\left(\frac{M_1}{M_2} - 1\right) + E^*\left(1 + \frac{M_1}{M_2}\right) - 2\,\frac{M_1}{M_2}\sqrt{E^0 E^*}\,\cos\theta,$$

CO_2

scattering angle

The Journal of Chemical Physics, Vol. 63, No.9, 1 November **1975**
Collisional ionization of Na, K, and Cs by CO2, COS, and CS2:
Molecular electron affinities

CO_2 activation: How was this measured?

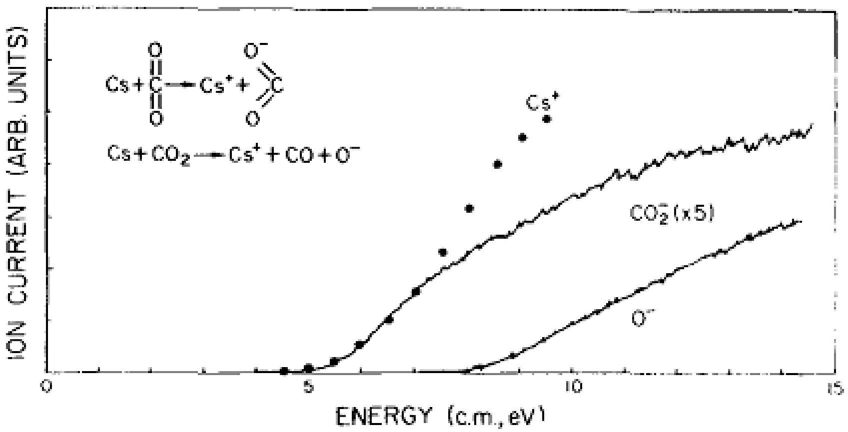


FIG. 2. Cs^+, CO_2^-, and O^- ion yields resulting from the collisions between Cs and CO_2 as a function of the relative energy. The Cs^+ and CO_2^- ion currents are normalized at 6 eV.

$$Cs + CO_2 \rightarrow Cs^+ + CO_2 + e, \qquad (1)$$

$$Cs + CO_2 \rightarrow Cs^+ + CO_2^{-*}, \qquad (2)$$

$$Cs + CO_2 \rightarrow Cs^+ + CO + O^-. \qquad (3)$$

Ionization potential Cs: 3.893 eV

Threshold for Cs^+ and CO_2^-: 4.6 ±0.2 eV

~ 0.7 eV

The Journal of Chemical Physics, Vol. 63, No.9, 1 November **1975**
Collisional ionization of Na, K, and Cs by CO2, COS, and CS2:
Molecular electron affinities

CO_2 Activation and Reduction

E_{tot} [kJ/mol]

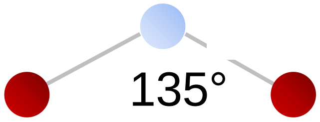
-1604

-1650

gas phase

e^-

$^*CO_2/CO_2^-$

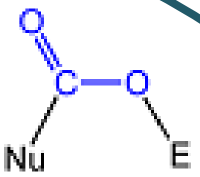


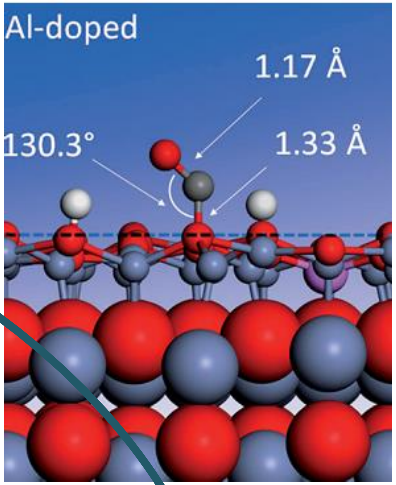
135°

R_{CO}=1.25 Å

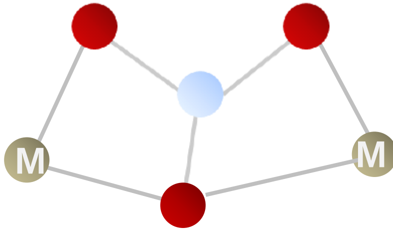
CO_2

R_{CO}=1.16 Å





$CO_3^{\delta-}$



tridentate carbonate

Al-doped ZnO (0001): -0.56 eV (Ea = 0.8 eV) [4]

ZnO (10-10): -0.5 to -0.7 eV [3]

MgO: -0.64 eV to 2.3 eV [Levchenko]

[1] Freund et al. *Surface Science Reports 25*, **1997**, 225-2 273

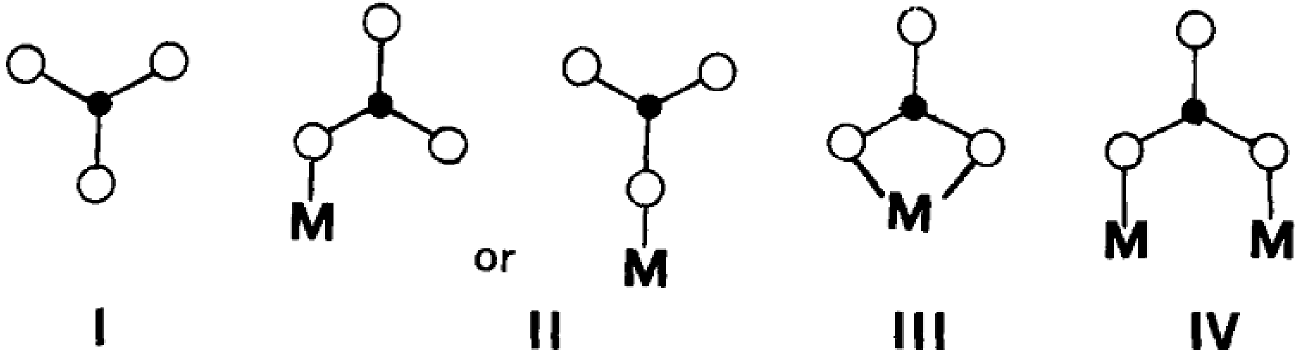
[2] *The Journal of Chemical Physics*, Vol. 63, No.9, 1 November **1975**
Collisional ionization of Na, K, and Cs by CO2, COS, and CS2: Molecular electron affinities*

[3] Wang et al. *Angew. Chem. Int . Ed.* **2007**, 46, 5624 –5627

[4] *ChemPhysChem* **2012**, 13, 3453 – 3456

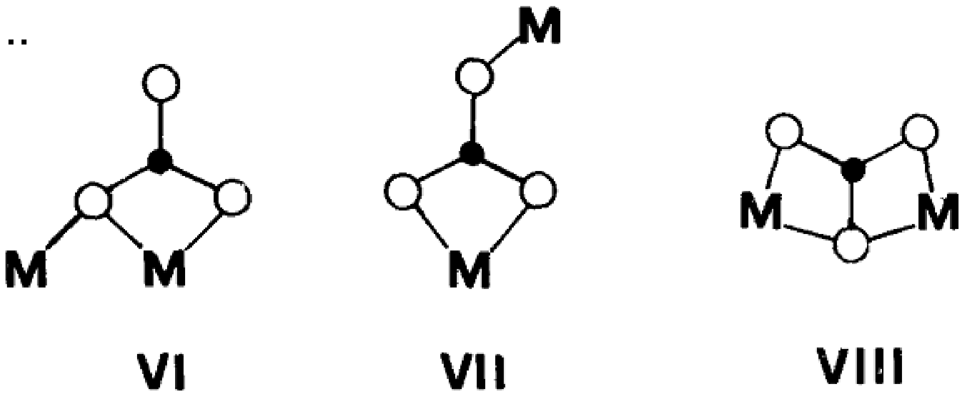
CO_2 chemisorption on surfaces

as carbonate



free/symm. mono- bi- bridged

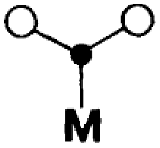
more complicated, polydentate…..



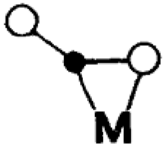
Materials Chemistry 7 (1982) 89 - 126

CO_2 chemisorption on surfaces

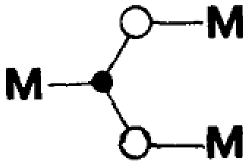
as carboxylates



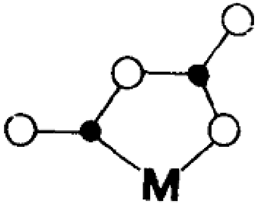
XIII



XIV

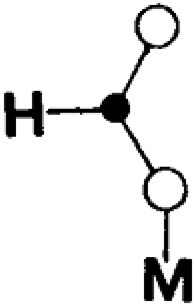


XV

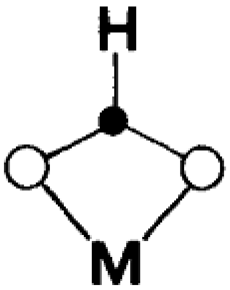


XVI

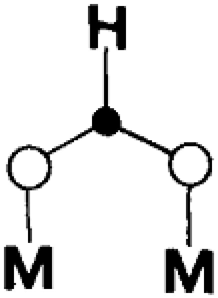
as formates



XX



XXI

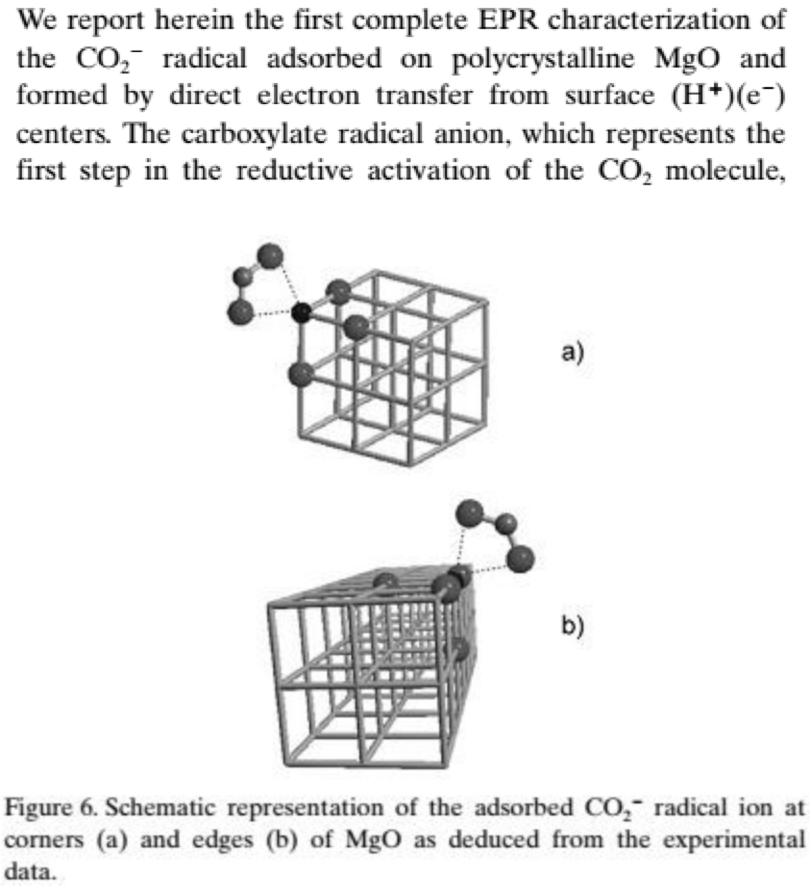


XXII

Materials Chemistry 7 (1982) 89 - 126

CO_2 chemisorption on metal oxides

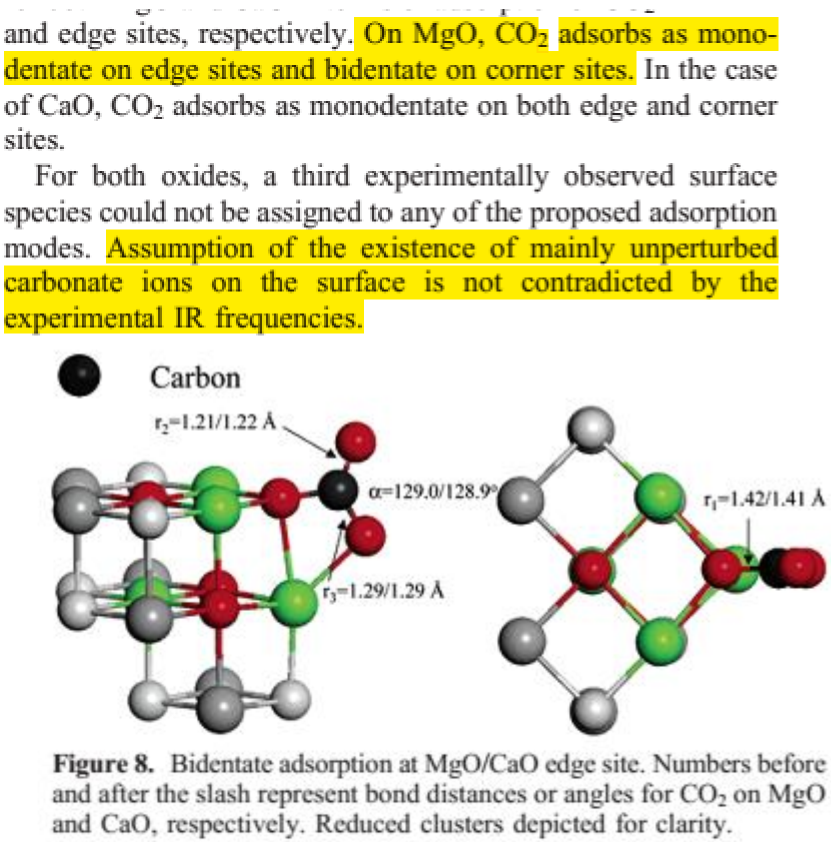
2 examples: **MgO** / ZnO



We report herein the first complete EPR characterization of the CO_2^- radical adsorbed on polycrystalline MgO and formed by direct electron transfer from surface $(H^+)(e^-)$ centers. The carboxylate radical anion, which represents the first step in the reductive activation of the CO_2 molecule,

Figure 6. Schematic representation of the adsorbed CO_2^- radical ion at corners (a) and edges (b) of MgO as deduced from the experimental data.

