

Sorption Mechanism for CO₂ on Hydrotalcites

For Sorption Enhanced Water Gas Shift processes

Soledad van Eijk

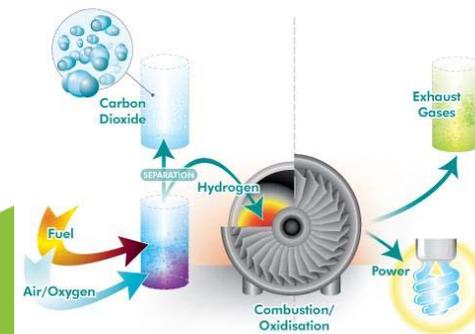
Veldhoven
11th February 2014

www.ecn.nl

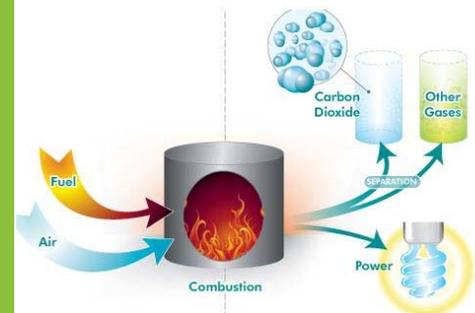
The world of SEWGS

pre-combustion capture

Pre-Combustion Capture

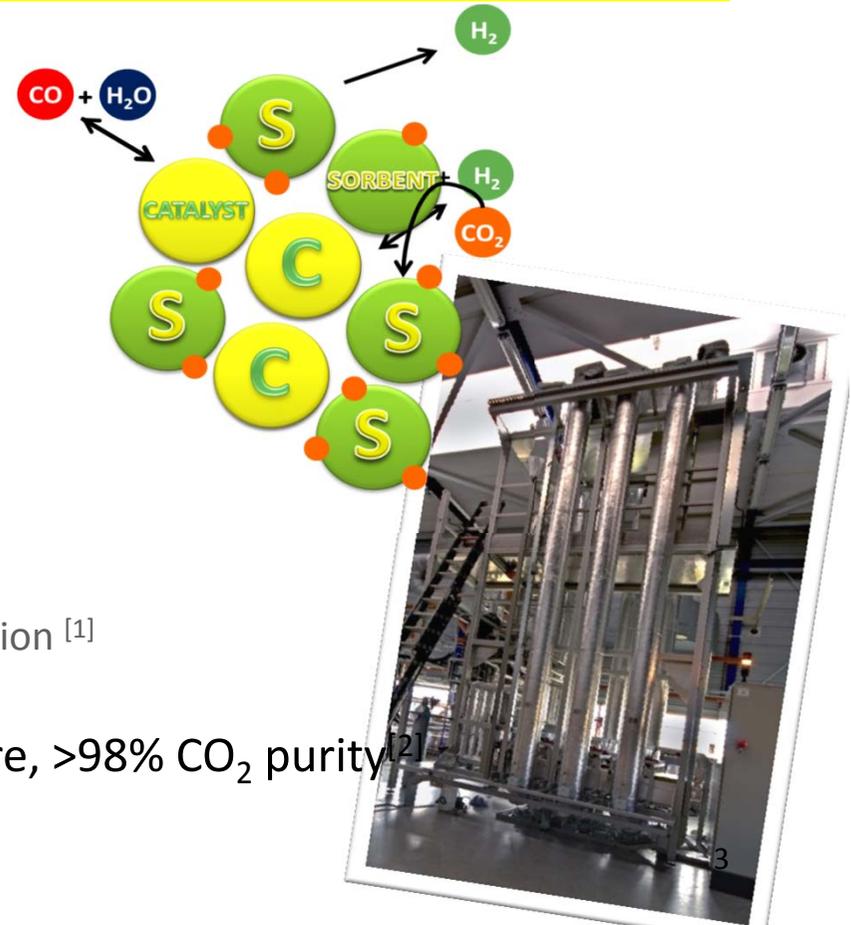


Post-Combustion Capture



What is SEWGS?

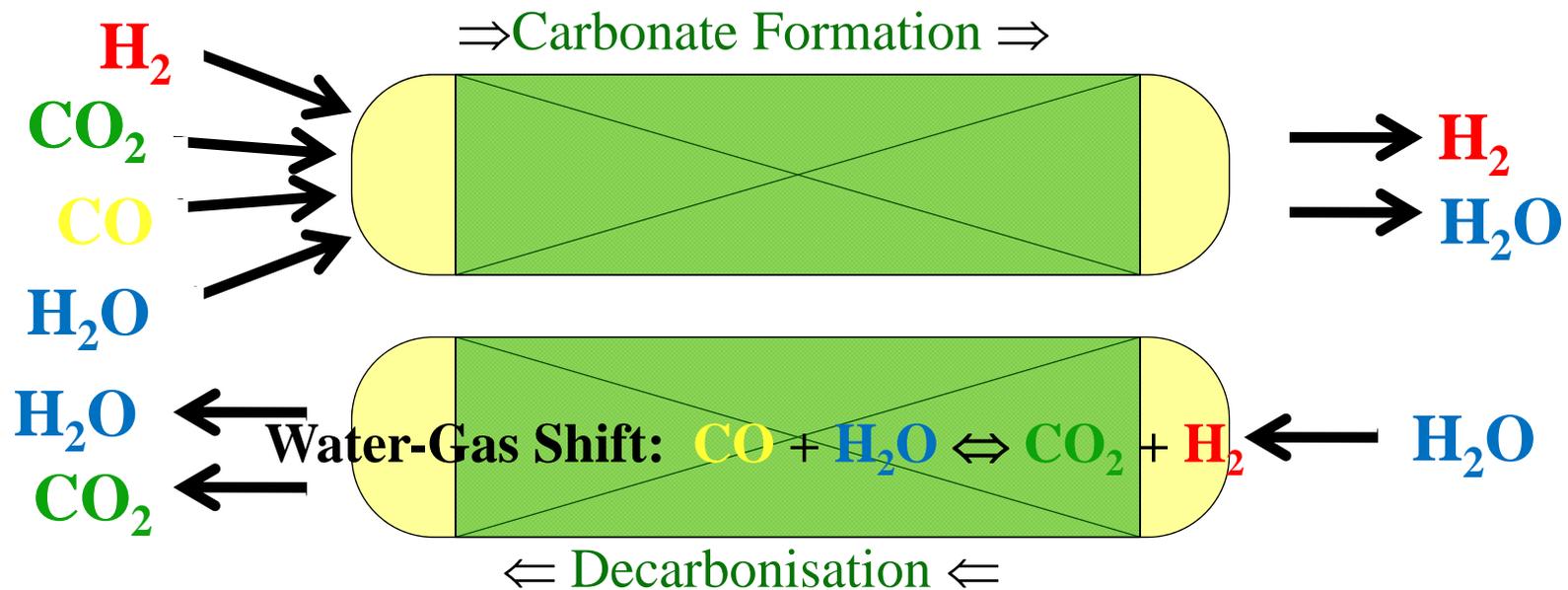
- Pre-combustion CO₂ capture
 - Pre-reformed gas mixture = syngas
- Sorption Enhanced Water Gas Shift
 - Water Gas Shift: $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$
 - Sorption Enhanced: Le Chatelier's Principle
- High pressure (35 bar)
- High temperature (400°C)
 - Lower energy penalty, H₂ ready for combustion ^[1]
- Specifications SEWGS: >95% CO₂ capture, >98% CO₂ purity^[2]



