CHARACTERIZATION OF COAL-BASED METAL CATALYSTS

Fernando Vallejos-Burgos
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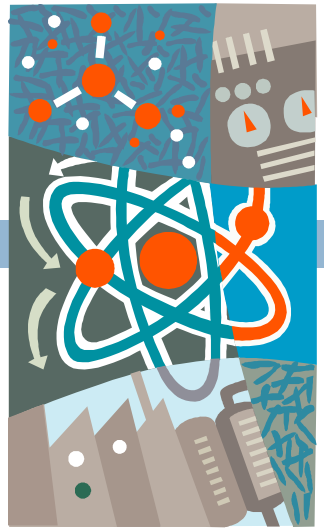
Introduction

- PhD Thesis: 'Oxygen transfer on carbon supported catalysts'
- Why my work is (or will be) important?
  - Fundamental: oxygen transfer mechanism
  - Practical: NO reduction in stationary (and mobile?) sources
- Key reactions:
  - $2C_f + 2NO = N_2 + 2C(O)$ Chemisorption
  - $2C_f + O_2 = 2C(O)$
  - $2C(O) = 2C_f + CO_2 (+ CO)$ Desorption

Preparation of samples



AR-C

As received carbon (coal)

Dem-C

Demineralized carbon

Dem-C-550 (…700, 850 and 1000 °C)

Pyrolyzed carbon

Dem-AC-1000 1h (…6h, 12.5h and 24h)

Activated carbon

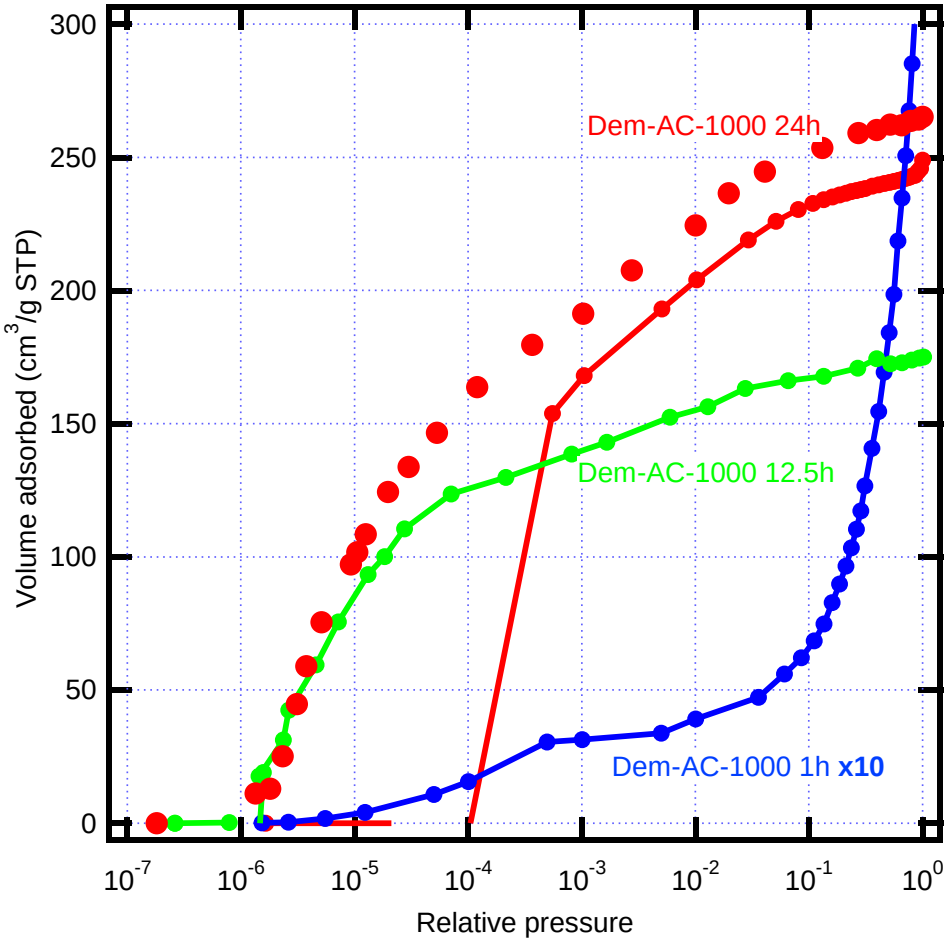
Incipient wetness impregnation

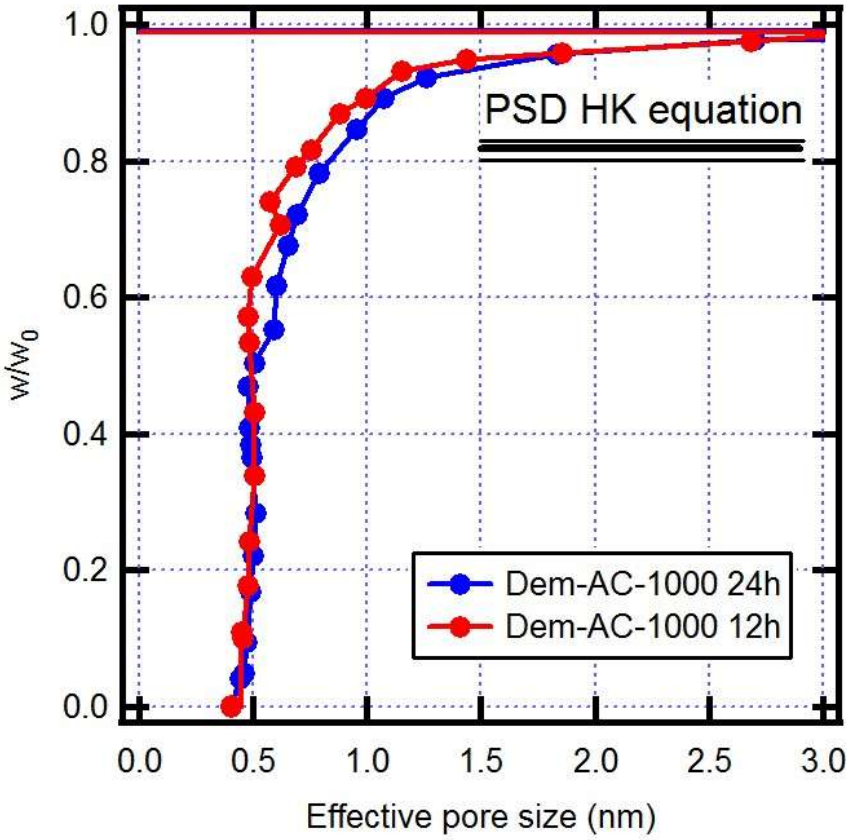
Co-IWI-1000 1h (…Cu and K)

Ion exchange (and oxidation)

Co-IE-1000 1h (…Cu and K)

Nitrogen adsorption on supports (77 K)





Dem-C-1000 → NO ADSORPTION (Dem-C-1000 is precursor of all Dem-AC)