Chem. Eur. J. **2007**, *13*, 1261 – 1267



and edge sites, respectively. On MgO, CO_2 adsorbs as monodentate on edge sites and bidentate on corner sites. In the case of CaO, CO_2 adsorbs as monodentate on both edge and corner sites.

For both oxides, a third experimentally observed surface species could not be assigned to any of the proposed adsorption modes. Assumption of the existence of mainly unperturbed carbonate ions on the surface is not contradicted by the experimental IR frequencies.

Figure 8. Bidentate adsorption at MgO/CaO edge site. Numbers before and after the slash represent bond distances or angles for CO_2 on MgO and CaO, respectively. Reduced clusters depicted for clarity.

J. Phys. Chem. B **2005,** *109,* 16774−16781

CO_2 chemisorption on metal oxides

2 examples: **MgO (100)** / ZnO

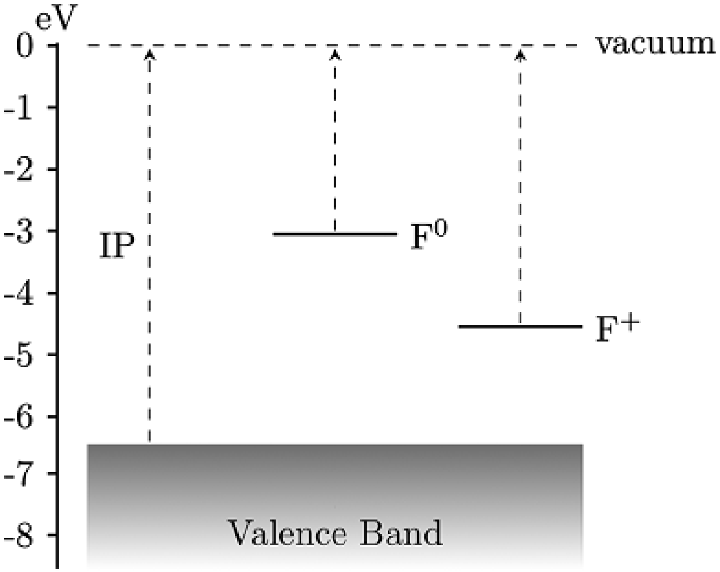
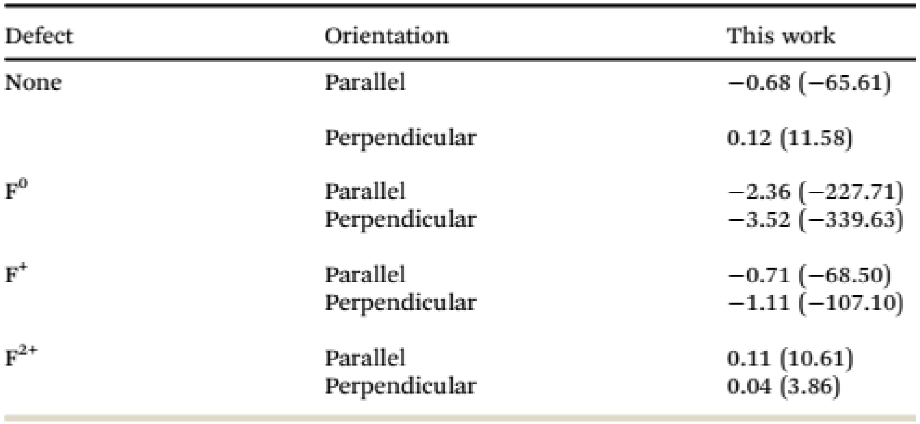
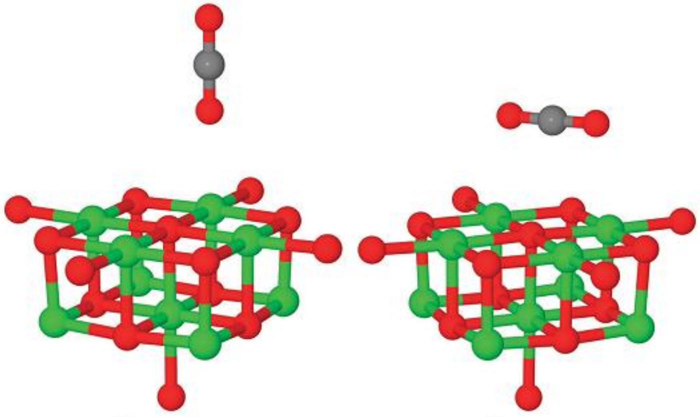


Fig. 4 Positions of defect levels of MgO and their vertical ionization potentials. MgO (100) terrace IP: 6.46 eV, F^0: 3.05 eV, F^+: 4.55 eV. Relaxation to the ground states corresponding to MgO^+, F^+ and F^{2+} gave values for the adiabatic ionization potentials of 5.52, 1.91 and 3.30 eV respectively.



Defect	Orientation	This work
None	Parallel	−0.68 (−65.61)
	Perpendicular	0.12 (11.58)
F^0	Parallel	−2.36 (−227.71)
	Perpendicular	−3.52 (−339.63)
F^+	Parallel	−0.71 (−68.50)
	Perpendicular	−1.11 (−107.10)
F^{2+}	Parallel	0.11 (10.61)
	Perpendicular	0.04 (3.86)



(a) Perpendicular (b) Parallel

Phys. Chem. Chem. Phys., 2014, **16**, 184–195

F^0 coulor center on the MgO (100) surface

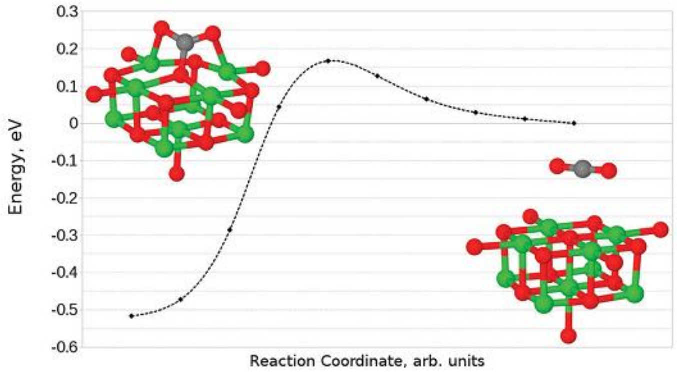


Fig. 9 Reaction profile for the conversion between parallel physisorbed and tridentate adsorbed CO_2 geometries on the defect-free MgO(100) terrace obtained using the NEB method with 10 images. A barrier of 0.17 eV (17.40 kJ mol^{-1}) is observed for the adsorption process.

activation barrier of 0.17 eV!

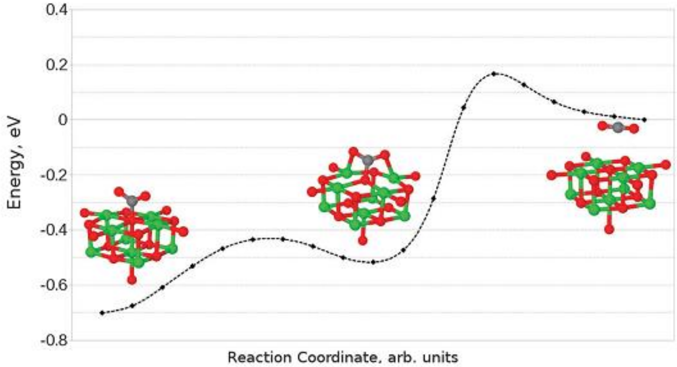
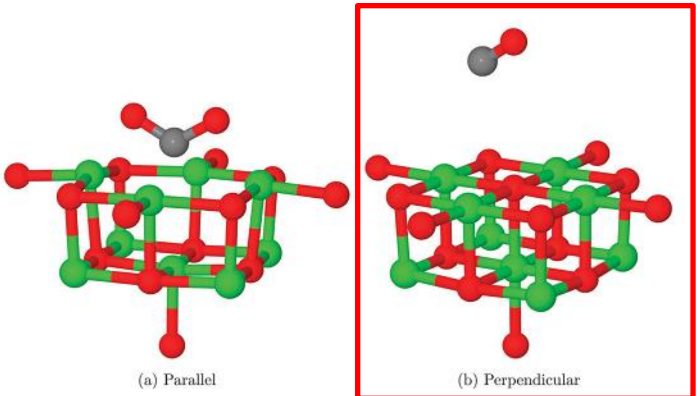


Fig. 10 Reaction profile for an alternative adsorption process, from physisorbed CO_2 to the monodentate chemisorbed species *via* a tridentate intermediate.

tridentate carbonate as intermediate!



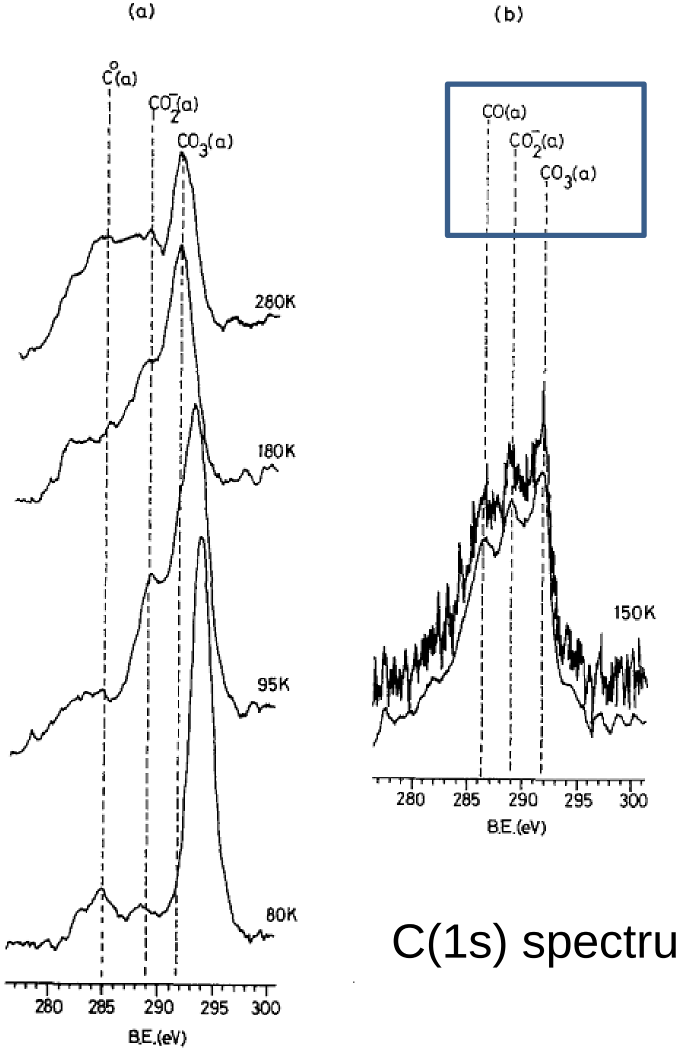
(a) Parallel (b) Perpendicular

Fig. 11 Structures obtained after relaxation of CO_2 in proximity to an F^0 centre. The internal angle of the adsorbate when in the parallel orientation is 120.8°, while the two $Mg_s{-}O_{ads}$ distances are 2.01 Å. In the perpendicular case, a defect-free MgO surface is formed and the CO molecule does not remain in close proximity to the surface. O atoms shown in red, Mg in green and C in grey.

