Adsorption of carbon dioxide on Cu(110) and on hydrogen and oxygen covered Cu(110) surfaces

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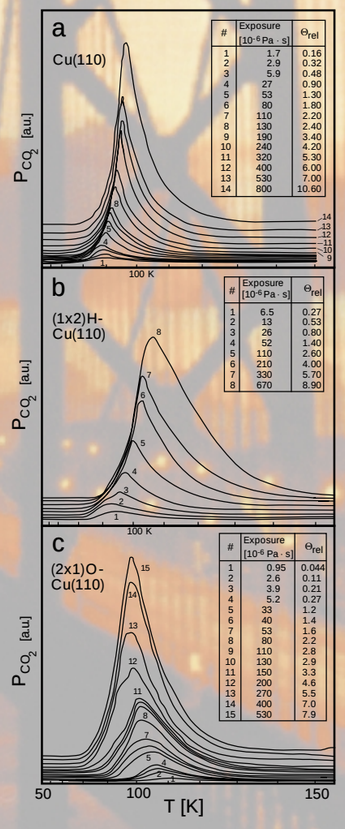
Outline

CO_2 may act as a precursor in methanol synthesis ($CO + 2H_2 \rightarrow CH_3OH$) over $Cu/ZnO/Al_2O_3$ catalysts. A bent CO_2^- anion and a formate species ($HCOO_{ad}$) were proposed as intermediates. Kinetic measurements of the r-WGS reaction ($H_2 + CO_2 \rightarrow H_2O + CO$) over Cu(110) showed a dramatic drop in turnover frequency with increasing CO_2 pressure. This could only be explained via substrate phase transition triggered by the H_2 coverage [1]. Dissociation into CO and oxygen were observed on stepped Cu-surfaces [2]. On Cu(110), however, there was still a controversy about any dissociation at low temperatures [3-5].

Under UHV conditions:
(a) Does CO_2 dissociate on Cu(110) below 100K?
(b) Can it be hydrogenated to $HCOO_{ad}$?
(c) What are the geometric structures of CO_2 on Cu(110) and on the reconstructed surfaces like (1x2)H/Cu(110) and (2x1)O/Cu(110)? Are there species like CO_2^- or CO_3^- ?

TDS

CO_2 coverage calibration: adsorption of HCOOH at 340K leads to a closed packed $HCOO_{ad}$ layer with $3.6 \cdot 10^{14}$ molec/cm^2). Subsequent TDS ($HCOO_{ad} \rightarrow CO_2 + H_2$) gives the respective CO_2 desorption signal at 470K (signal area assigned to θ_{rel}=1).



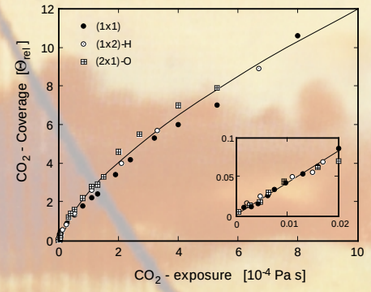
#	Exposure [10^{-6} Pa · s]	Θ_{rel}
1	1.7	0.16
2	2.9	0.32
3	5.9	0.48
4	27	0.90
5	53	1.30
6	80	1.80
7	110	2.20
8	130	2.40
9	190	3.40
10	240	4.20
11	320	5.30
12	400	6.00
13	530	7.00
14	800	10.60

#	Exposure [10^{-6} Pa · s]	Θ_{rel}
1	6.5	0.27
2	13	0.53
3	26	0.80
4	52	1.40
5	110	2.60
6	210	4.00
7	330	5.70
8	670	8.90

#	Exposure [10^{-6} Pa · s]	Θ_{rel}
1	0.95	0.044
2	2.6	0.11
3	3.9	0.21
4	5.2	0.27
5	33	1.2
6	40	1.4
7	53	1.6
8	80	2.2
9	110	2.8
10	130	2.9
11	150	3.3
12	200	4.6
13	270	5.5
14	400	7.0
15	530	7.9

TD spectra of various CO_2 coverages on (a) Cu(110), (b) (1x2)H/Cu(110), and (c) (2x1)O/Cu(110).