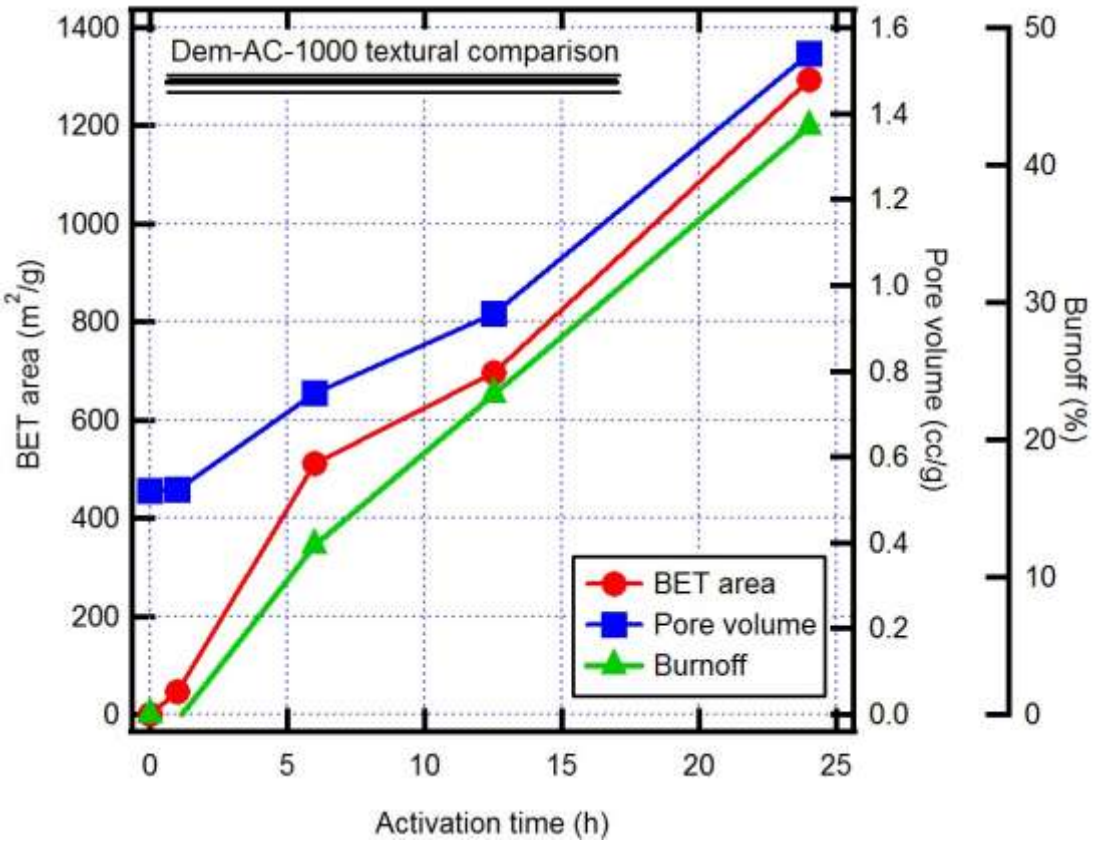
CO_2 activation: textural properties

BURNOFF indicates the % of sample consumed during activation

Carbon supports have very different BET surface areas (ranging from ~20 to ~1200 m^2/g)

Pore volume (adding drops of water) increases with burnoff

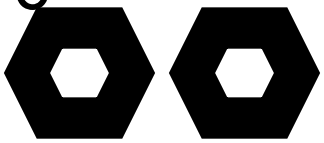
Burnoff is linear with activation (reaction) time



IWI: Does water penetrate inside pores?

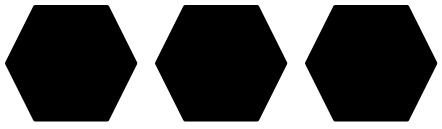
- Pore volume (by water addition): have to compare the same number of particles (weight normalization!)

- If pore volume per gram of actual sample:

weight  = weight  = weight 

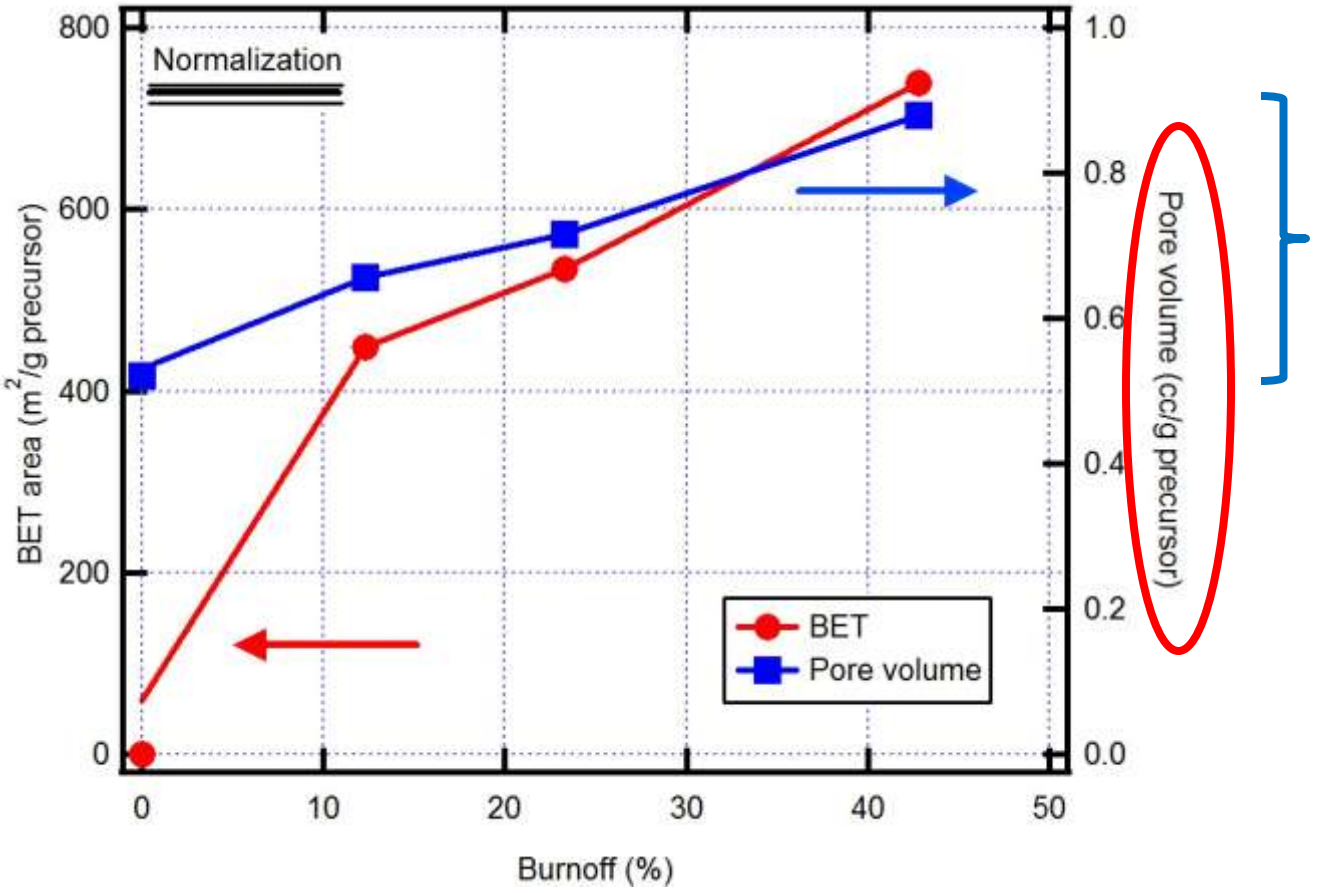
→ not fair for less porous (heavy) particles

- OK, so let's normalize considering the yield

 =  = 

Now, if pore volume increases, it is due to H_2O penetration

IWI: Does water penetrate inside pores?