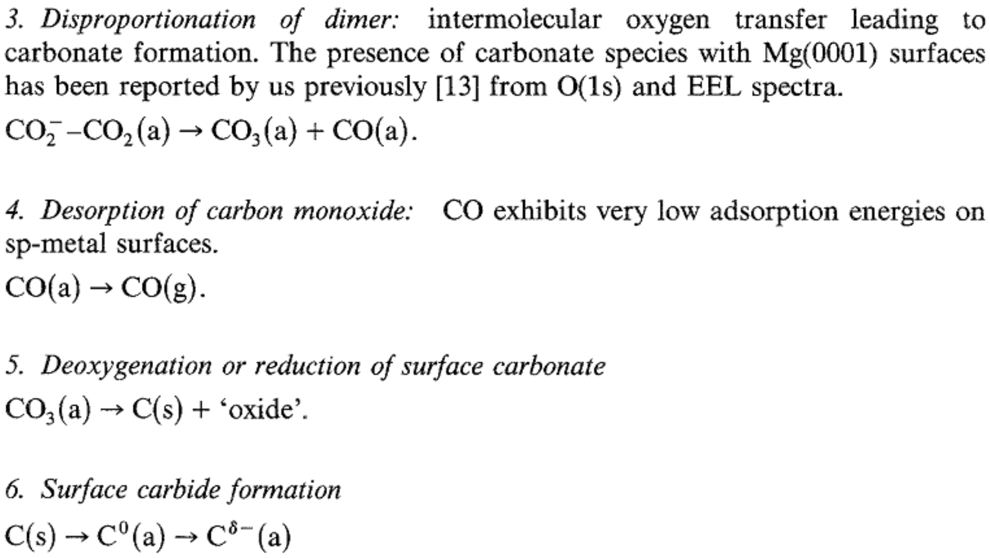
F^0 centers show a limited usefulness:
Perpendicular CO_2 would poison the catalyst

CO_2 chemisorption on metal oxides

2 examples: **MgO (0001)** / ZnO



Estimated by the surface stoichiometries (O:C ratios)



3. *Disproportionation of dimer:* intermolecular oxygen transfer leading to carbonate formation. The presence of carbonate species with Mg(0001) surfaces has been reported by us previously [13] from O(1s) and EEL spectra.

$$CO_2^- - CO_2(a) \rightarrow CO_3(a) + CO(a).$$

4. *Desorption of carbon monoxide:* CO exhibits very low adsorption energies on sp-metal surfaces.

$$CO(a) \rightarrow CO(g).$$

5. *Deoxygenation or reduction of surface carbonate*

$$CO_3(a) \rightarrow C(s) + \text{'oxide'}.$$

6. *Surface carbide formation*

$$C(s) \rightarrow C^0(a) \rightarrow C^{\delta -}(a)$$

C(1s) spectrum exposed to 100 L CO_2 at 80K

Catalysis Letters 1 (1988) 11–20

CO_2 chemisorption on metal oxides

2 examples: MgO / **ZnO (10-10)**

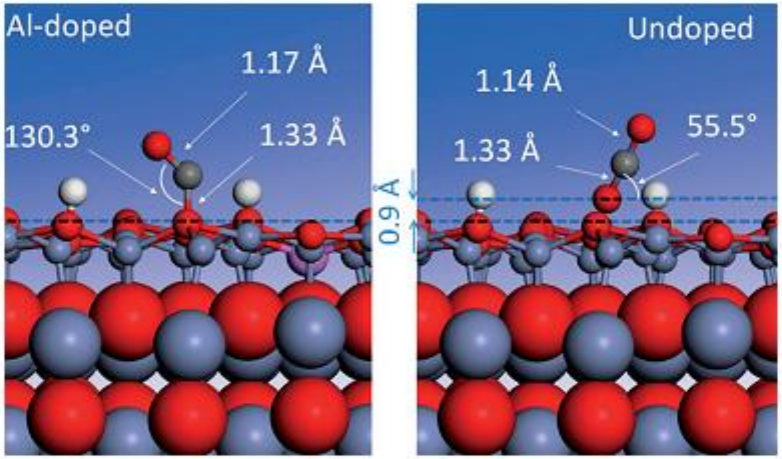
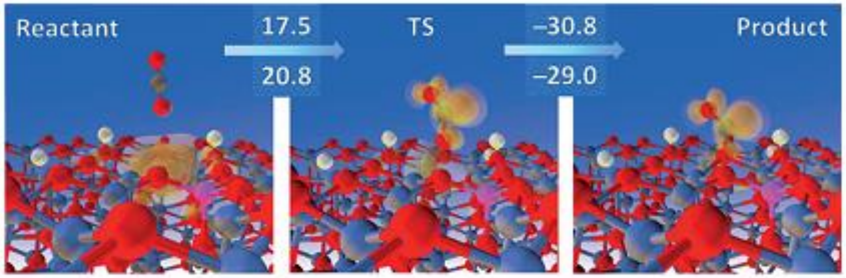
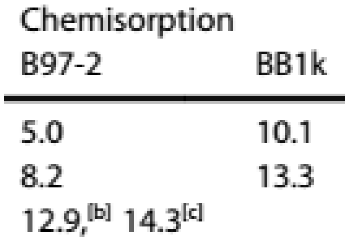


Figure 3. Molecular structure of carbon dioxide adsorbates in active, negatively charged, and inactive neutral forms, on the left and on the right.

- undoped ZnO seems to be inactive
- bent CO_2^- structure
- huge activation barriers of ~ 0.8 eV
- Adsorption energy of ~ 0.5 eV



$$CO_2(g) + VOISS^- \xrightleftharpoons{CO_2^- \cdots VOISS} CO_2(a)$$



Chemisorption B97-2	BB1k
5.0	10.1
8.2	13.3
12.9,[b] 14.3[c]	

ChemPhysChem **2012**, *13*, *3453–3456*

CO_2 chemisorption on metal oxides

2 examples: MgO / **ZnO (10-10)**

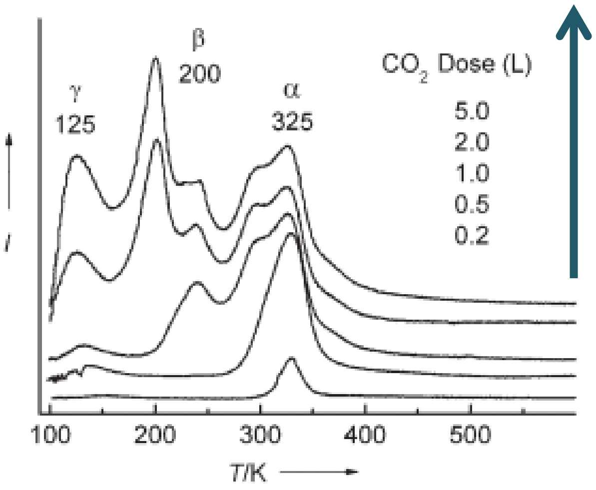


Figure 3. TDS data of CO_2 for various CO_2 exposures on ZnO(10$\bar{1}$0) at 95 K. The heating rate was 1 K s^{-1}.

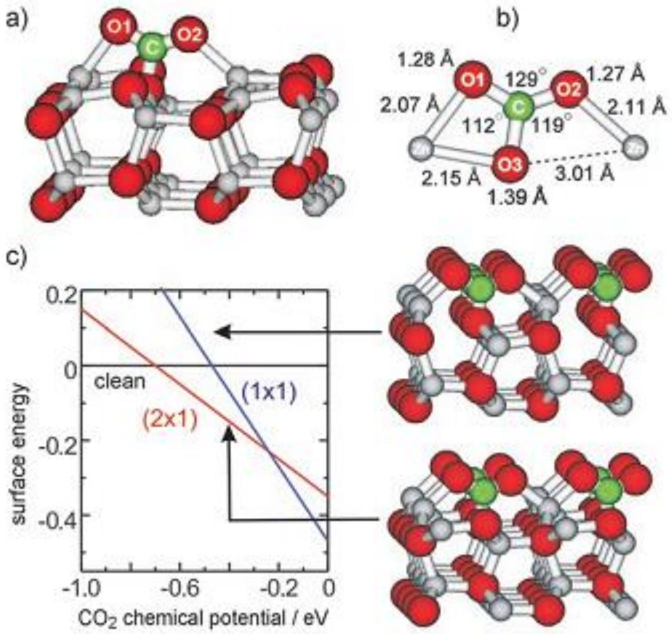


Figure 5. a, b) Side view of the atomic structure of an isolated carbonate ion on ZnO(10$\bar{1}$0) formed upon CO_2 adsorption. c) Relative thermodynamic stability of the half- and full-monolayer CO_2 coverage.

γ: weakly physisorbed CO_2
α + β : strong adsorbed carbonates, coverage depending existence:
C atom surface O / both O of CO_2 interact with neighb. Zn

Angew. Chem. Int. Ed. **2007**, *46*, 5624–5627

Different species due to repulsion of CO_2: 2x1 and 1x1

CO_2 chemisorption on metal oxides: Conclusion I.

- Anionic activation of CO_2 coupled with an electron transfer

- Many metal oxides activate or stabilze CO_2:

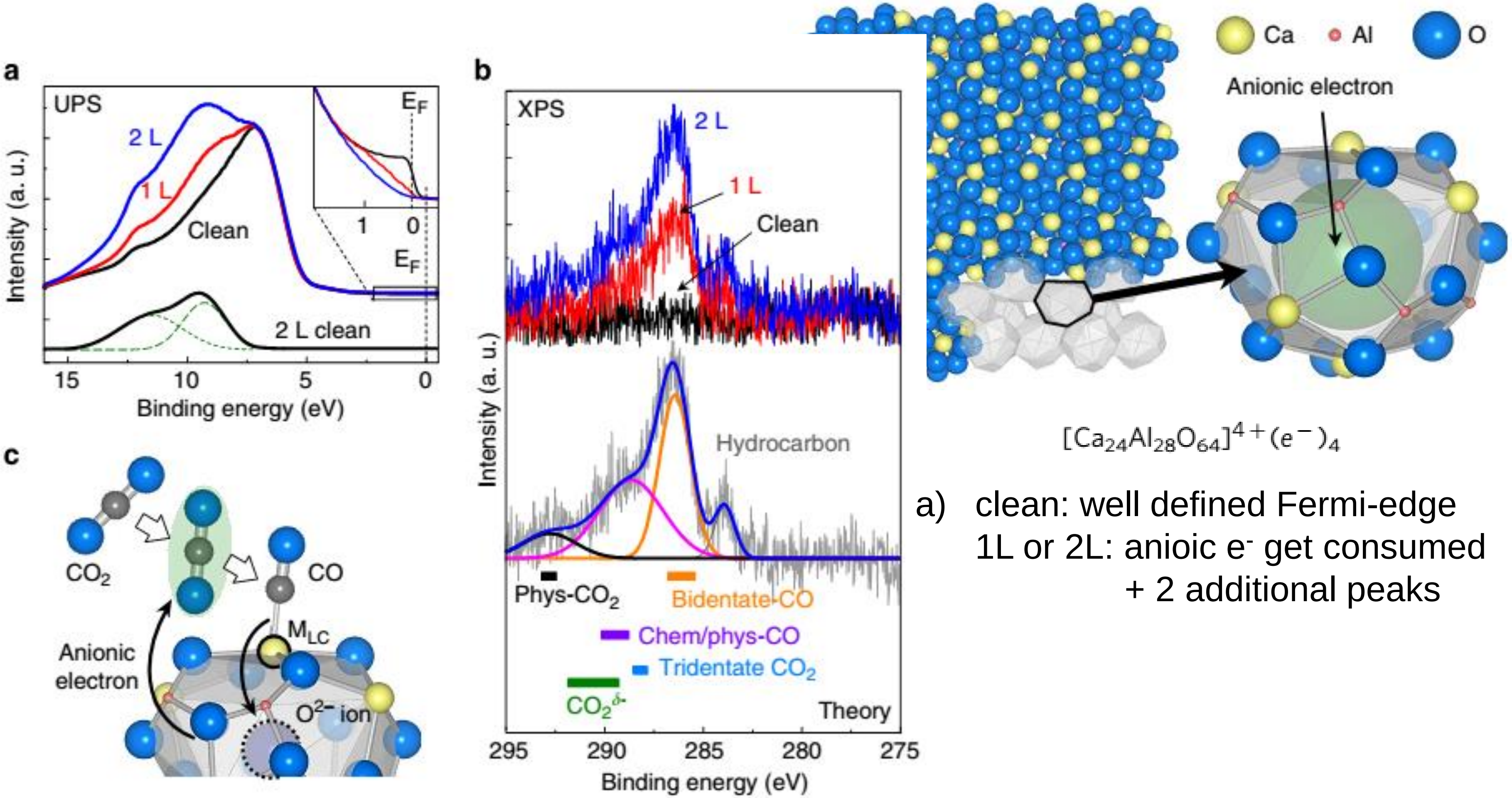
  MgO to BaO / Cr_2O_3/ Na_2O / NiO / TiO_2 / ZnO / CeO_x / ZrO_2 etc.