[1] M.Gazzani et.al., international journal of greenhouse gas control (12 A.D.).

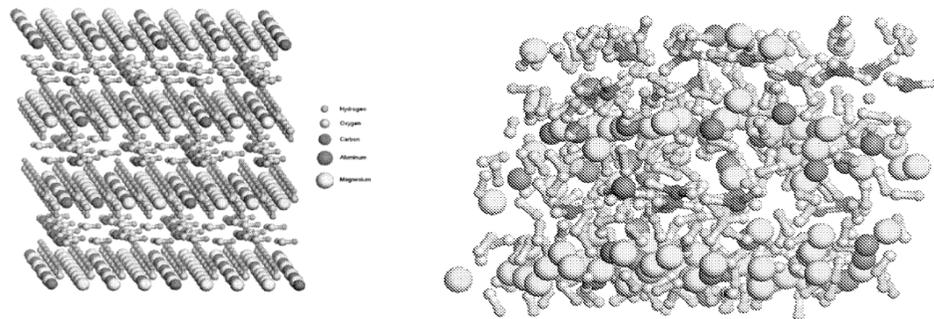
The reactor proces

High temperature (400°C), high pressure (35 bar) production of H₂ from Syngas.



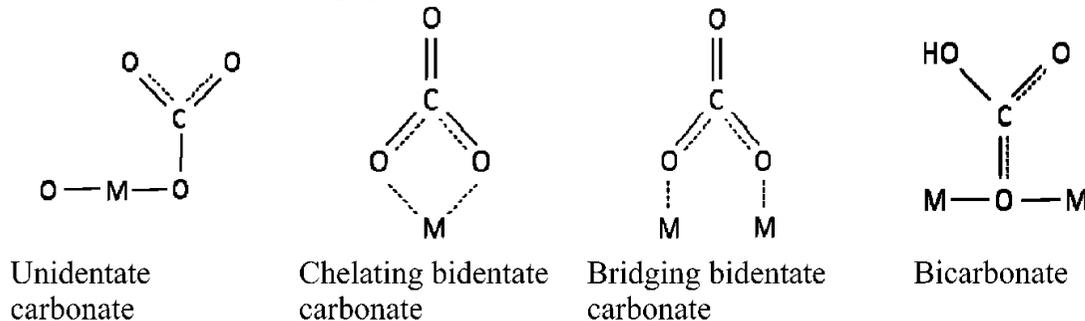
The CO₂ adsorbent

- At ECN a sorbent is developed: Alkasorb +
- This is based on Hydrotalcite [2]
 - Two dimensional sheets of mixed hydroxides (M²⁺ & M³⁺)
 - With interlayer H₂O & charge compensating anions
 - **Mg₆Al₂(OH)₁₆CO₃·4H₂O**
- At this temperature HTC converts into its active form [3]
 - @100°C layered HTC → @400°C amorphous mixed oxide → @900°C spinel



How does CO₂ adsorb?

- What is the mechanism behind the CO₂ adsorption
 - Some of the bonding geometries known^[4]