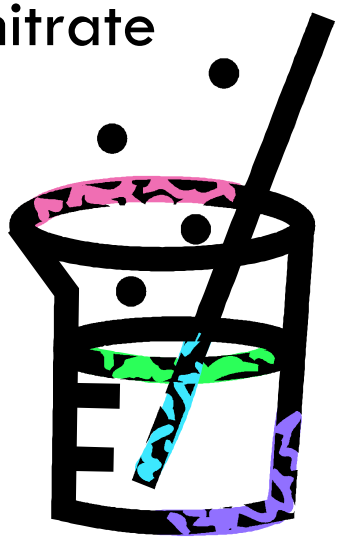
Samples:
Activated carbons
(All Dem-AC-1000 **h)

The water DOES penetrate into pores!

Incipient wetness impregnation

- Addition of catalyst (Co, Cu or K) to support (active carbon)
- Target metal content : 8% by weight

- Aqueous solution of:
  - Cobalt nitrate / Copper nitrate / Potassium nitrate

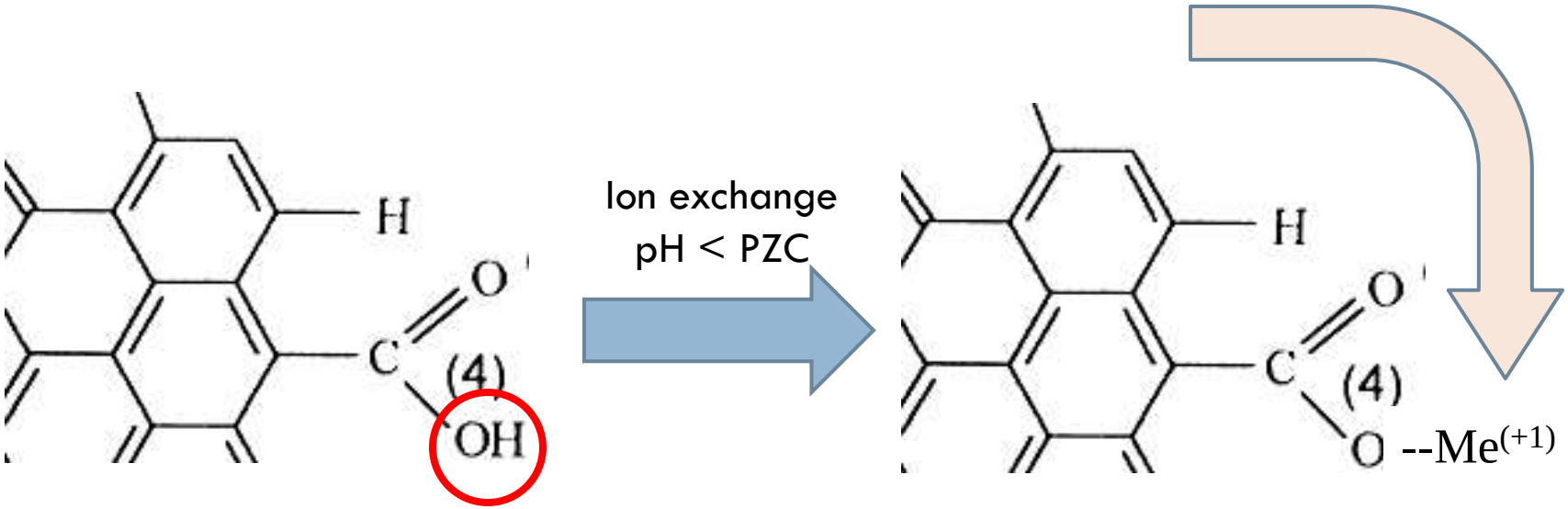


Ash as measure of metal content

- Just burning the carbon in the sample (500 °C, 2h)
- Demineralization: 15.5% (AR-C) → <0.3% (Dem-C)
- Cobalt (considering Co_3O_4)
  - IWI=8.4-7.3%
  - IE= 0.2-0.4% (!?)
- Copper (considering Cu^0)
  - IWI= 7.8-7.0%

Ion exchange

- Consists in EXCHANGING IONS on the carbon surface with ions in solution
- Which ions?
  - CARBON: H^+ (carboxylic groups)
  - SOLUTION: Metal cations



Carbon acid treatment

- But… samples were heat-treated at high temperatures and original carboxylic groups decomposed around 250 °C[Figueiredo 1999]
- So… have to add these carboxylic groups again

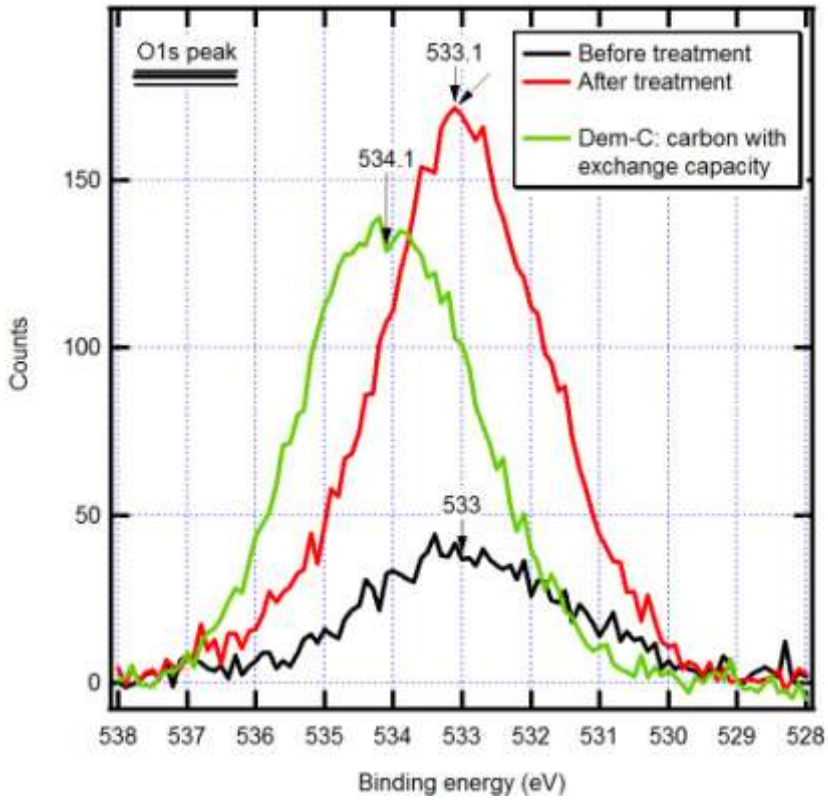
  → HNO_3 treatment
- XPS results:

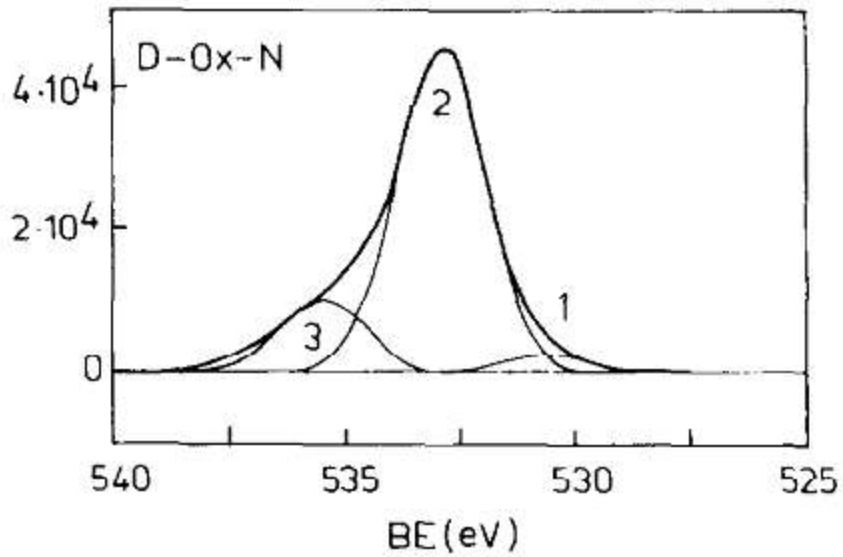
Sample	C%	N%	O%	Metal%
Dem-AC-1000 24h	94.5	0.6	5.0	-
Dem-AC-1000 24h Ox	83.9	1.4	14.7	-

- If all carboxylic H^+ could exchange with Co^{2+}, metal loading would be around 15 wt% Co

What went wrong? (oxidation or ion exchange?)

- But cobalt loading (after overnight at initial pH=4.0) was only around 0.3%. (The pH_{PZC} of the support was 4.3)
- C=O appears at ~531.1 eV / C-OH at ~532.8 eV



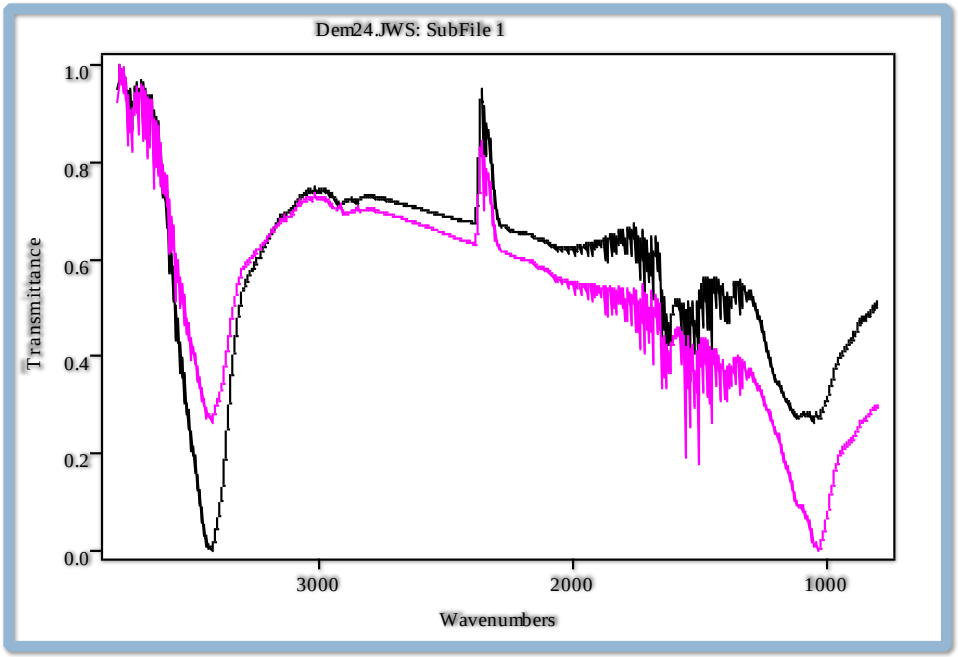


(1) C=O; (2) C–OH, C–O–C; (3) chemisorbed water or oxygen.

Biniak, Carbon 1997

FTIR results (ざんねん)

- Particle size was too big (around 100 microns) → no useful spectra

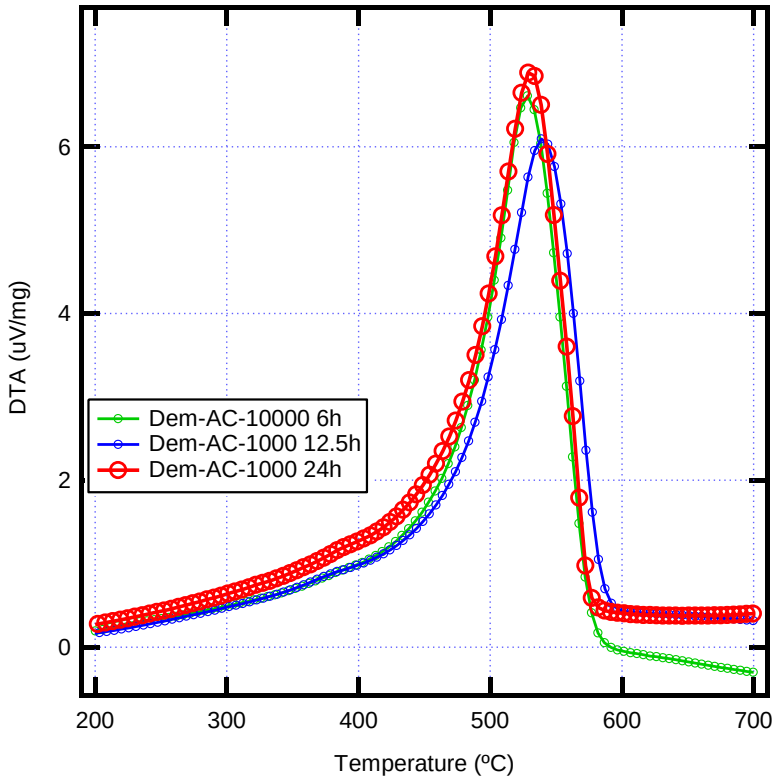


millimeter thickness. Transmission infrared spectroscopy can be applied if the bulk of the catalyst absorbs weakly. This is usually the case with typical oxide supports for wavenumbers above about 1000 cm^{-1}, whereas carbon-supported catalysts cannot be measured in transmission mode. Another condition is that the support particles are smaller than the wavelength of the infrared radiation, otherwise scattering losses become important.