- Most of the metal oxides stabilize CO_2 as carbonates non-diss.

- Strongly depending on the cristall. orientation and defect situation (coulor centers etc.)

- Surface termination: terraces, edges, steps

CO_2 chemisorption: alternatives



$[Ca_{24}Al_{28}O_{64}]^{4+}(e^-)_4$

a) clean: well defined Fermi-edge
1L or 2L: anioic e^- get consumed
+ 2 additional peaks

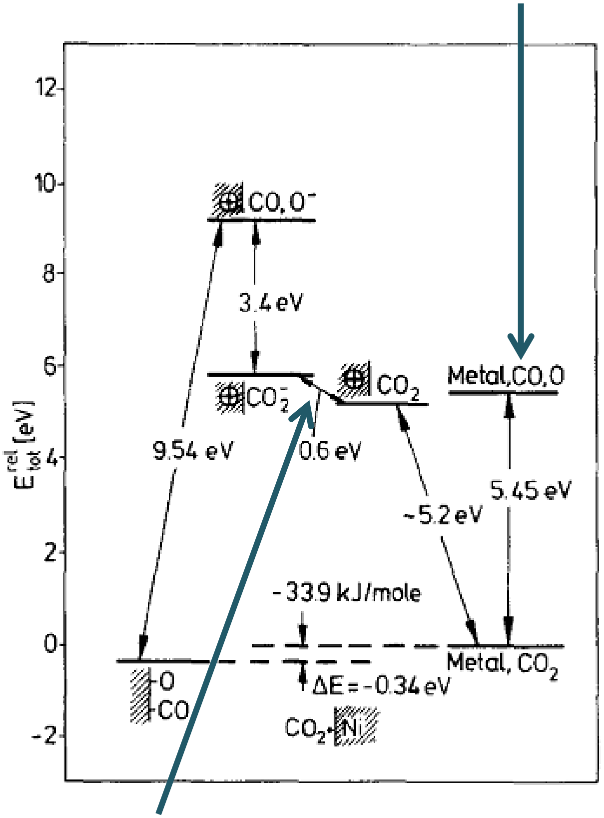
dissociative CO_2 adsorption at RT

NATURE COMMUNICATIONS | 4:2378 | DOI: 10.1038/ncomms3378 | www.nature.com/naturecommunications

CO_2 chemisorption on transition metals

Table 2 (continued)

	CO_2(phys.)	CO_2^-(chem.)	Dissociation	Carbonate	Oxalate	Ref.
Magnesium						
Mg(0 0 0 1)	x		x	x		[88]
Mg(0 0 0 1)	x	x	x	x		[106]
Nickel						
Ni(1 0 0)	x		x			[131,132]
Ni(1 1 0)	x	x	x			[39,81,131,133]
Ni(1 1 1)	x					[134]
Ni(1 0 0) + O	x			x		[135,136]
Ni(1 1 0) + O	x			x		[39]
Ni(1 1 1) oxidized	x	x	x	x		[137]
Palladium						
Pd(1 0 0)	x					[138]
Pd(1 1 1)	x					[139–142]
Pd(1 0 0) + K	x	x	x	x		[143]
Pd(1 1 1) + Na, $\theta < 0.25$	x		x			[139–141]
Pd(1 1 1) + Na, $\theta > 0.25$	x			x		[139–141]
Pd(1 1 1) + K	x	x		x		[142]
Pd(1 1 1) + K	x	x	x			[144]
Platinum						
Pt(foil)	x					[145,146]
Pt(FEM-tip)	x					[147]
Pt(1 1 1)	x					[148–150]
Pt(1 1 1) + K	x	x		x		[150,151]
Rhenium						
Re(0 0 0 1)	x	x	x			[75,152–154]
Re(0 0 0 1) + Cu	x		x			[153]
Rhodium						
Rh(film)	x					[64]
Rh(poly)	x					[155]
Rh(Alumina-supp.)	x					[156]
Rh(FEM-tip)	x	x				[147]
Rh/B-impurities	x	x				[157,158]
Rh(1 1 1)	x					[152,153,157,158]
Rh(1 1 1) + K	x	x	x	x		[159–163]
Ruthenium						
Ru(0 0 1) + K	x	x	x	x	x	[164]

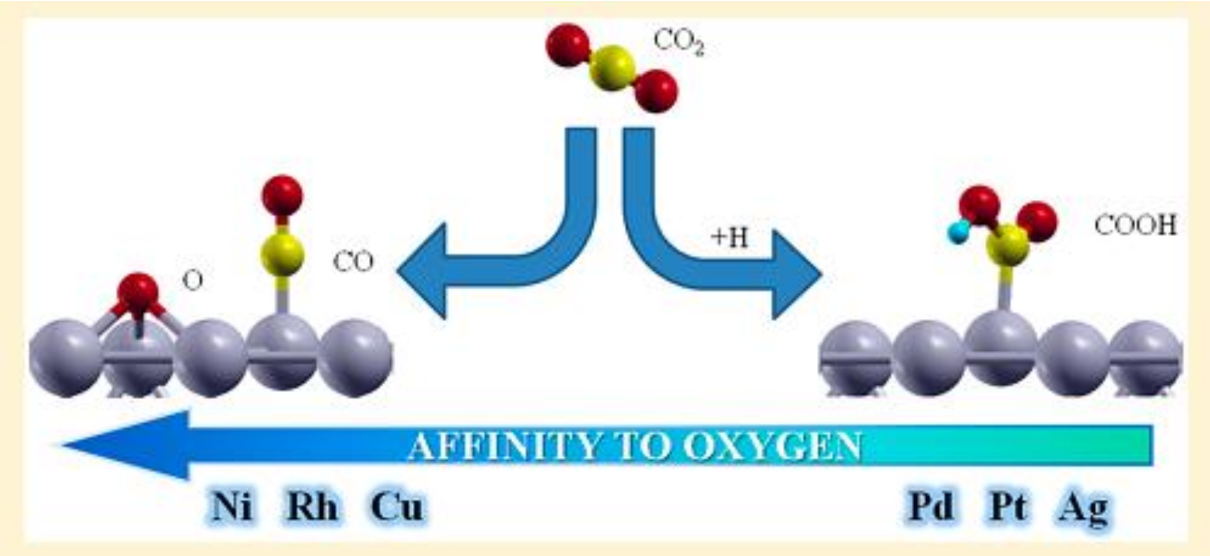


cleavage of a bond

neg EA

- work function of the metal
- structural parameters

CO_2 chemisorption on transition metals

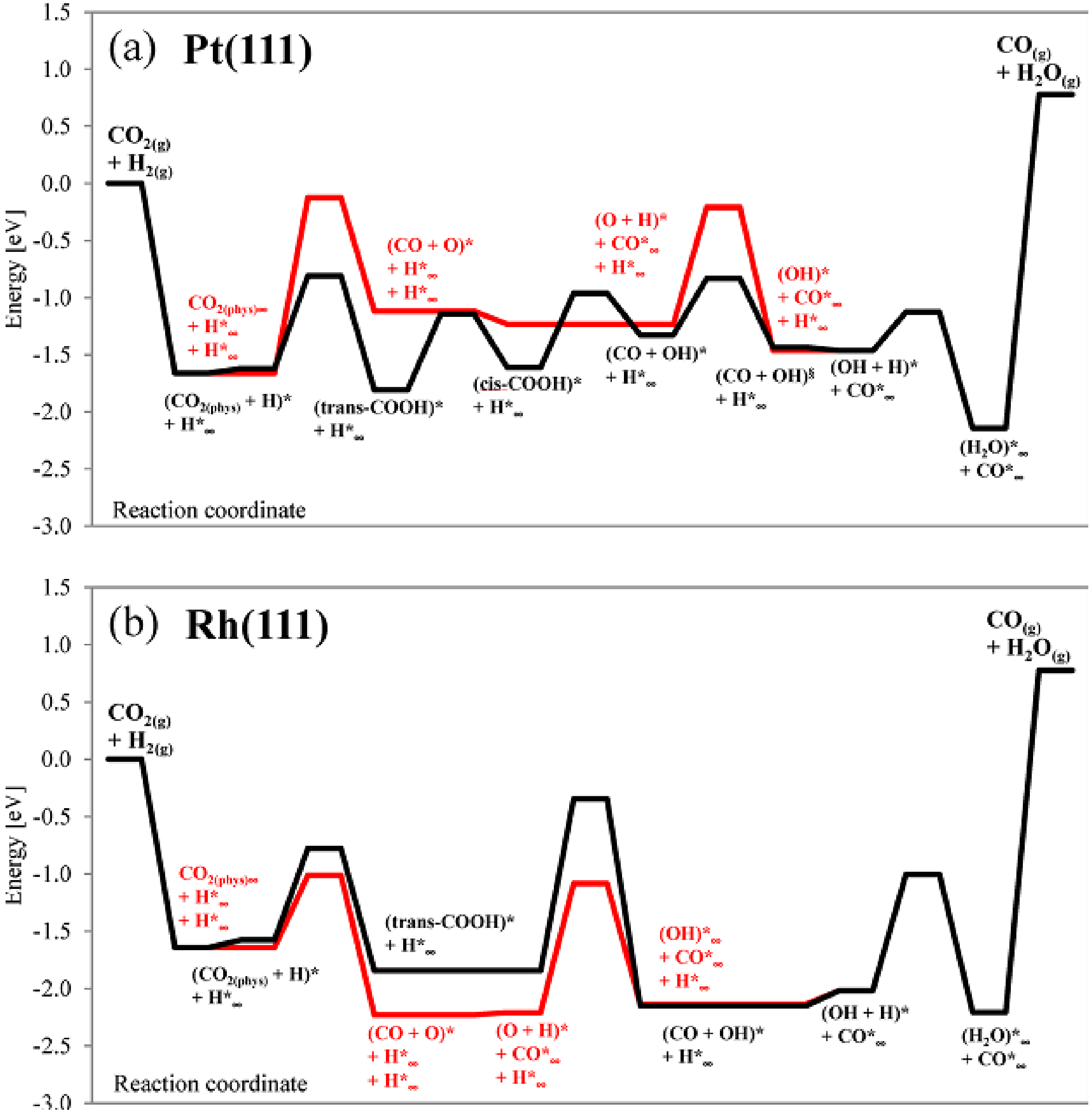


Mechanistic Insights into CO_2 Activation via Reverse Water–Gas Shift on Metal Surfaces

Luca Dietz,[†] Simone Piccinin,[*,‡] and Matteo Maestri[*,†]

DOI: 10.1021/jp512962c
J. Phys. Chem. C 2015, 119, 4959–4966

CO_2 chemisorption on transition metals



hydrogenation

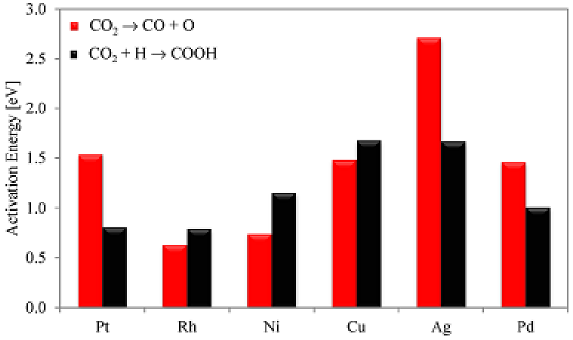


Figure 2. Dissociation (red bars) and hydrogenation (black bars) activation energies on Pt(111), Rh(111), Ni(111), Cu(111), Ag(111), and Pd(111) metals.