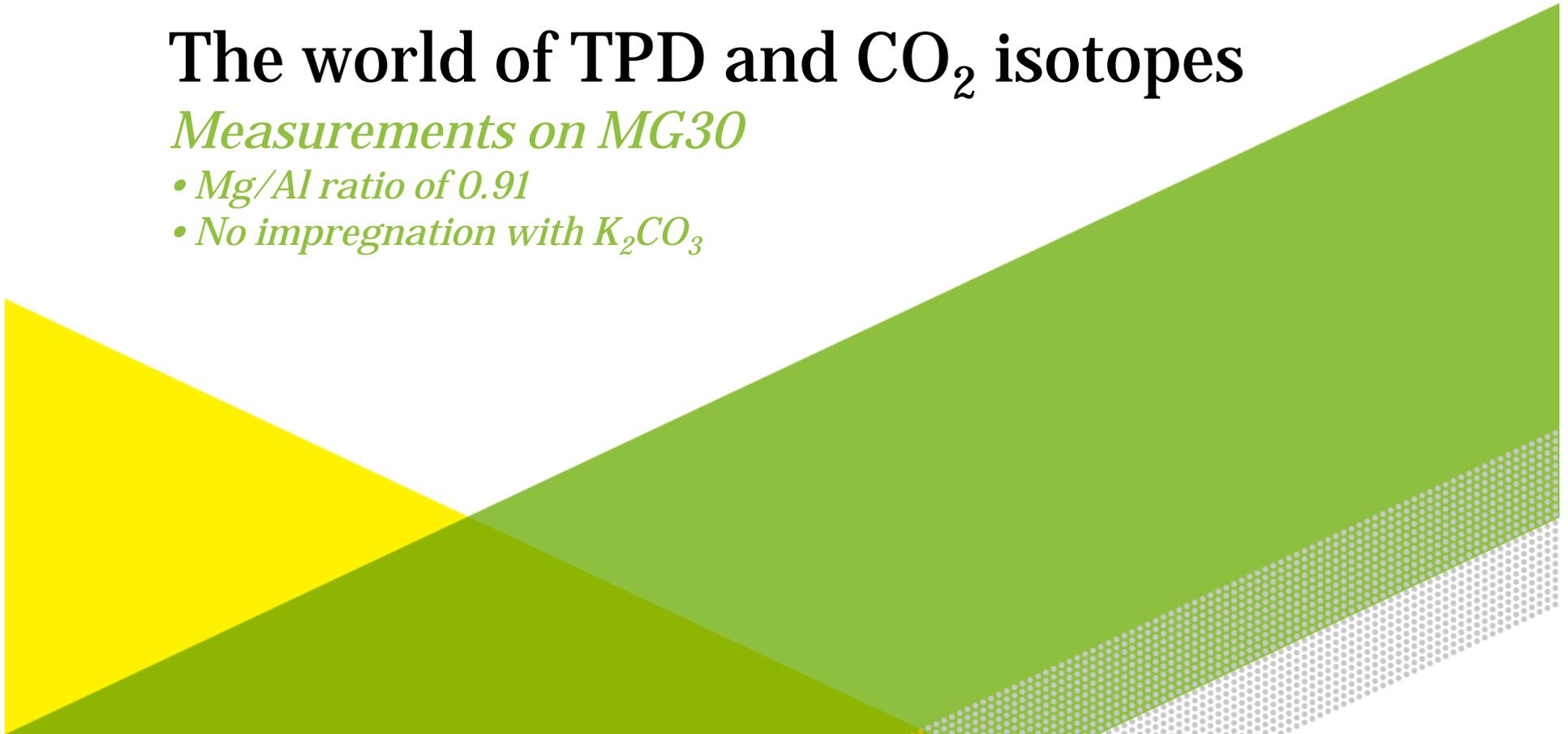
- What is the influence of the material composition
 - The **Mg/Al** ratio and distribution have effect on possible bonding geometries (= sites)
 - Impregnation with **K₂CO₃** improves capacity by factor 4
- What is the influence of the process conditions
 - **Steam** is always present and is also adsorbed, however seems to enhance capacity as well
 - **Syngas** is the starting condition and Alkasorb showed to have catalytic properties

[4] M.Leon et.al., *Industrial & Engineering Chemistry Research* 49 (2010) 3663-3671.

The world of TPD and CO₂ isotopes

Measurements on MG30

- *Mg/Al ratio of 0.91*
- *No impregnation with K₂CO₃*

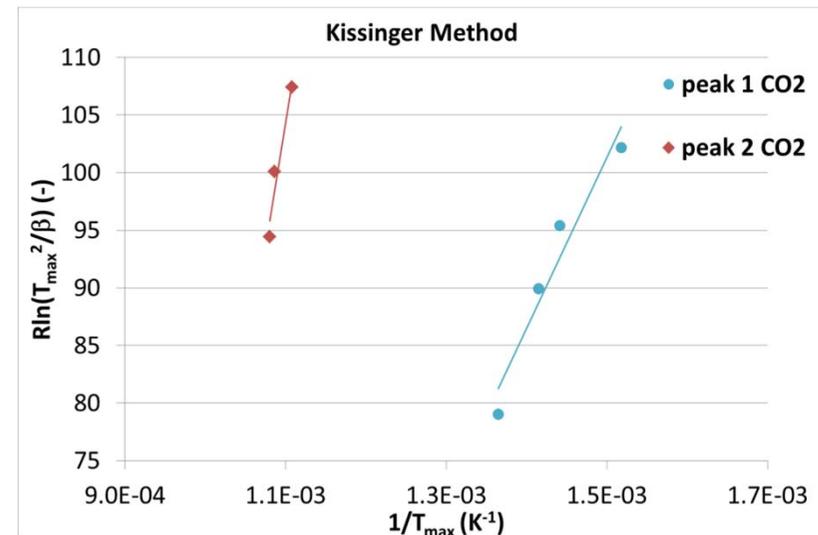
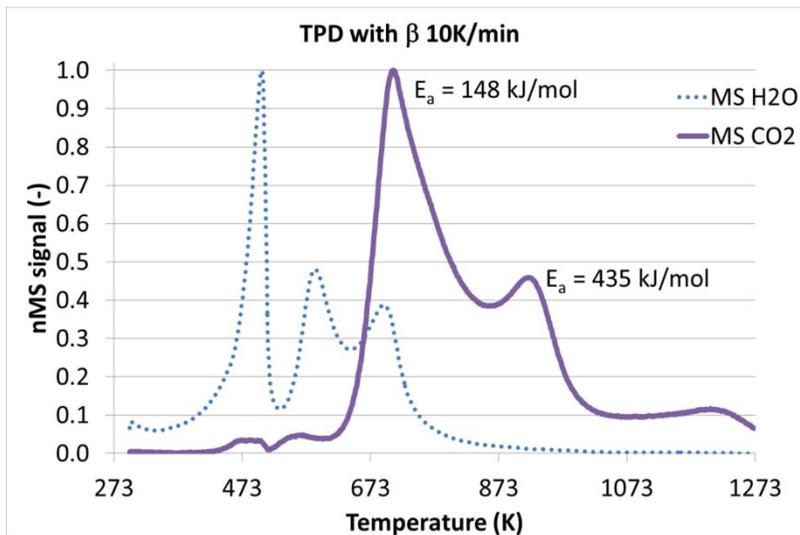


TPD: with green HTC

- Decomposition of HTC with several heating rates (β)

- Resulted in **two sites for CO₂** (*H₂O results in 3 sites*)
- With Kissinger method^[5] E_a was determined from the slope
 - This corresponds to the **decomposition** sites of HTC
 - Need info on adsorption site(s) of Mixed Oxide, **other measurements setup**