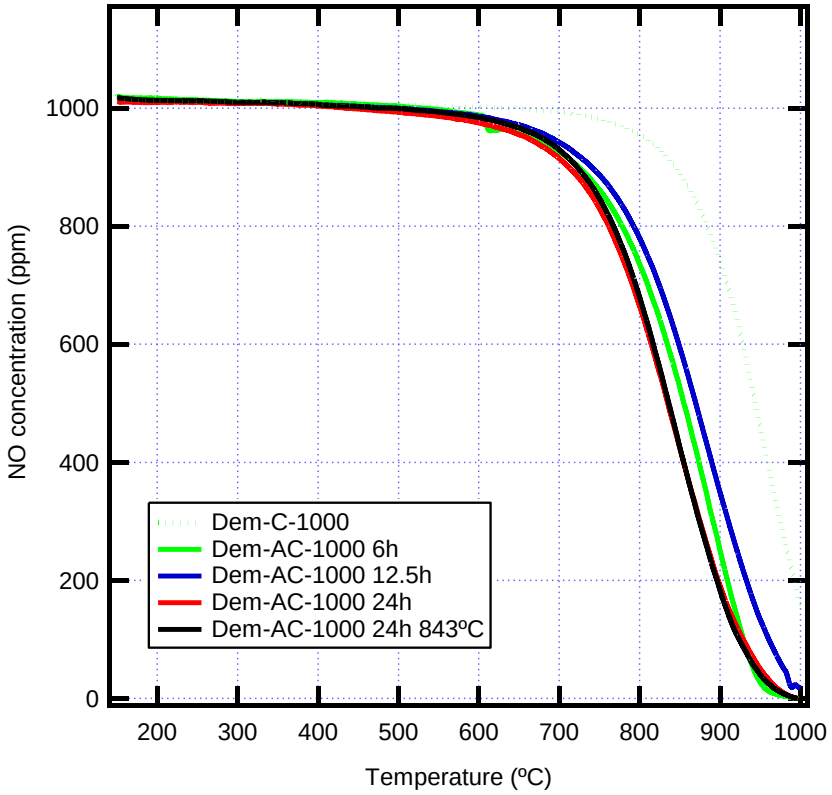
J. W. Niemantsverdriet
Spectroscopy in Catalysis

Reactivity: Dem-AC (Chile)

Oxygen reduction



NO reduction



Carbon reactivity (*without catalyst*) does not depend on surface area → BURNOFF vs ACTIVATION TIME

Why reactivity does not depend on S.A.? (at least for demineralized samples)

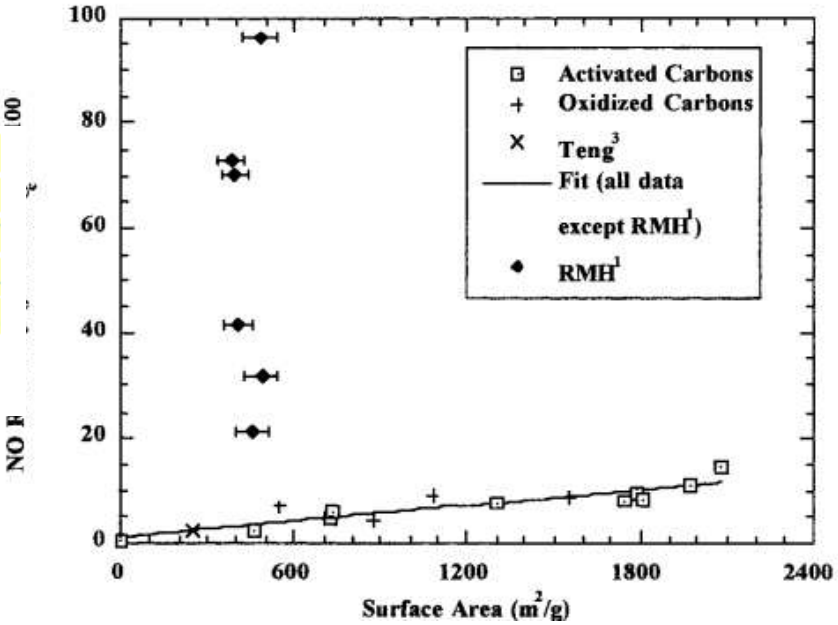
- (Probably) samples has the same REACTIVE surface area

The Role of Surface Area in the NO–Carbon Reaction

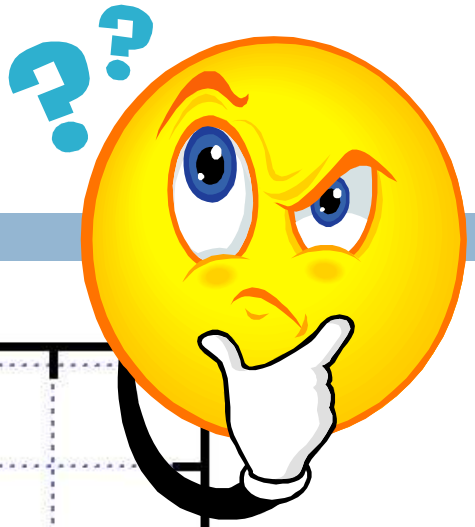
J. M. Calo,* E. M. Suuberg, and I. Aarna