dissociation

CO_2 chemisorption on transition metals

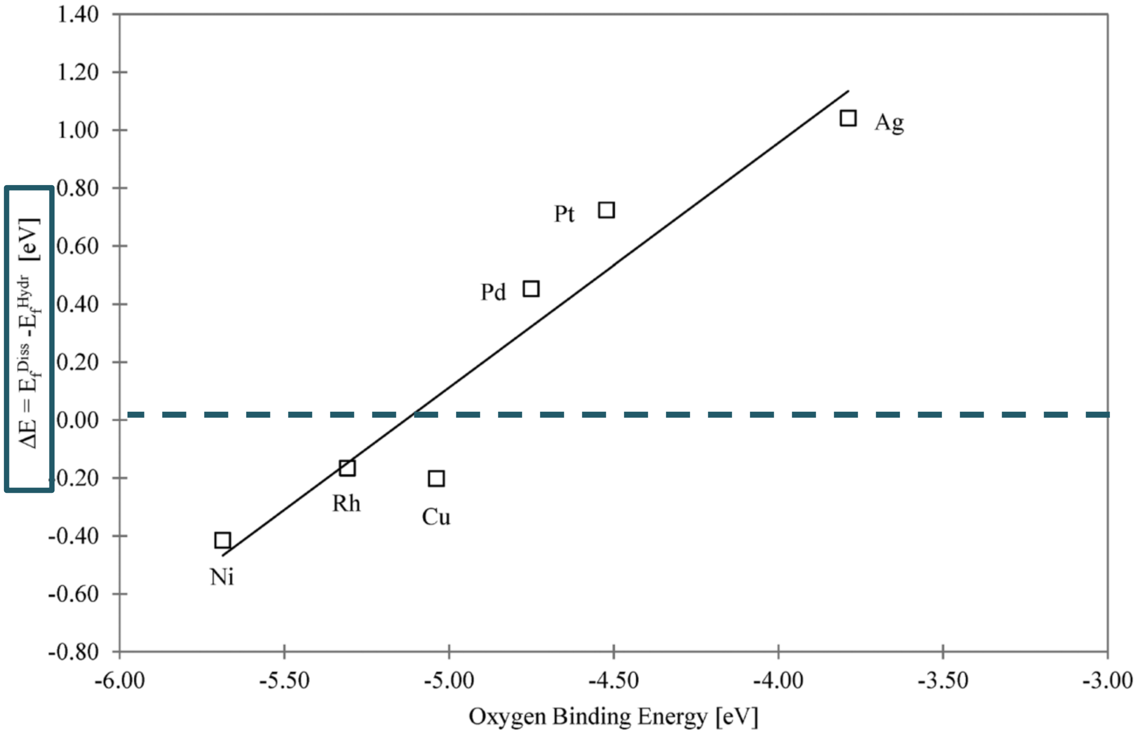


Figure 9. Correlation between the binding energy of oxygen and difference of the activation energies for the dissociation and hydrogenation reactions. Fitting model: y = 0.8436x + 4.3307; R^2 = 0.9114.

Different mechanisms steered by CO_2 dissociation barrier

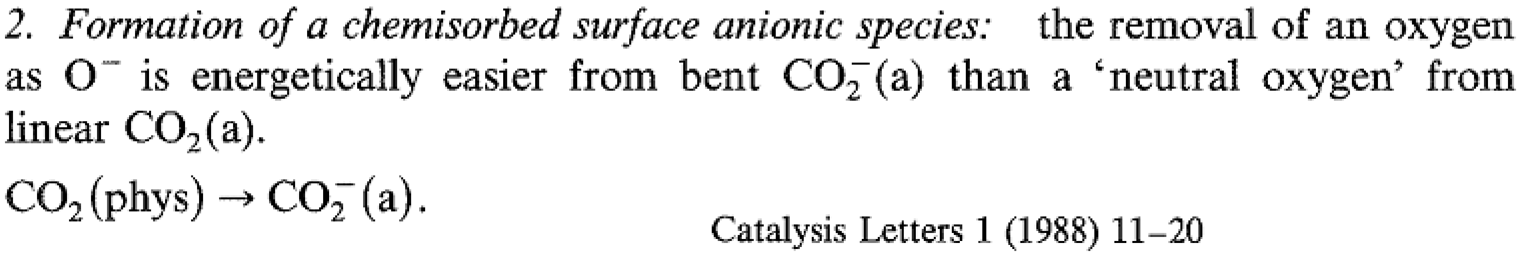
The stronger the metal-O Interaction, the lower the barrier: see BEP relation

Oxygen affinity as descriptor for the pathway

CO_2 chemisorption on transition metals: Conclusion II.

- CO_2 adsorbs on metals often dissociatively
- with hydrogen are formate or carboxylate adsorbates possible
- Many parameters like the work function, defectivity, oxophilicity and carbophilicity influence the CO_2 adsorption

Not discussed:
complexes, homogeneous catalysts, enzymes, electrochemical reduction

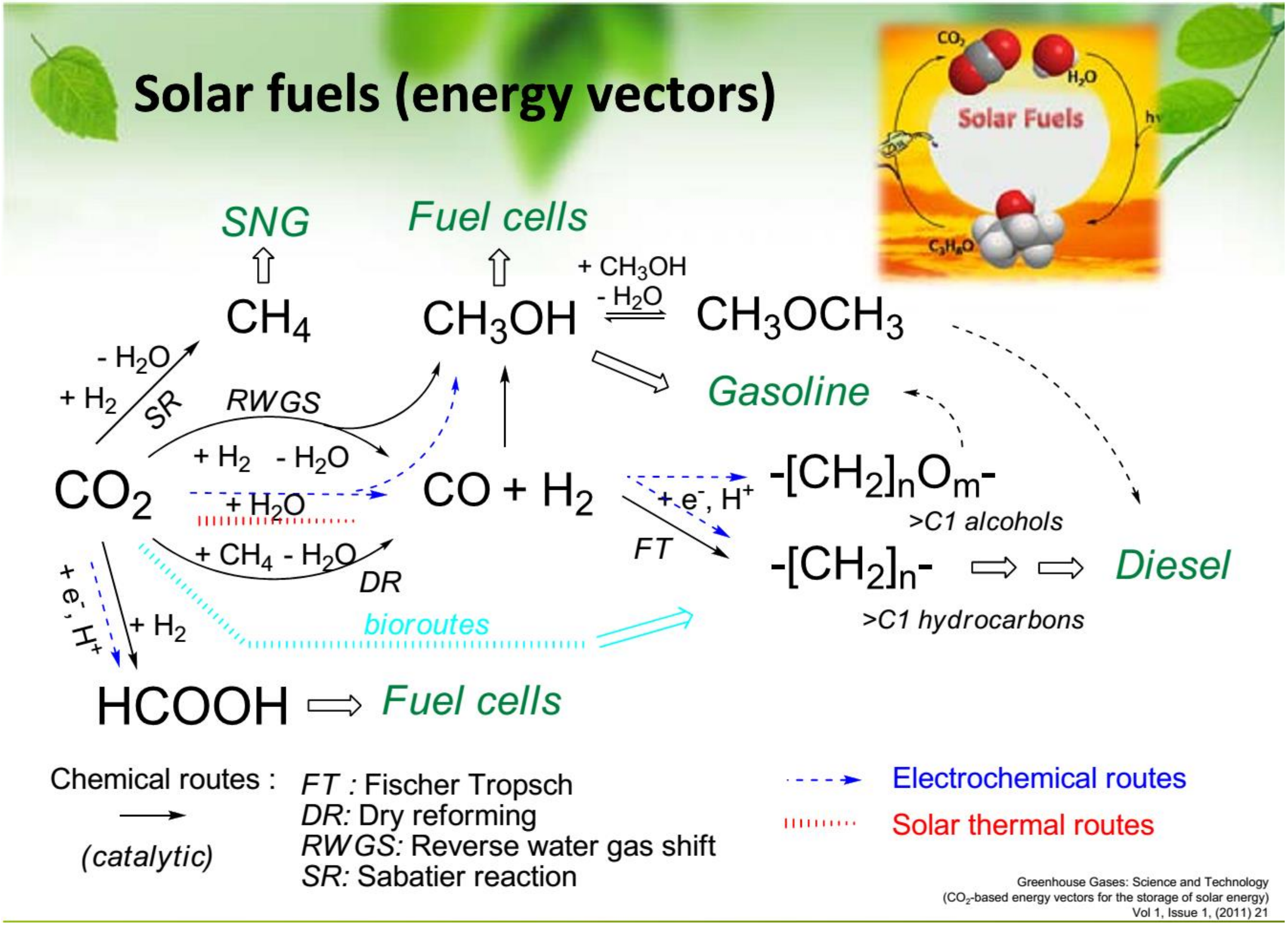


2. *Formation of a chemisorbed surface anionic species:* the removal of an oxygen as O^- is energetically easier from bent $CO_2^-(a)$ than a ‘neutral oxygen’ from linear $CO_2(a)$.

$CO_2(phys) \rightarrow CO_2^-(a)$.

Catalysis Letters 1 (1988) 11–20

CO_2 conversion with heterogeneous catalysts: metals + metal oxides



Solar fuels (energy vectors)

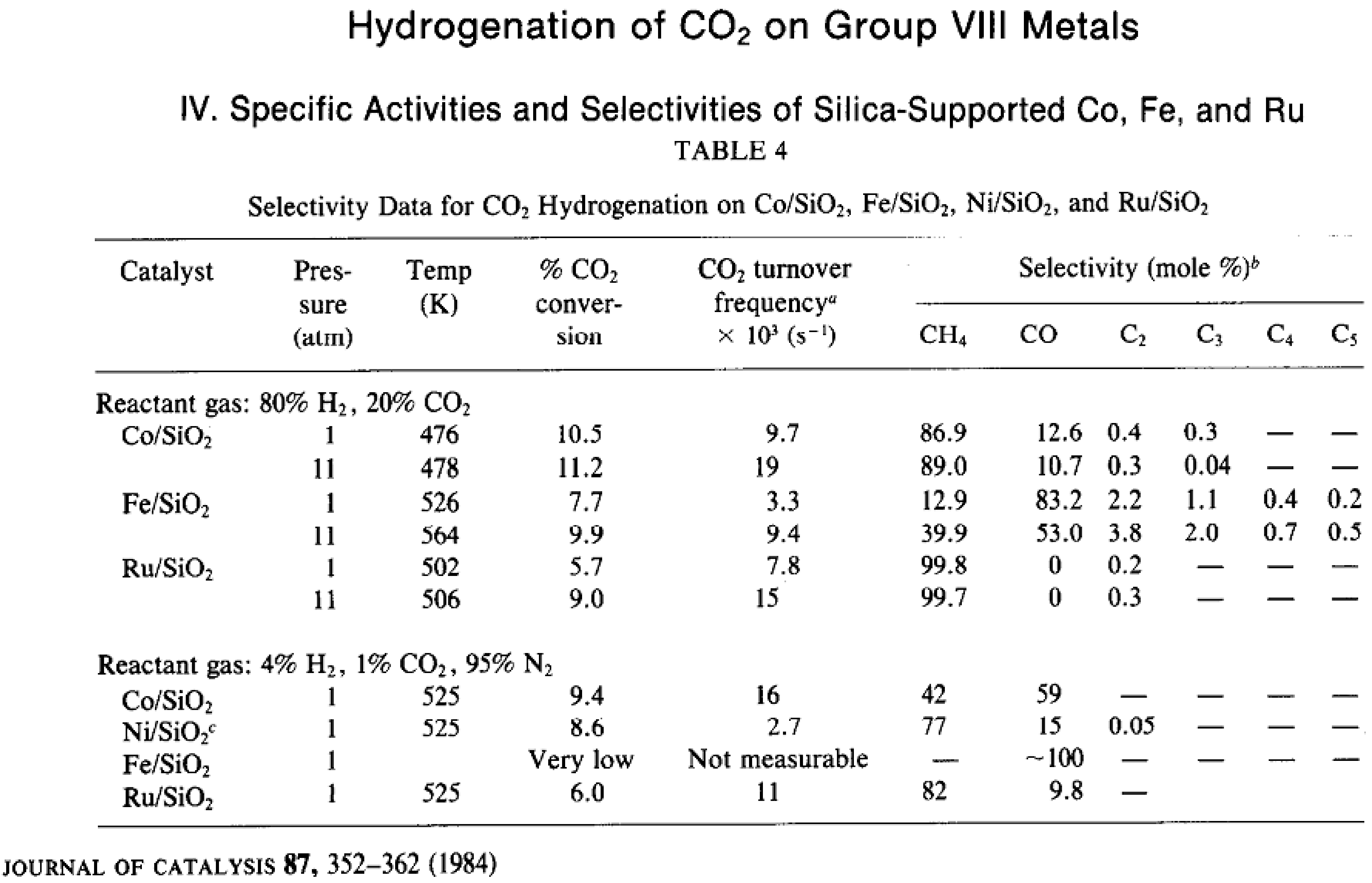
Chemical routes : → (catalytic)