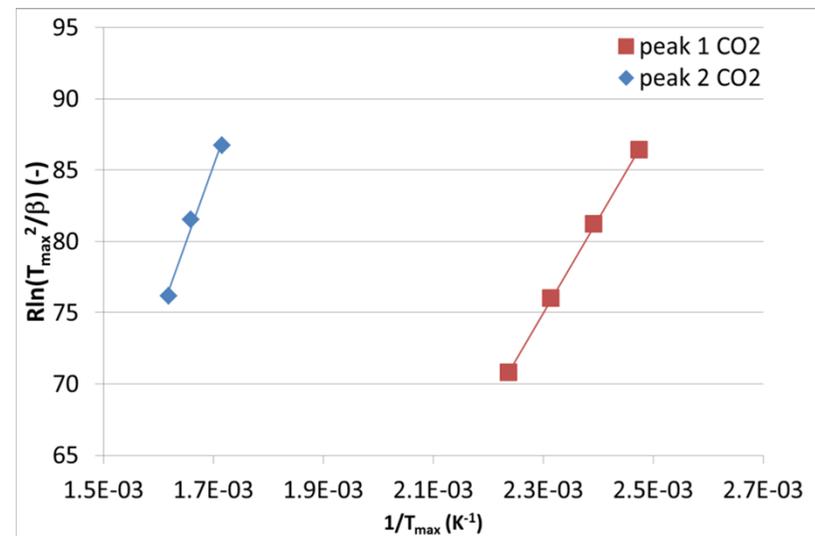
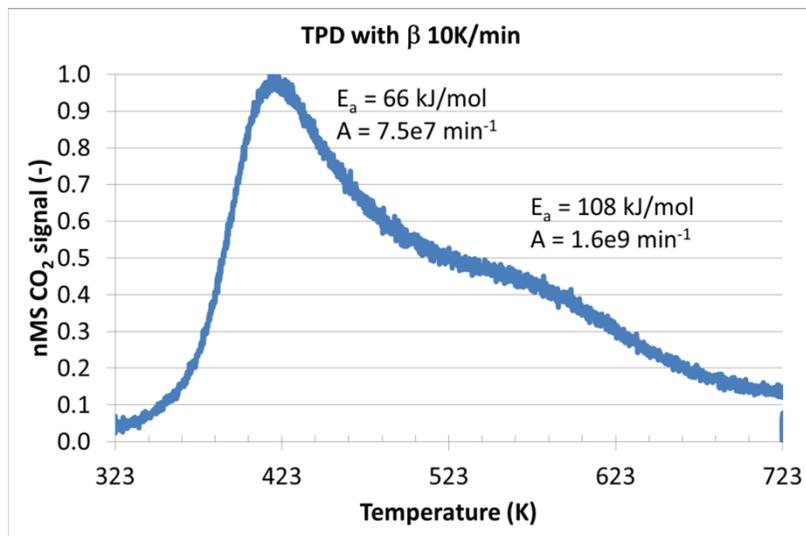
$$\frac{d\left(\ln \frac{\beta}{Tm^2}\right)}{d\left(\frac{1}{T}\right)} = -\frac{E_a}{R}$$



[5] H.E.Kissinger, Anal.Chem. 29 (1957) 1702-1706

TPD: with Mixed Oxide

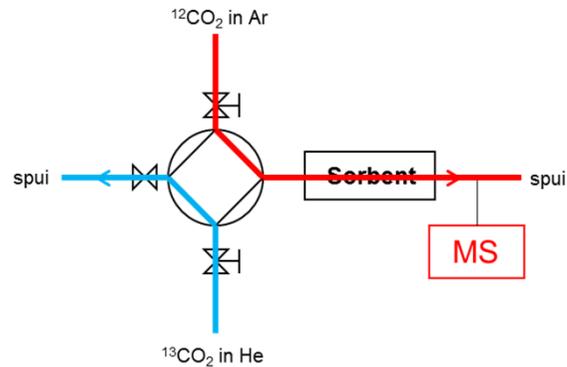
- Mixed oxide (derived from HTC) saturated with CO₂ at 50°C
 - TPD with several heating rates (β)
 - With Kissinger the E_a can be determined from the slope
 - A can be determined^[6] when all sites are occupied ($f(\theta)=1$) → $A = \frac{E_a}{Rf(\theta)} e^{-b/R}$
 - Determined E_a and A can be used in mathematical models



[6] M.Leon et.al., Chem.Eng.J. 175 (2011) 341-348.

SSITKA: Steady State Isotopic Transient Kinetic Analysis

Step 1: Saturation of sorbent with $^{12}\text{CO}_2$

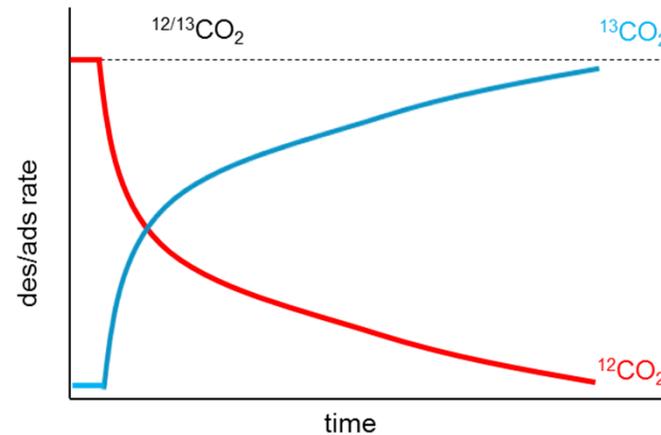
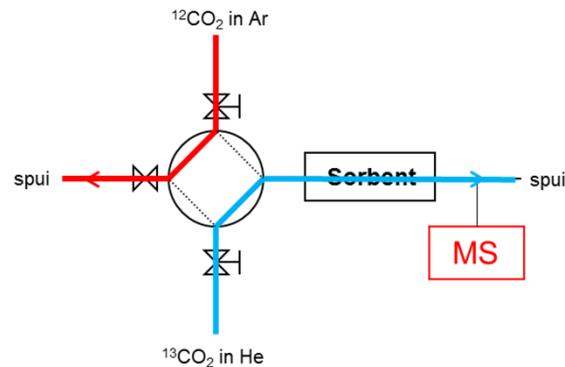


Follow ads reaction in complete equilibrium
 → All (possible) sites are occupied with CO_2