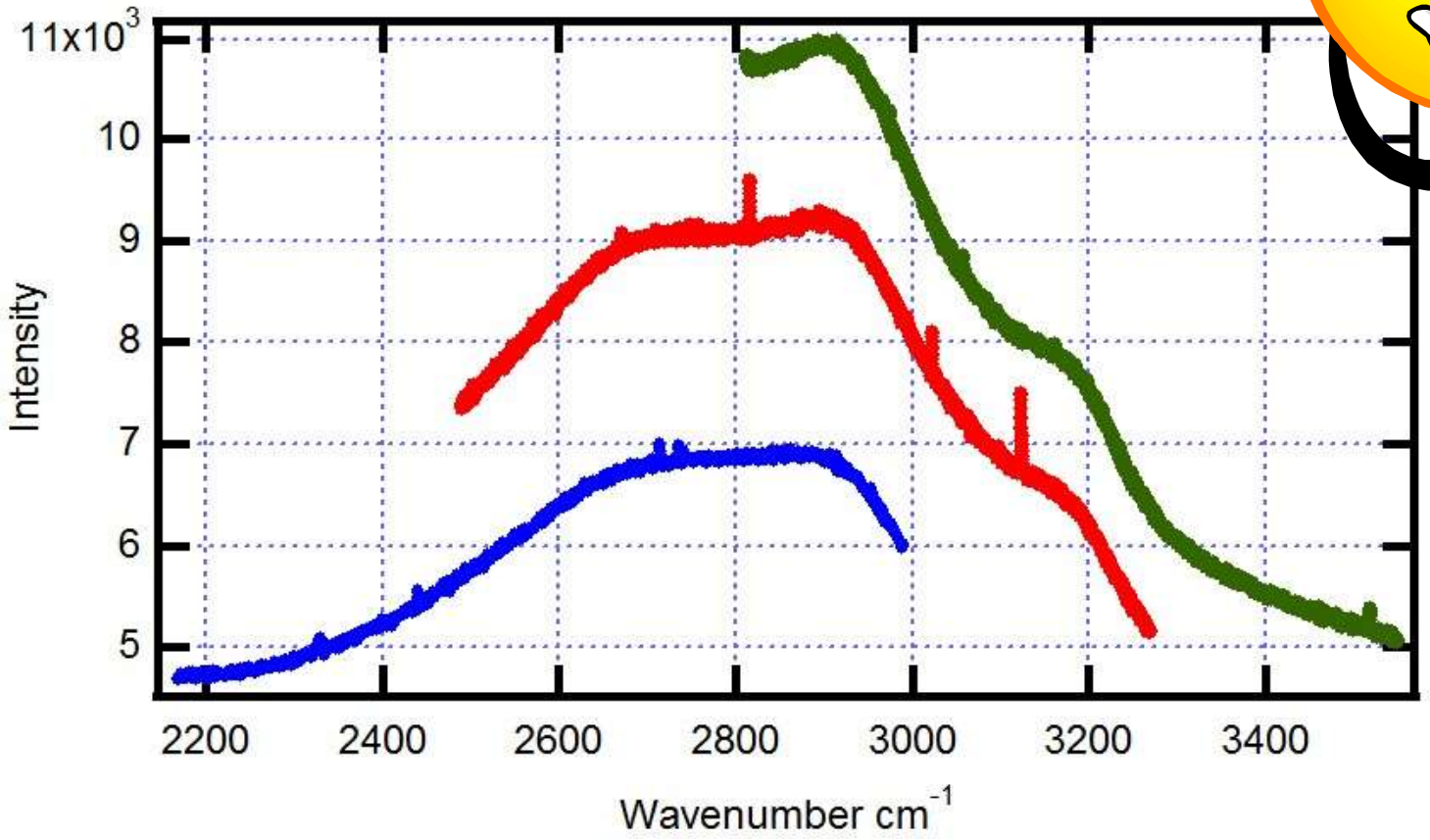
Energy & Fuels **1999,** *13,* 761–762

The issue of whether the NO–carbon reaction utilizes all the available or accessible porosity in a carbon, the details of the reaction mechanism, and how these vary with various parameters, are important issues from a number of fundamental and practical viewpoints, and, consequently, these are topics of current debate in the literature. In our view, however, the conclusions of RMH