FT : Fischer Tropsch
DR: Dry reforming
RWGS: Reverse water gas shift
SR: Sabatier reaction

- - -► Electrochemical routes
ııııııııı Solar thermal routes

Greenhouse Gases: Science and Technology
(CO_2-based energy vectors for the storage of solar energy)
Vol 1, Issue 1, (2011) 21

CO_2 conversion with heterogeneous catalysts: Selectivities



Hydrogenation of CO_2 on Group VIII Metals

IV. Specific Activities and Selectivities of Silica-Supported Co, Fe, and Ru

TABLE 4

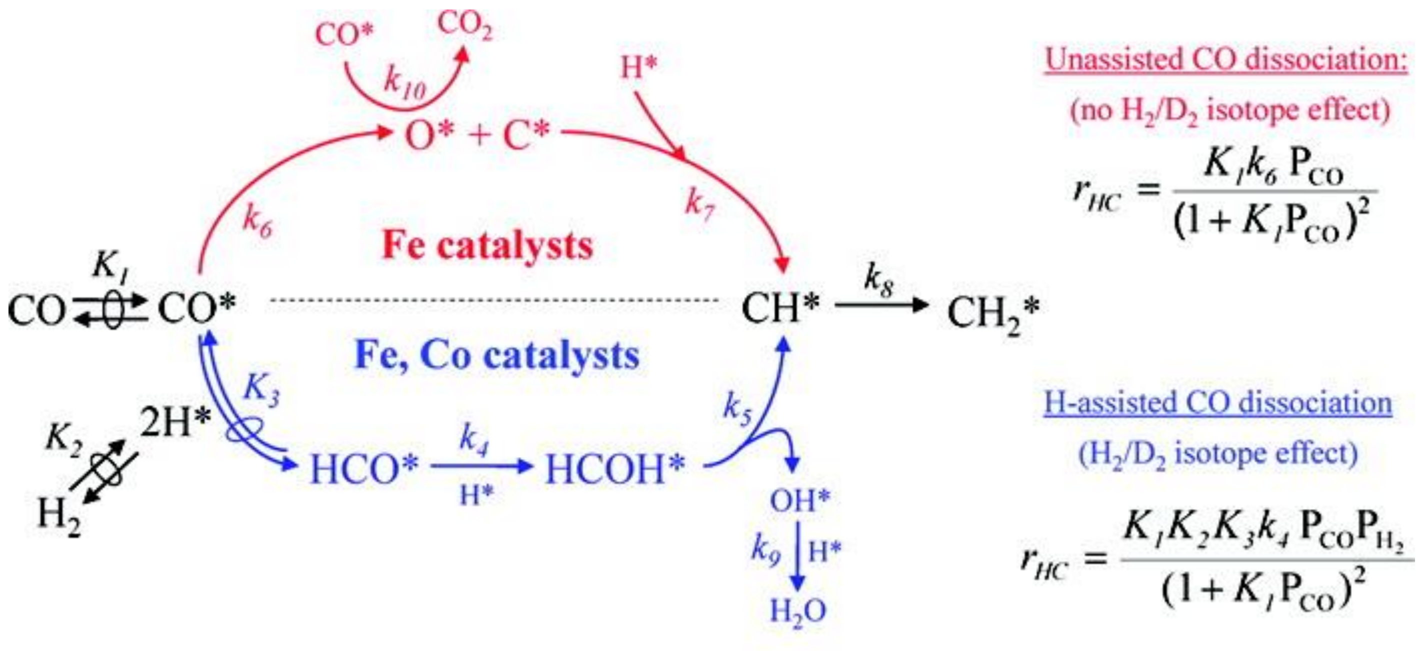
Selectivity Data for CO_2 Hydrogenation on Co/SiO_2, Fe/SiO_2, Ni/SiO_2, and Ru/SiO_2

Catalyst	Pressure (atm)	Temp (K)	% CO_2 conversion	CO_2 turnover frequency[a] $\times 10^3$ (s^{-1})	Selectivity (mole %)[b]					
					CH_4	CO	C_2	C_3	C_4	C_5
Reactant gas: 80% H_2, 20% CO_2										
Co/SiO_2	1	476	10.5	9.7	86.9	12.6	0.4	0.3	—	—
	11	478	11.2	19	89.0	10.7	0.3	0.04	—	—
Fe/SiO_2	1	526	7.7	3.3	12.9	83.2	2.2	1.1	0.4	0.2
	11	564	9.9	9.4	39.9	53.0	3.8	2.0	0.7	0.5
Ru/SiO_2	1	502	5.7	7.8	99.8	0	0.2	—	—	—
	11	506	9.0	15	99.7	0	0.3	—	—	—
Reactant gas: 4% H_2, 1% CO_2, 95% N_2										
Co/SiO_2	1	525	9.4	16	42	59	—	—	—	—
Ni/SiO_2[c]	1	525	8.6	2.7	77	15	0.05	—	—	—
Fe/SiO_2	1		Very low	Not measurable	—	~100	—	—	—	—
Ru/SiO_2	1	525	6.0	11	82	9.8	—			

JOURNAL OF CATALYSIS **87**, 352–362 (1984)

CO_2 conversion with heterogeneous catalysts: Selectivities

FT catalysts have to adsorb also CO dissociatively!



Unassisted CO dissociation:

(no H_2/D_2 isotope effect)

$$r_{HC} = \frac{K_1 k_6 P_{CO}}{(1 + K_1 P_{CO})^2}$$

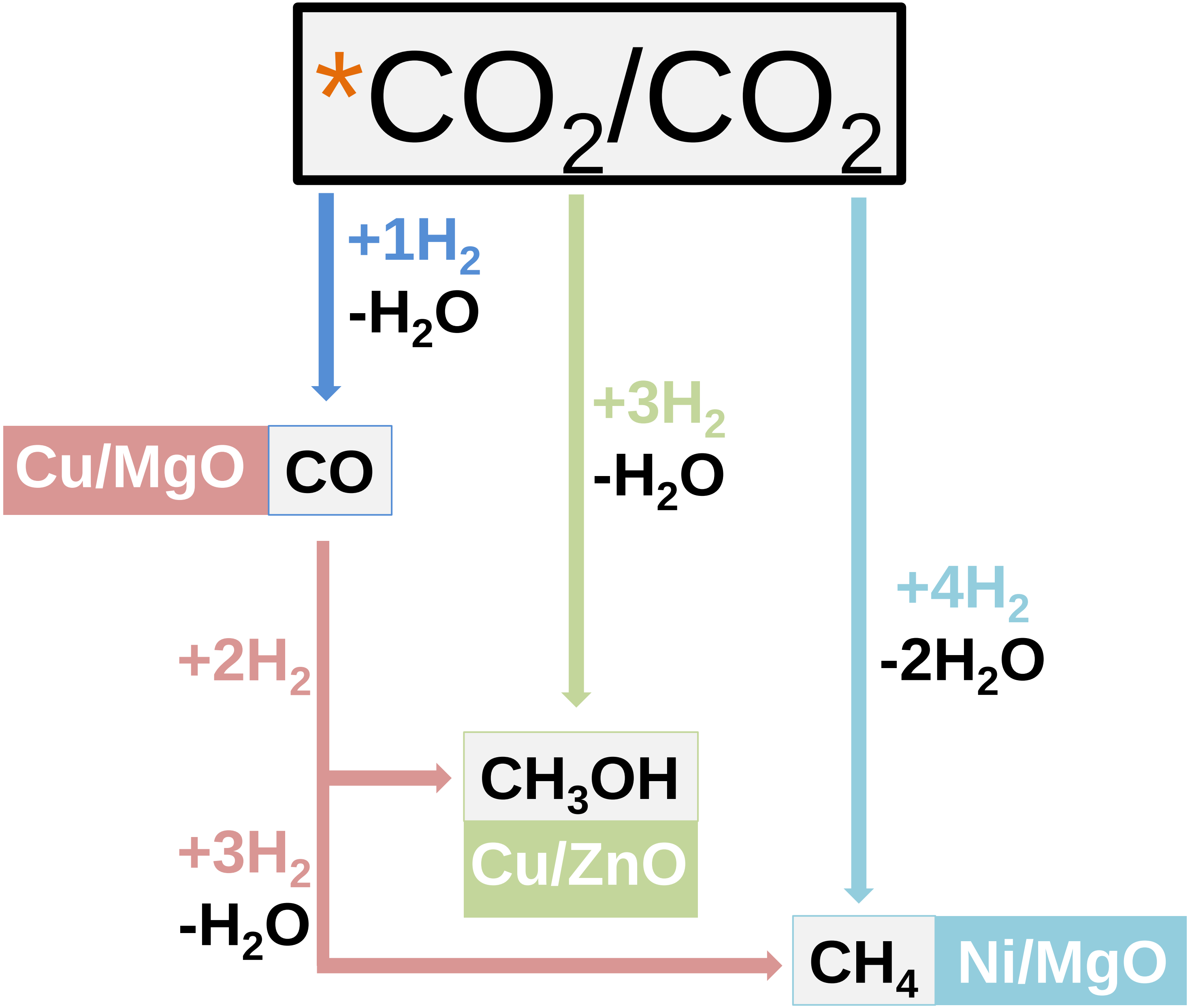
H-assisted CO dissociation

(H_2/D_2 isotope effect)

$$r_{HC} = \frac{K_1 K_2 K_3 k_4 P_{CO} P_{H_2}}{(1 + K_1 P_{CO})^2}$$

H_2/D_2 isotope effect : $\frac{r_H}{r_D} = \frac{K_2^H}{K_2^D} \cdot \frac{K_3^H}{K_3^D} \cdot \frac{k_4^H}{k_4^D}$ → **0.56 (Fe)**, → **0.80 (Co)**

J. Phys. Chem. C 2010, 114, 19761–19770



*CO_2/CO_2

$+1H_2$
$-H_2O$

Cu/MgO CO

$+2H_2$

$+3H_2$
$-H_2O$

$+3H_2$
$-H_2O$

CH_3OH
Cu/ZnO

$+4H_2$
$-2H_2O$

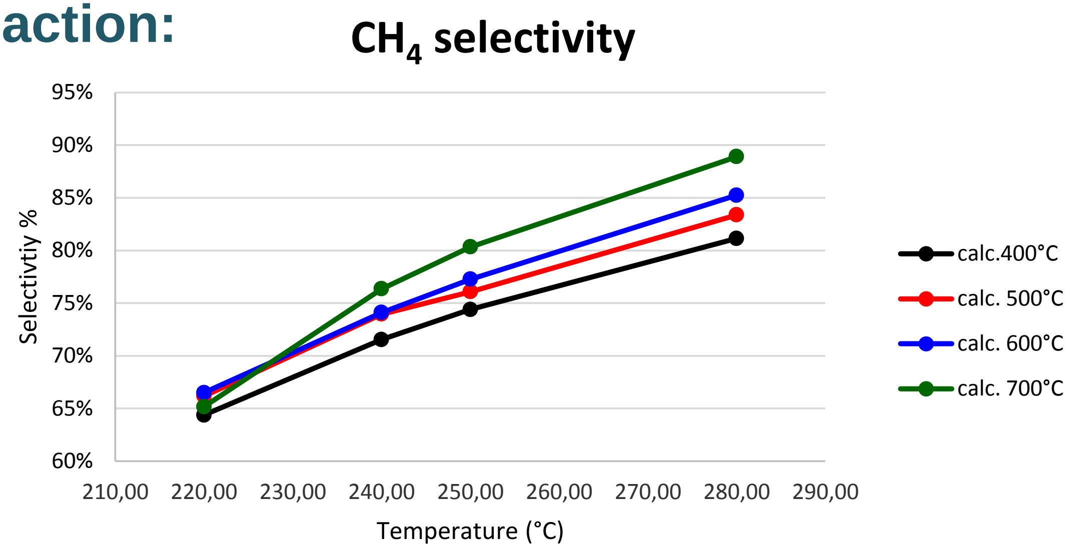
CH_4 Ni/MgO

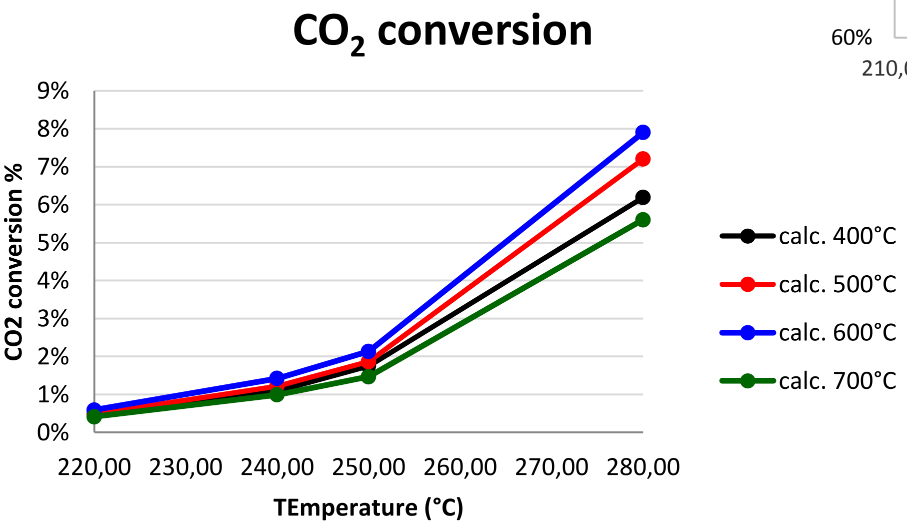
CO_2 conversion with Ni catalyst: Selectivity