Follow exchange of $^{12}\text{CO}_2$ with $^{13}\text{CO}_2$

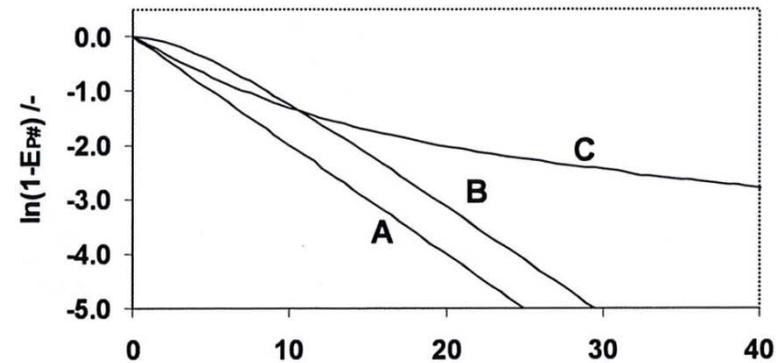
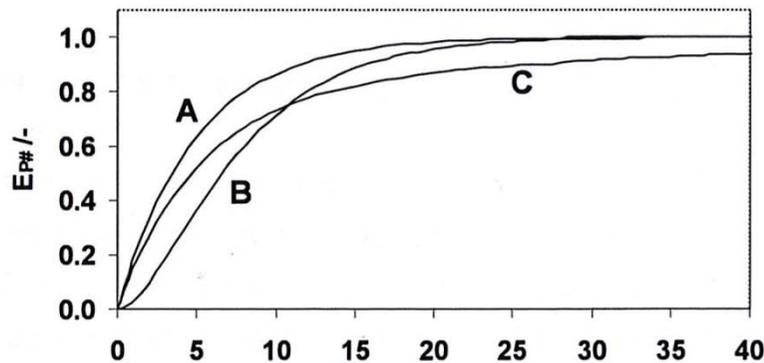
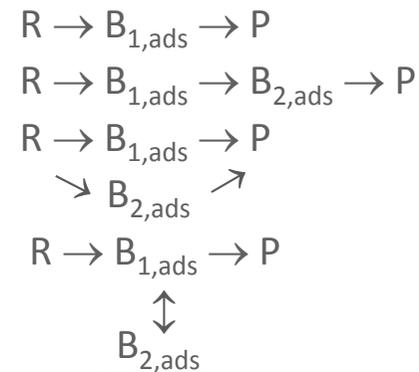
- Information on number of sites and
- Mathematical input (reaction mech./kinetics)

Step 2: Exchange of $^{12}\text{CO}_2$ with $^{13}\text{CO}_2$



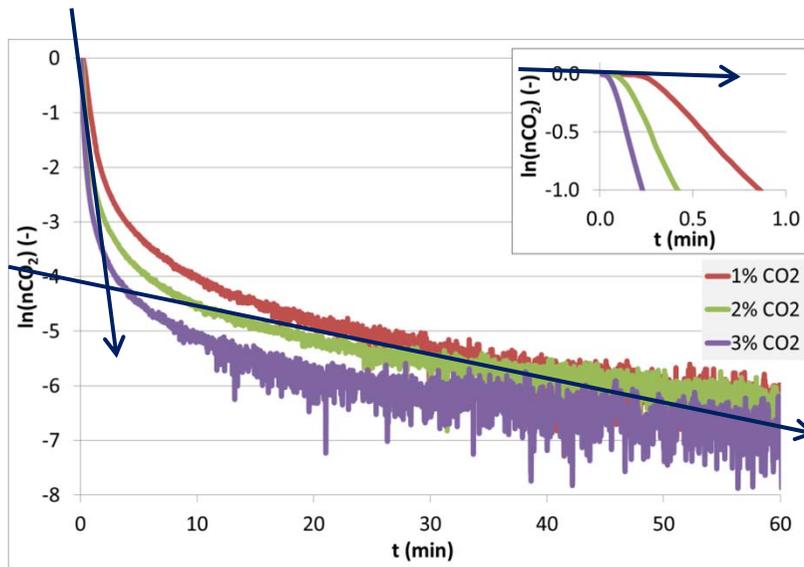
Interpretation of SSITKA

- Indication of number of site types
 - Done by calculating $\ln(1-N_{\text{signal}})$
 - A. Simple mechanism:
 - B. Mechanism with 2 surface species in serie
 - C. Mechanism with parallel route
or buffer step

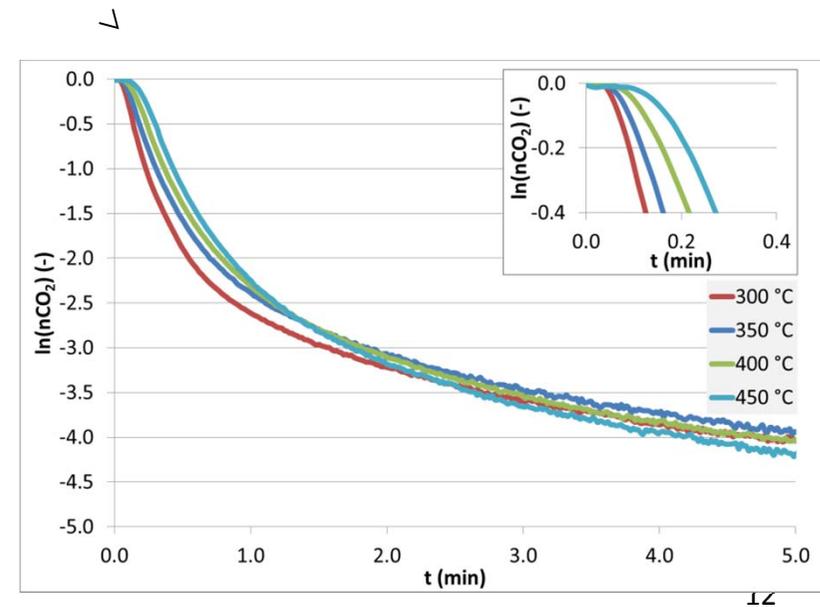


Results of SSITKA

- Experiments varying $P[\text{CO}_2]$
 - At least 3 sites
 - As $P[\text{CO}_2]$ increases more capacity is used
 - Type of sites remains the same