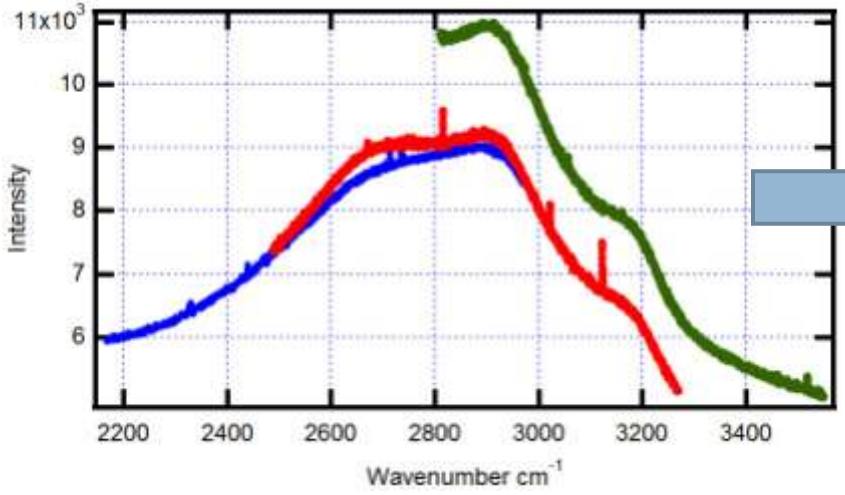
Raman second order

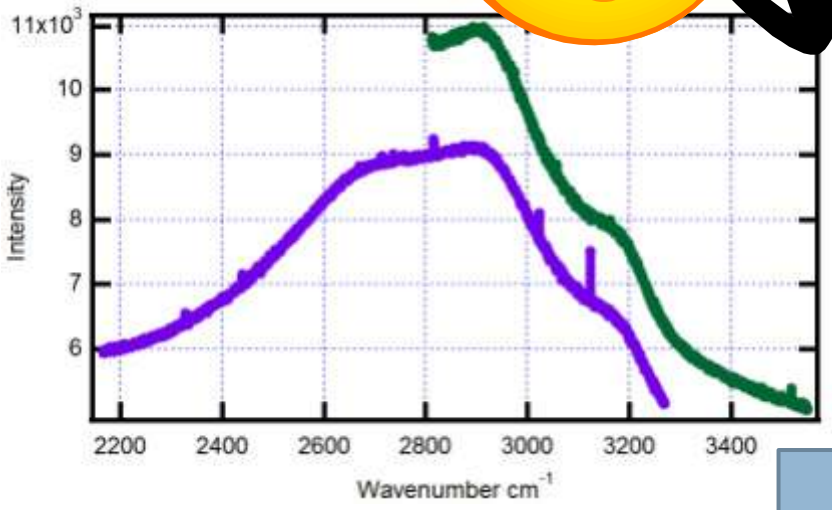


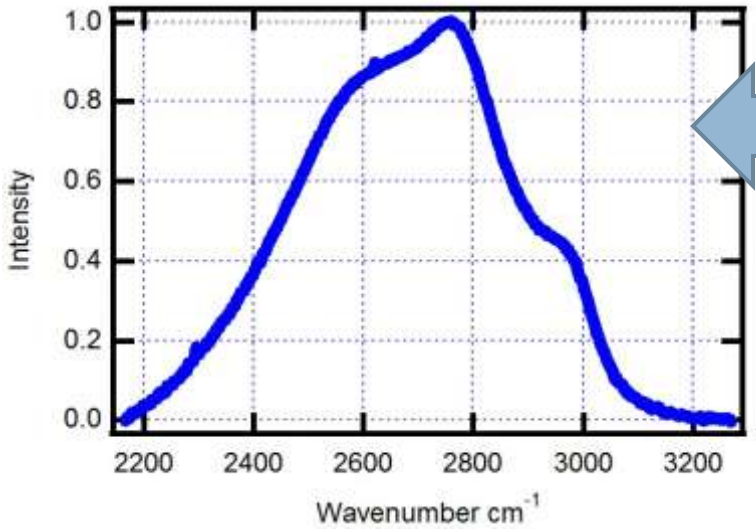


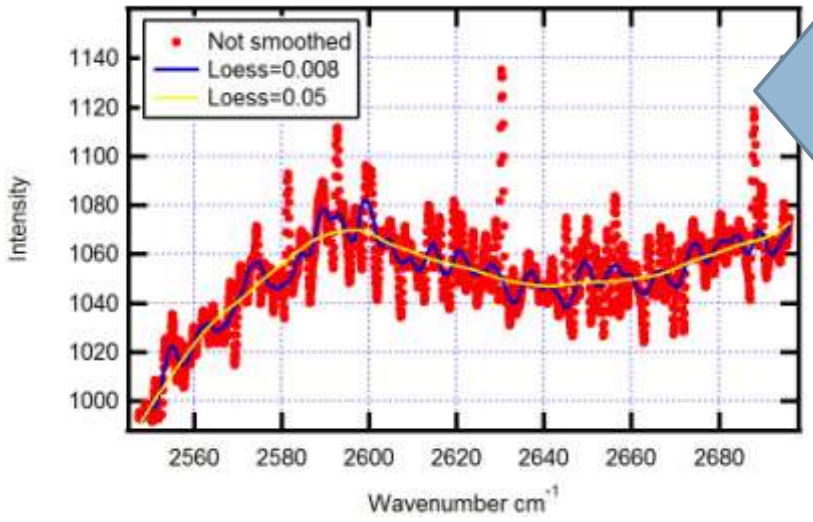
Raw data, second order phonons

Raman data treatment

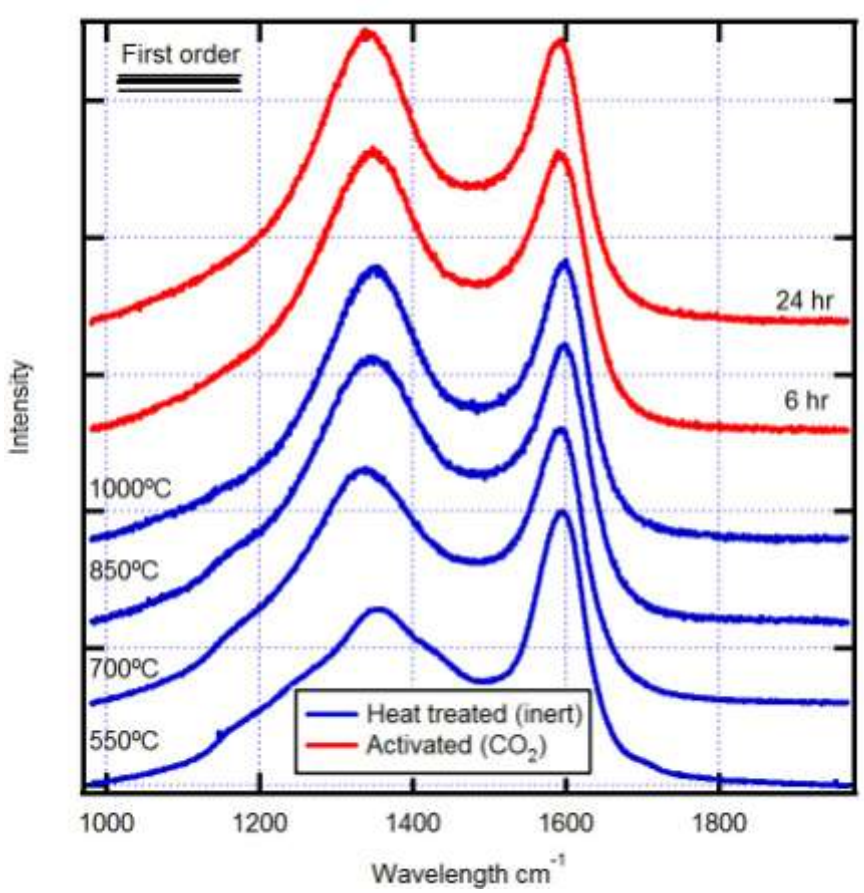


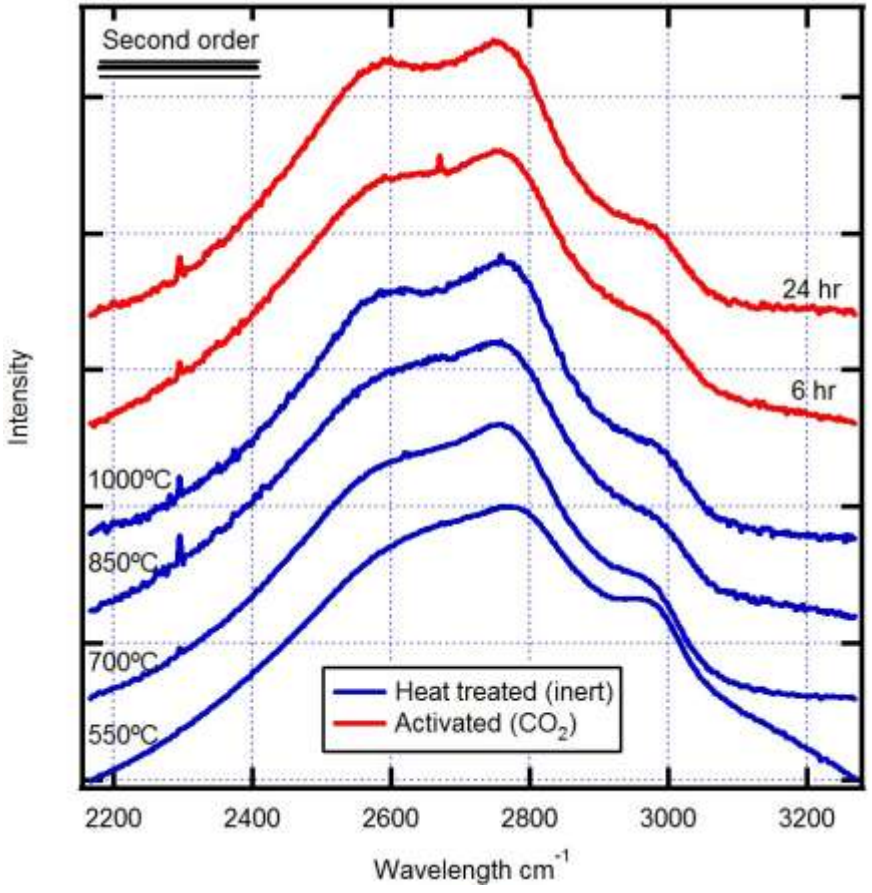




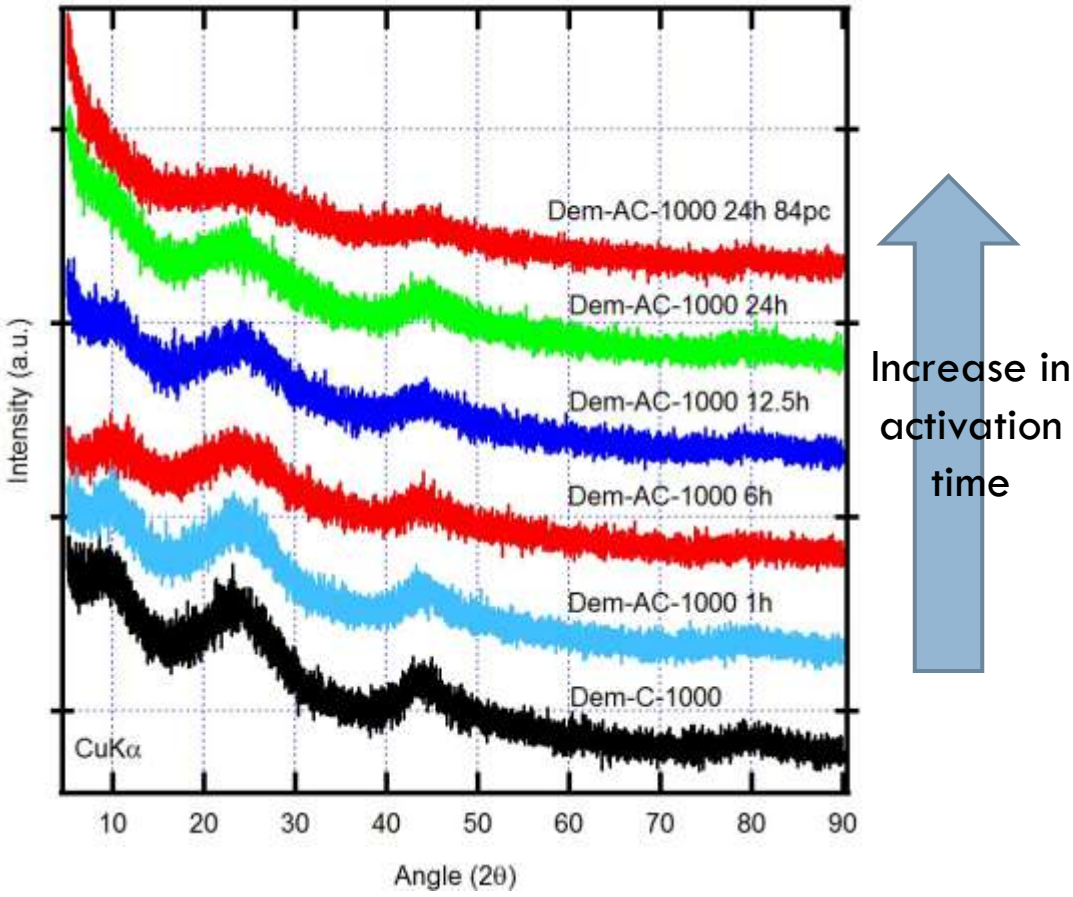


Raman 1st and 2nd order results





XRD: any effect of activation burnoff?