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad \Delta H_0 = 41\ \text{kJ mol}^{-1}$$

NiMgO catalyst for Sabatier reaction:

- $4H_2$ / 1 CO_2 at 1 bar
- CH_4 and CO as products

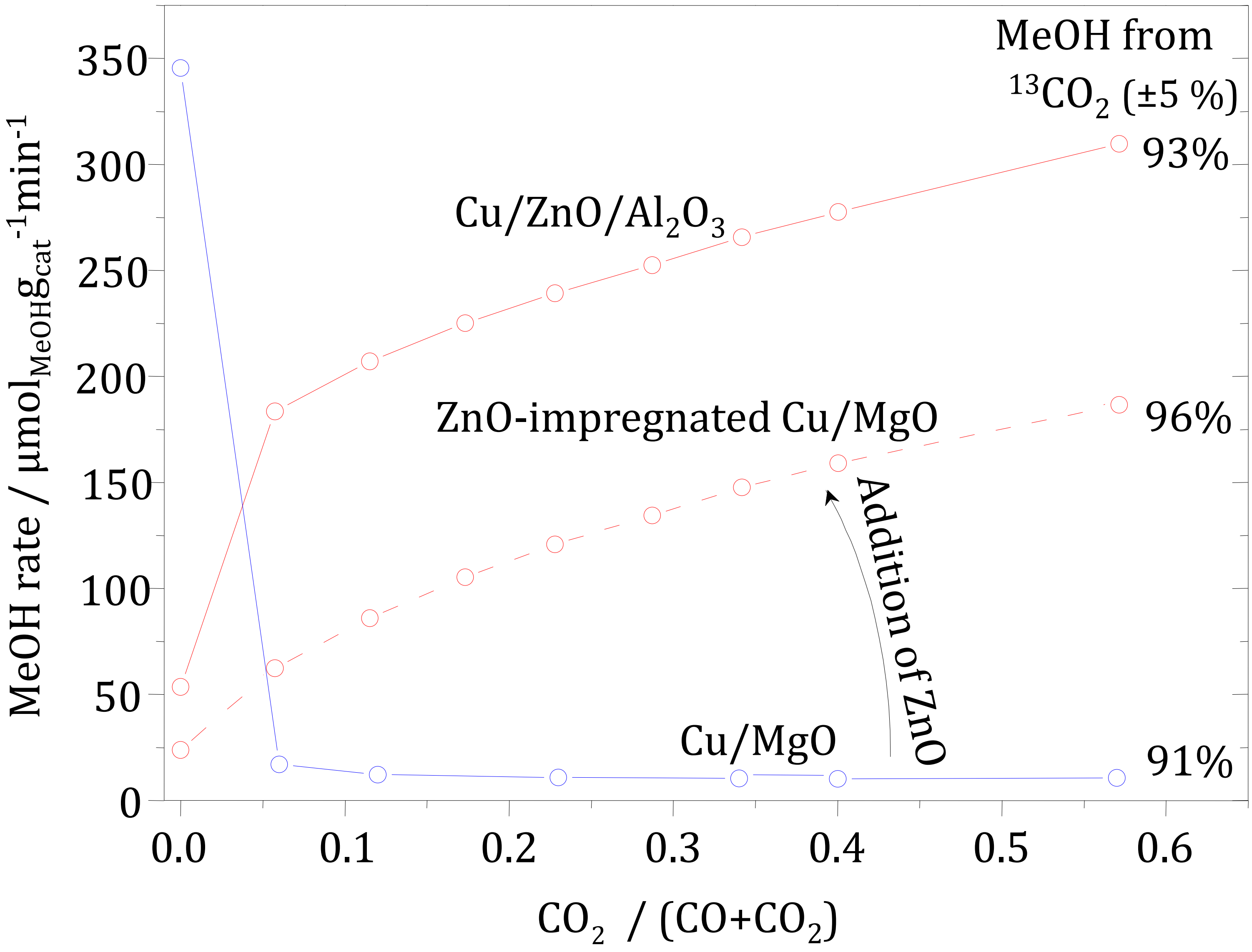




PhD-Thesis M.-M. Millet

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \qquad \Delta H_{298} = -165{,}12\ \text{kJ/mol}$$

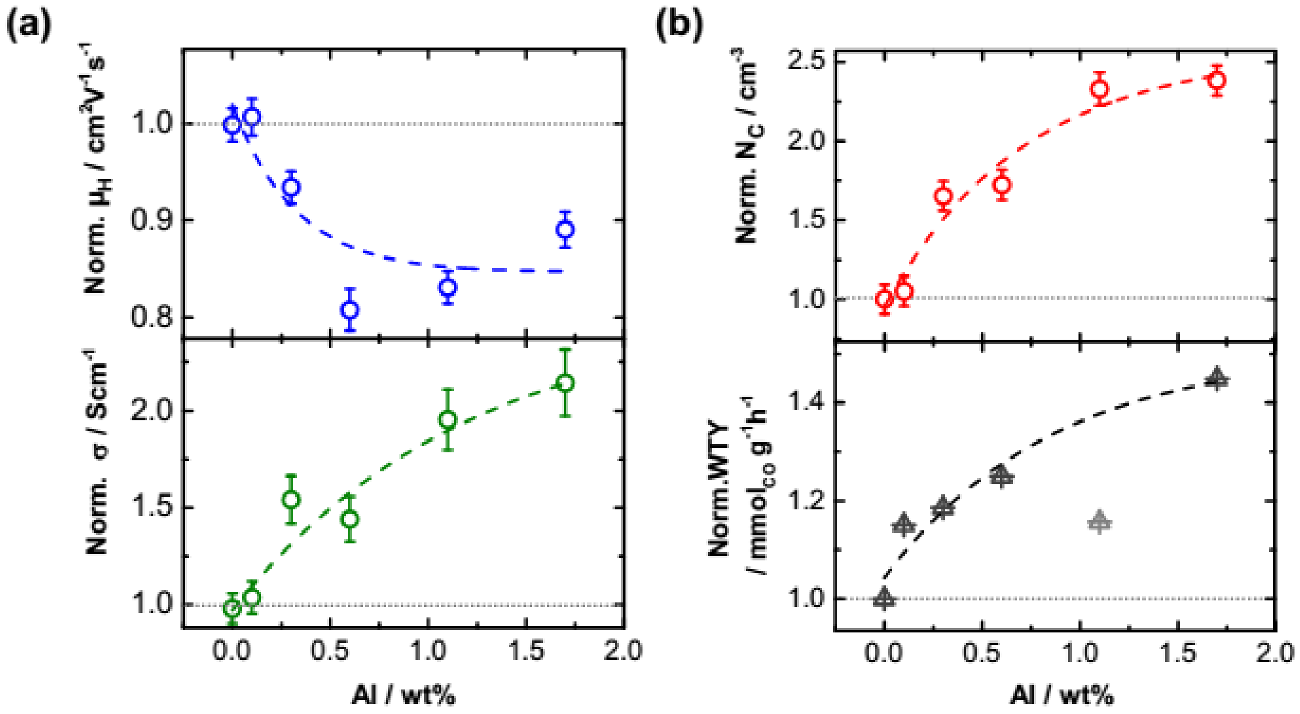
CO_2 / CO conversion with Cu catalysts



Behrens, Frei, Schlögl et al., ChemCatChem 2015, 7, 1105 – 1111

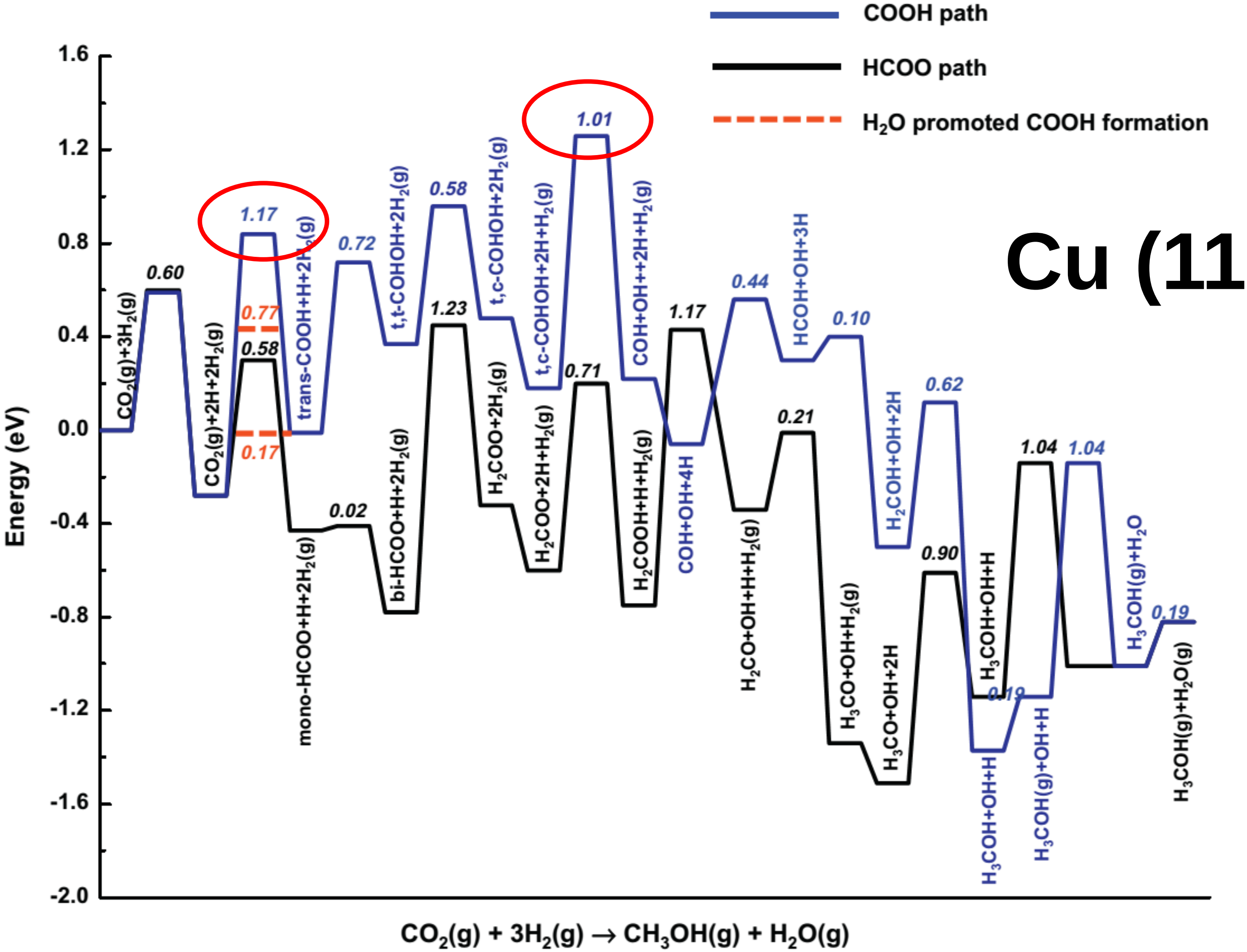
Al doped ZnO + Cu in rWGSR:

- more charge carriers
- more active in CO_2 activation / CO-production
- decrease of the app. E_a