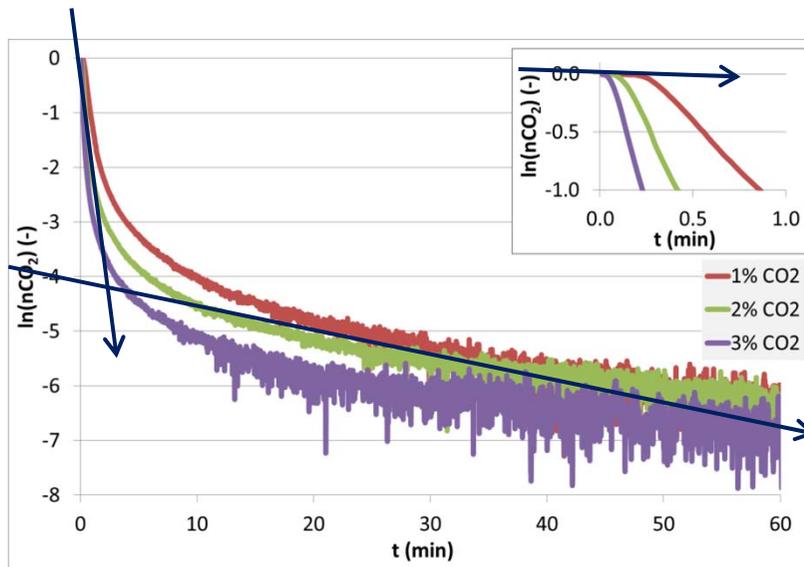


- Experiments varying T
 - Type of different sites remains the same
 - Effects of both kinetics and thermodynamics are visible with increasing T

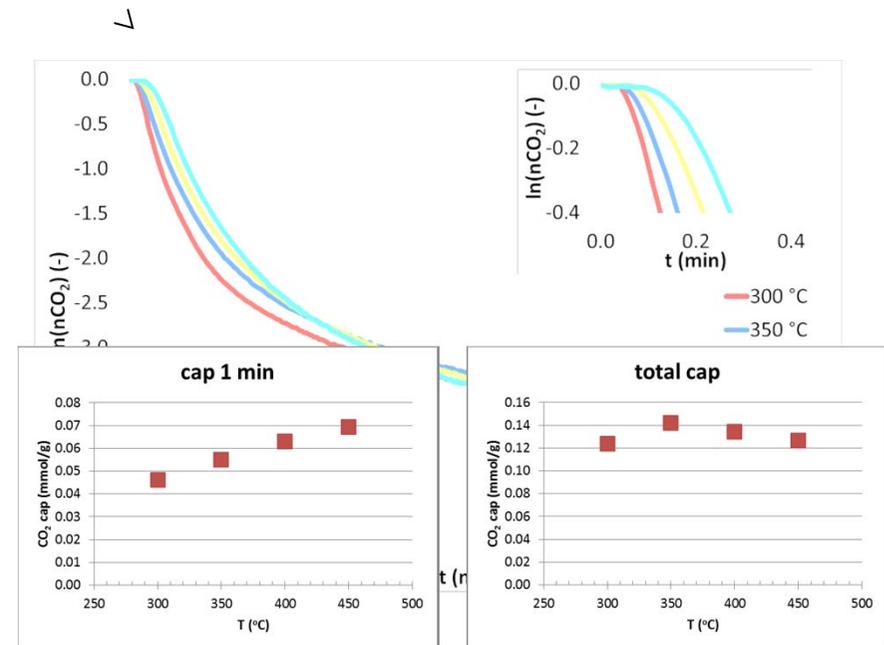


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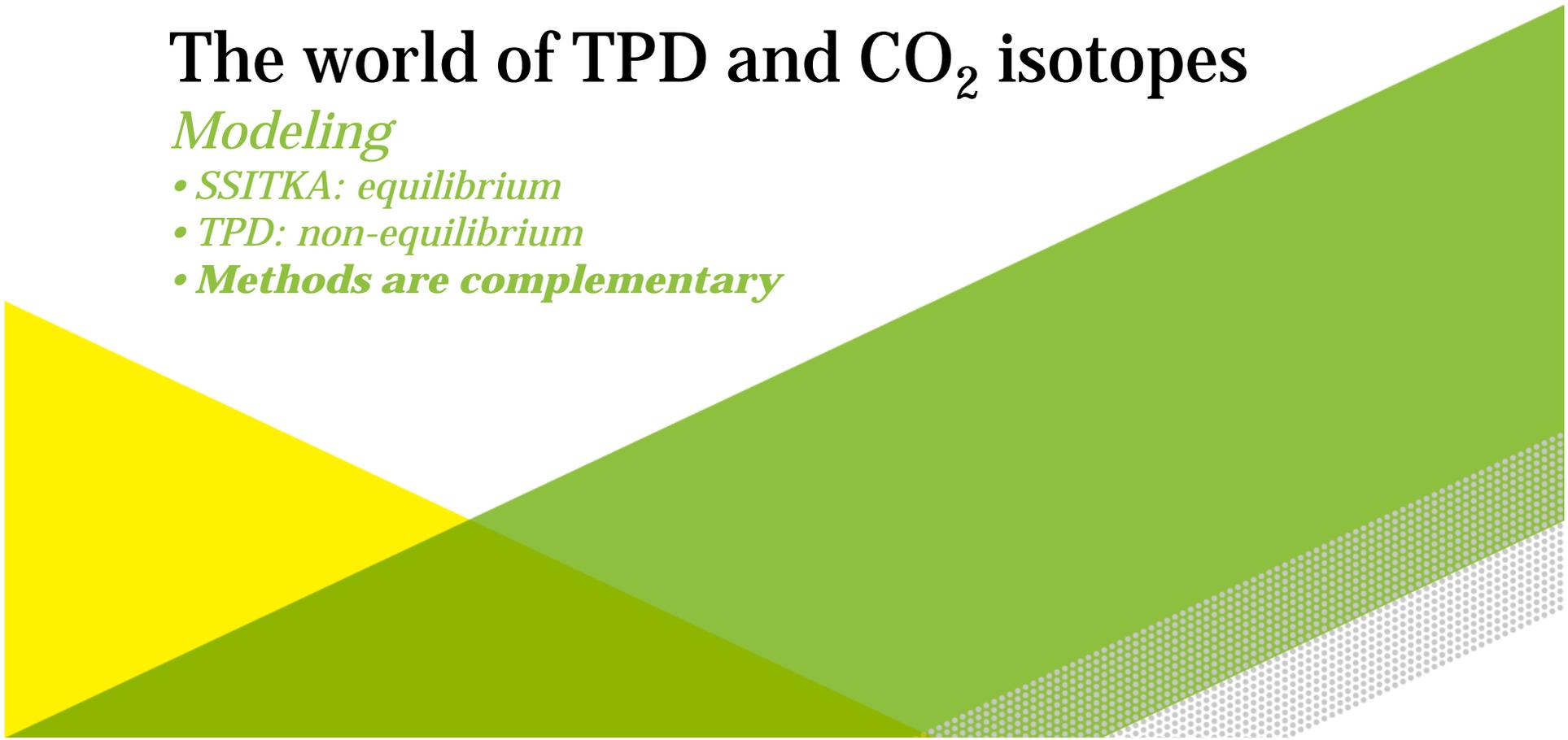
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The world of TPD and CO₂ isotopes