Activation energies of desorption at low coverage (assuming 1st order desorption kinetics): Cu(110): 21 kJ/mol; (1x2)H/Cu(110): 22.5 kJ/mol; (2x1)O/Cu(110): 26 kJ/mol. Common leading edge at higher coverages indicates zero-order desorption kinetics, but it shifts to higher temperatures with higher coverages!



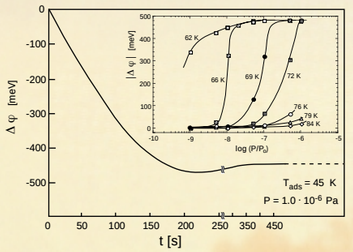
The coverage-exposure dependence does not show significant differences in sticking coefficient.

TDS experiments on all three substrates using $C^{18}O_2$ did not show $C^{18}O$.
After CO_2 adsorption on (1x2)H/Cu(110), neither H_2 nor CO_2 desorption at 470K was observed.

LEED

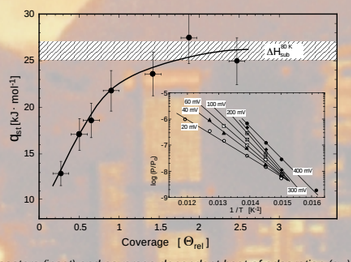
No superstructure between 30K and 100K was observed.
=> no lateral long range order

Work Function ($\Delta\varphi$)



$\Delta\varphi$ with increasing CO_2 exposure obtained via the Kelvin method. The inset shows adsorption isotherms.

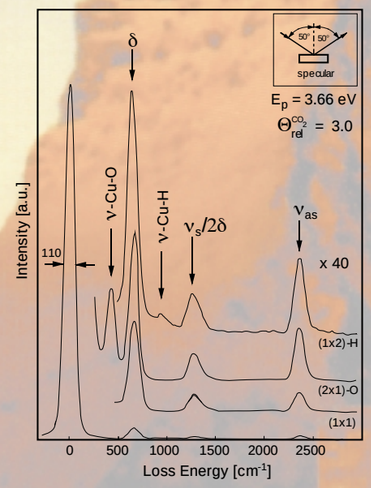
Rapid adsorption occurs when a critical pressure is exceeded.
⇒ condensation of CO_2 into islands



Isosters (inset) and coverage dependent heat of adsorption (q_{st}).

The increase of q_{st} from 13 to 25 kJ mol^{-1} ($\approx$ CO_2 sublimation enthalpy) shows that the CO_2–CO_2 interaction is stronger than the CO_2–Cu interaction.

HREELS



HREEL spectra for CO_2 on Cu(110), on (1x2)H/Cu(110), and on (2x1)O/Cu(110), respectively. The bands are located at δ = 660 cm^{-1} (deformation mode) $\nu_S/2\delta$ = 1270/1360 cm-1 (Fermi resonance), and ν_S = 2360 cm^{-1} (antisymmetric stretch mode).

Only vibrational bands for the linear molecule are observed. No differences for CO_2 vibrations on all three substrates at all coverages were found. Angular dependent off-specular measurements revealed that ν_S and δ are dipol active.
⇒ random or tilted adsorption geometry
Weak interaction, since the Fermi resonance is still observed.
⇒ small perturbation of the molecule upon adsorption

Conclusions

- CO_2 is physisorbed on all three sub strates.
- Neither dissociation nor hydrogenation of CO_2 was observed.
- The CO_2 molecular geometry is linear in all cases (no CO_2^-).
- CO_2-CO_2 interaction is stronger than CO_2- Cu interaction.
- CO_2 islands (3-dimensional?) are formed already at low coverages ($< \theta = 0.1$).

References

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