PhD-Thesis, Maria Heenemann

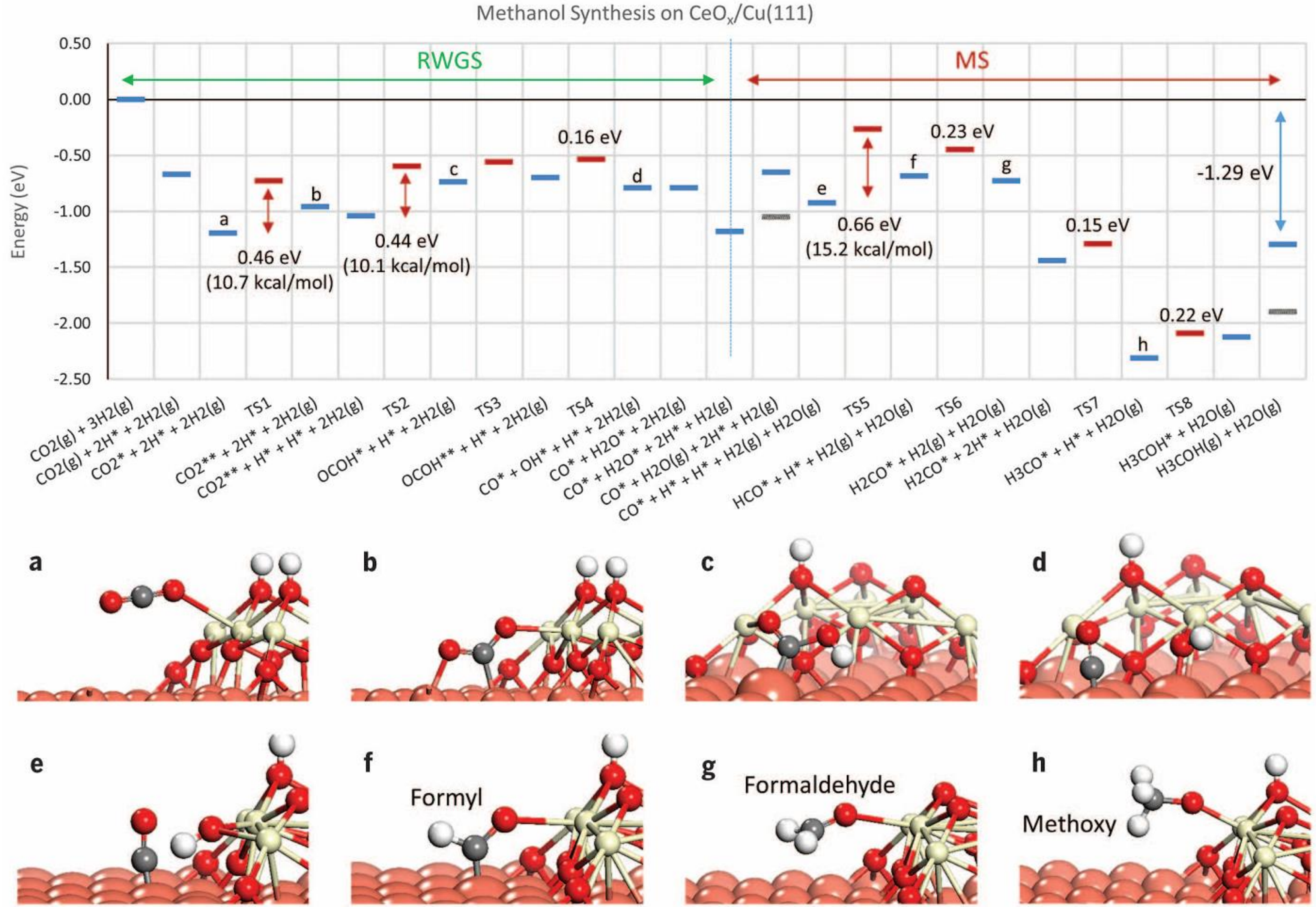
The importance of a metal/metal oxide interface



Cu (111)

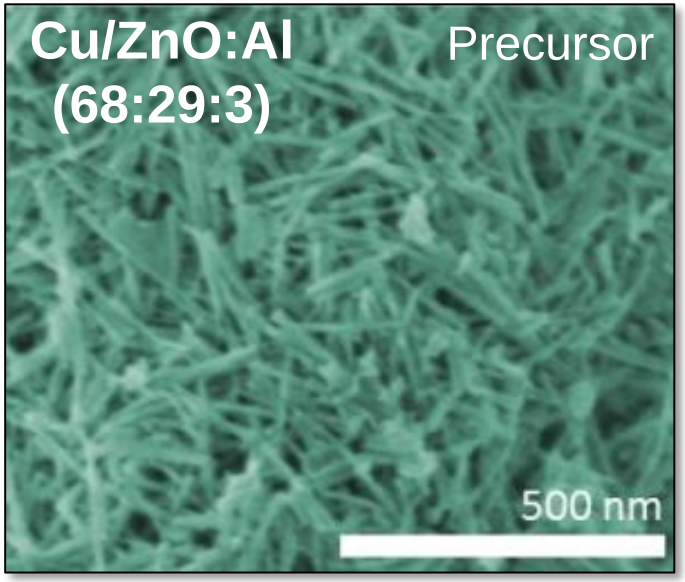
Y.-F. Zhao et al. / Journal of Catalysis 281 **2011** 199–211

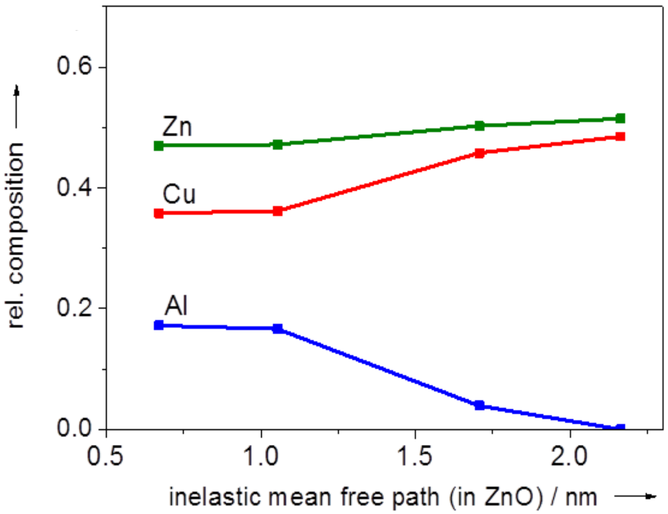
The importance of a metal/metal oxide interface

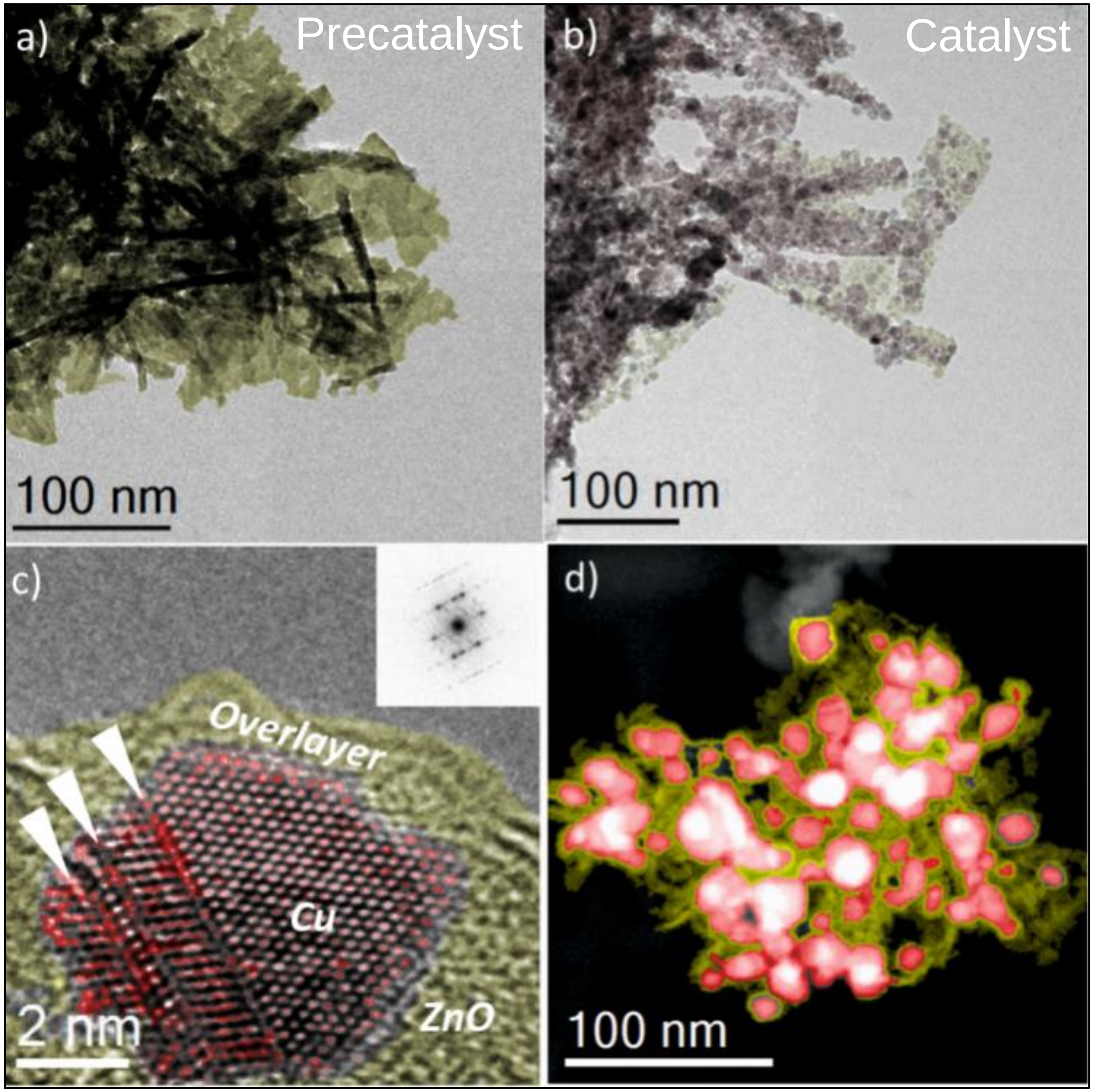


Science 1 AUGUST **2014**•VOL 345 ISSUE 6196

The importance of a metal/metal oxide interface







Schumann et al., ChemCatChem, Vol.6, Issue 10, 2889-2897, 2014

CO_2 activation and conversion: Conclusion III.

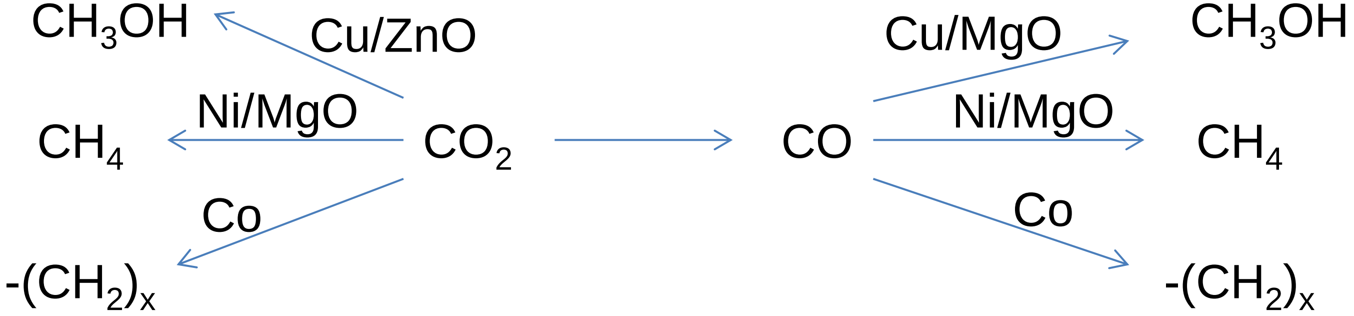
1. **Electron transfer for the anionic CO_2 activation: metal or metal oxide (see ZnO)**

2. **On metal oxides rather as carbonate on metals dissociativly adsorbed (or as formiate / carboxylate)**

3. **Heterogenous catalysts exist of metals + metal oxides (support or co-catalyst)**

4. **Interface between metal and metal oxide plays an important role: i.e. methanol**

5. **Depending on the metal, its electr. structure and the defectivity: prod. selectivity**


CH_3OH Cu/ZnO Cu/MgO CH_3OH

CH_4 Ni/MgO CO_2 $\rightarrow$ CO Ni/MgO CH_4

Co Co

$-(CH_2)_x$ $-(CH_2)_x$

Not discussed: DRM / Hydrogen activation