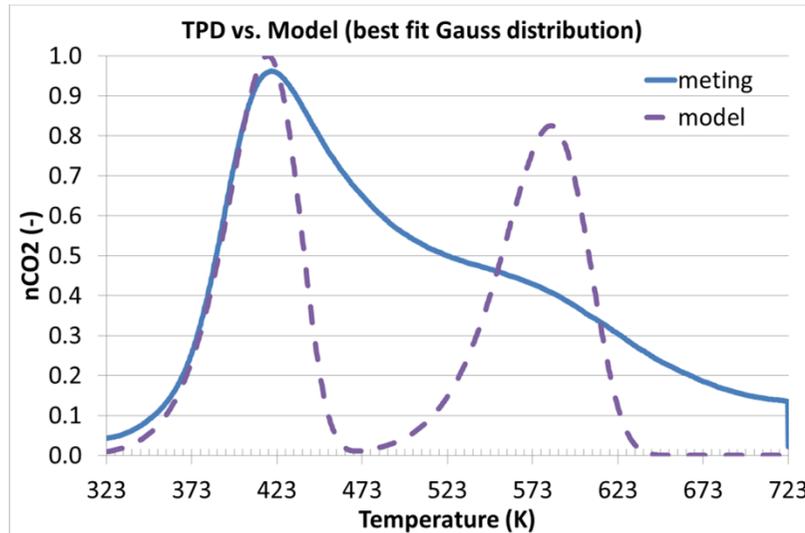
Modeling

- *SSITKA: equilibrium*
- *TPD: non-equilibrium*
- ***Methods are complementary***



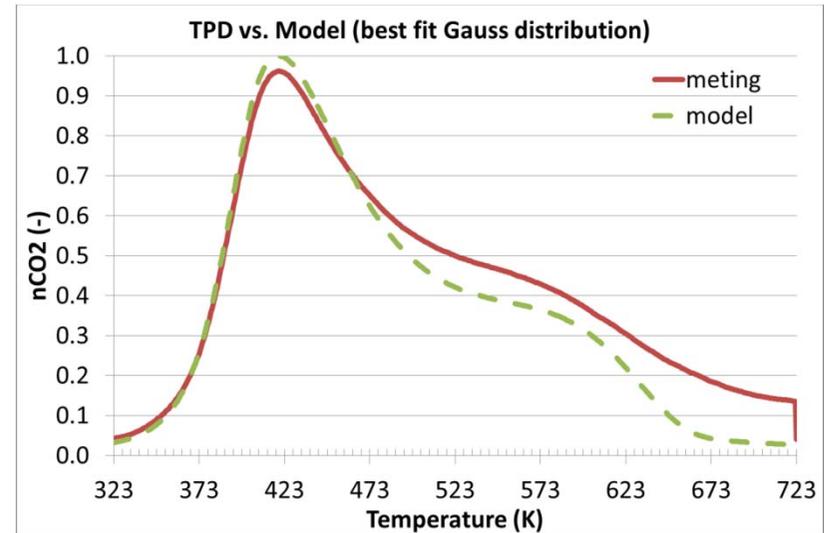
Model fitting of TPD

- E_a and A found with Kissinger's method
 - Site 1: $E_a = 66$ kJ/mol; $A = 7.5e7$ min⁻¹
 - Site 2: $E_a = 108$ kJ/mol; $A = 1.6e9$ min⁻¹
- $\frac{d[CO_2]}{dT} = A \exp^{-E_a/RT}$



- T_m model corresponds with measurements
- Shape is not corresponding

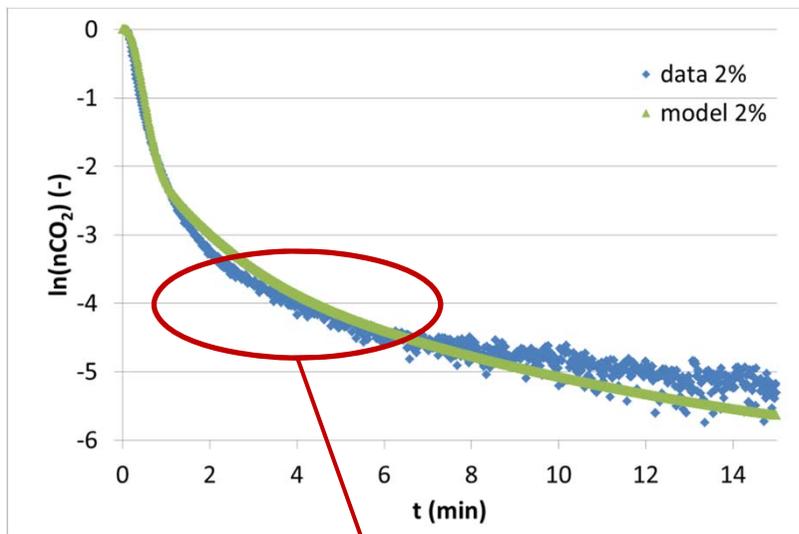
- Gauss distribution of E_a
 - with correlating A
- $\frac{d[CO_2]}{dT} = A_{f(E_a)} \exp^{-E_{a_gauss}/RT}$



- Shape is corresponding
- Changes in E_a and correlating A needed

Model fitting of SSITKA

- E_a and A from TPD as starting values



$$k_{ads} = A_{ads} \exp^{-E_{a_{ads}}/RT}$$

$$k_{des} = A_{des} \exp^{-E_{a_{des}}/RT}$$

$$\frac{d[^{12}CO_2]}{dt} = k_{ads} * [^{12}CO_2] * [1 - f(\theta^{12})] + k_{des} * [f(\theta^{12})]$$

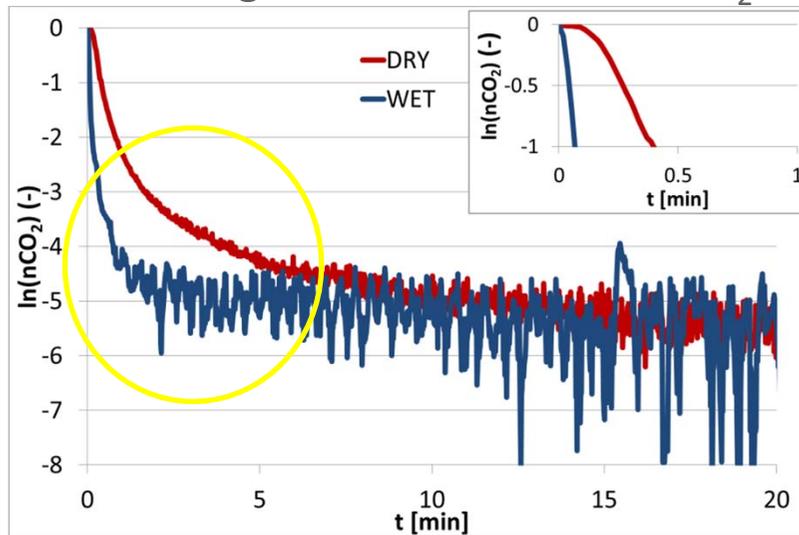
$$\frac{d[^{13}CO_2]}{dt} = k_{ads} * [^{13}CO_2] * [1 - f(\theta^{13})] + k_{des} * [f(\theta^{13})]$$

- There is a “transition” region → like the Gauss distribution in TPD
 - To obtain this result 4 sites were implemented in the model

Before... Conclusions and Future

The effect of H₂O on measurements

- H₂O increases capacity (of K-promoted) HTC
- Also adsorbing on sites available for CO₂



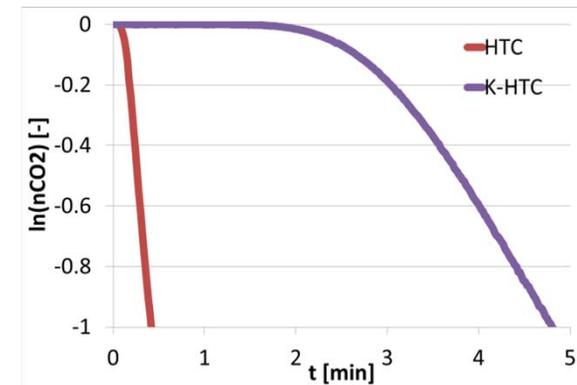
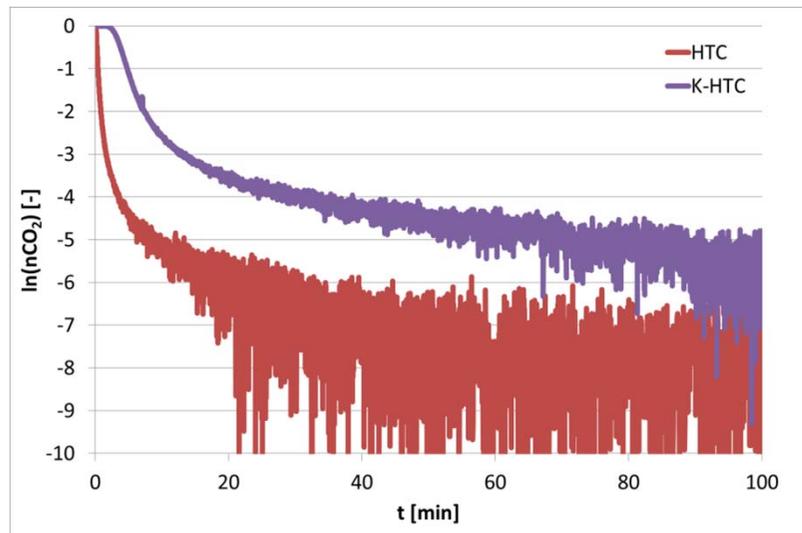
- Addition of 10% H₂O
 - No longer a chromatographic effect
 - The “transition” region is no longer present

Before... Conclusions and Future

The effect of Potassium promotion (K_2CO_3)



- Impregnation of HTC with K_2CO_3 enhances the capacity by a factor 4



- Addition of 20wt% K_2CO_3
 - A very long chromatographic effect
 - Increased capacity

Conclusions and Future

- Combination of TPD and SSITKA results in good method for describing the adsorption mechanism for these complex structures
- Three main sites can be determined
 - Chromatographic, fast, slow
- As well a distribution of E_a (Gaussian) for these sites
 - Inhomogeneous surface structure
- Focus on type of distribution of E_a for model TPD and SSITKA
- TPD and SSITKA measurements on K promoted HTC
- TPD and SSITKA measurements with additional steam
 - first experiments look promising
- Other techniques (like in-situ IR/RAMAN) → adsorption geometry.



Thank you!

Sponsor:



Institutes involved:



Co-autors:

J.J.C. Geerlings

W.G. Haije

P.D. Cobden

Functions θ

n th Order	θ^n
Random nucleation, unimolecular decay law	$(1 - \theta)$
Phase boundary controlled reaction (contracting area)	$(1 - \theta)^{1/2}$
Phase boundary controlled reaction (contracting volume)	$(1 - \theta)^{2/3}$
Two-dimensional growth of nuclei	$2(1 - \theta)(-\ln(1 - \theta))^{1/2}$
Three-dimensional growth of nuclei	$3(1 - \theta)(-\ln(1 - \theta))^{2/3}$
One-dimensional diffusion, sharp interface	$1/2\theta$
Two-dimensional diffusion, sharp interface	$-1/\ln(1 - \theta)$
Three-dimensional diffusion, sharp interface	$3/[2 \left((1 - \theta)^{-1/3} - 1 \right)]$
Three-dimensional diffusion	$\frac{[3(1-\theta)^{\frac{2}{3}}]}{[2(1-(1-\theta)^{\frac{1}{3}})]}$