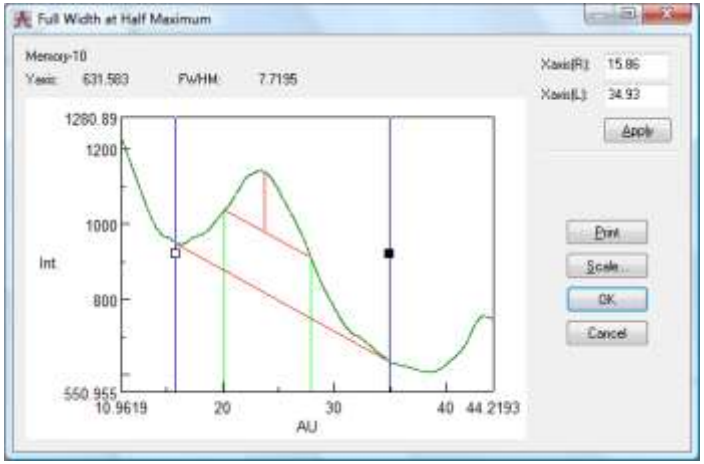


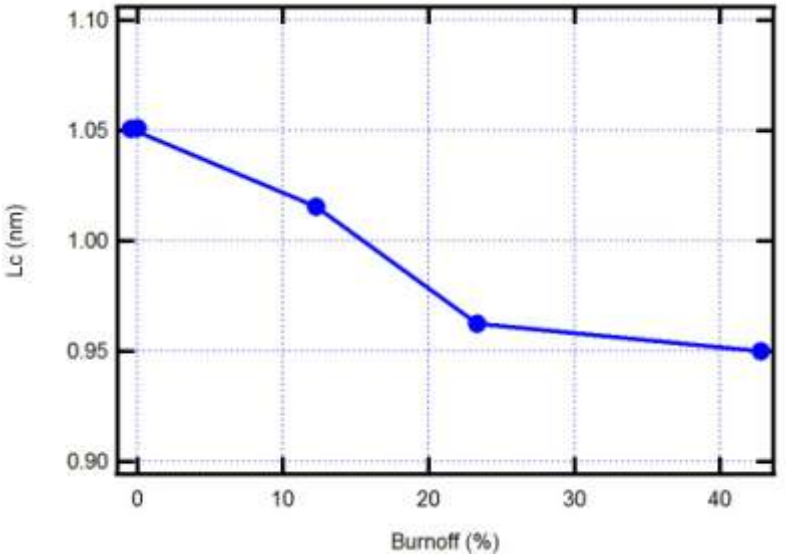
- Increase in small angle scattering due to increase in porosity
- Analysis of (002) carbon peak
- What is peak at $2\theta=10°$? (0.88 nm)

MiniFlex

XRD: FWHM (Full width at half maximum) for (002) plane

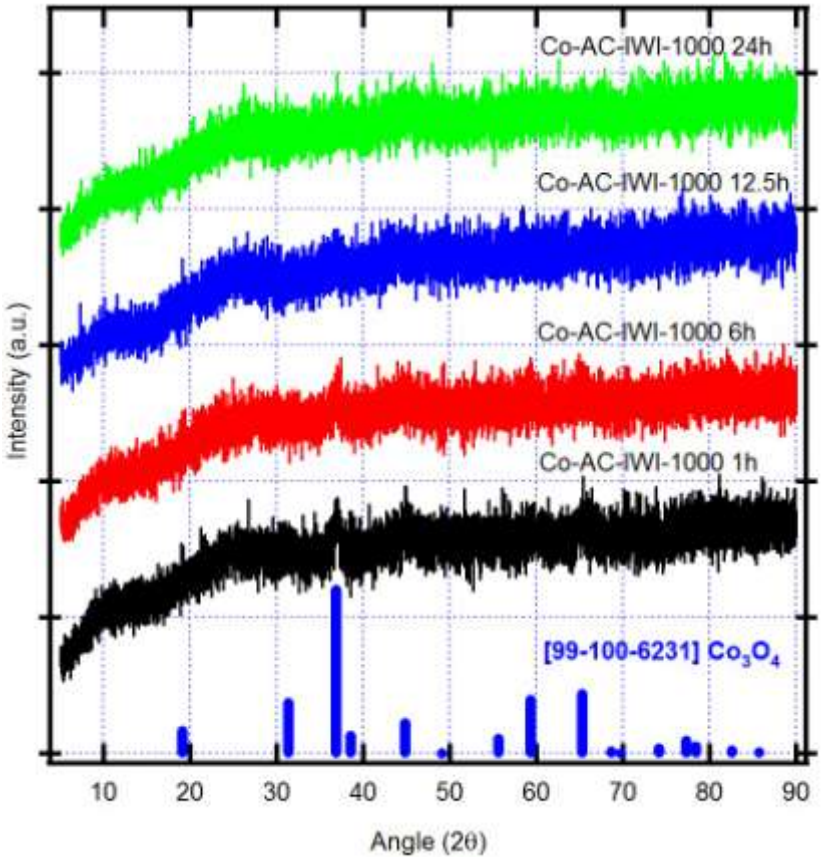
- Average number of parallel graphene layers in the microcrystals decreases with burnoff
- Not related with reactivity?
- Similar study of (10) peak (diameter of graphene) → need slow scan data



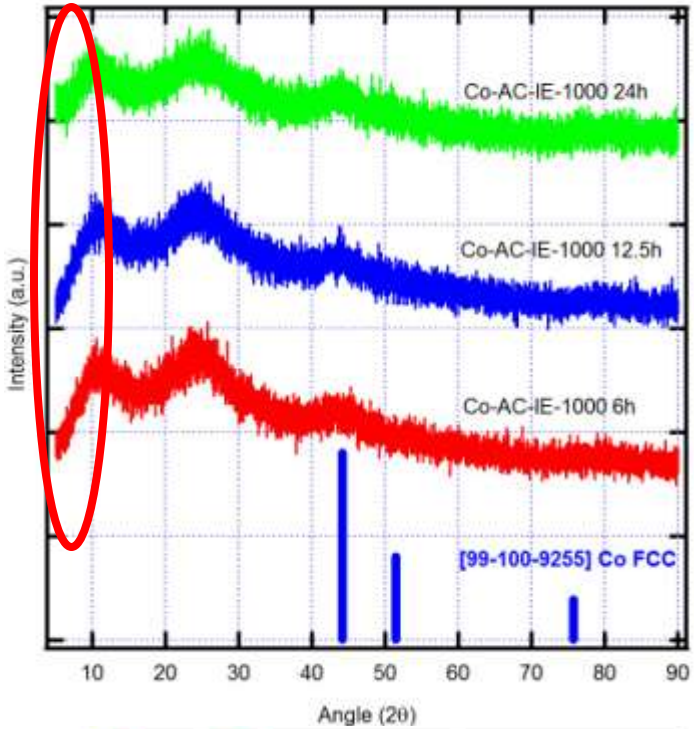


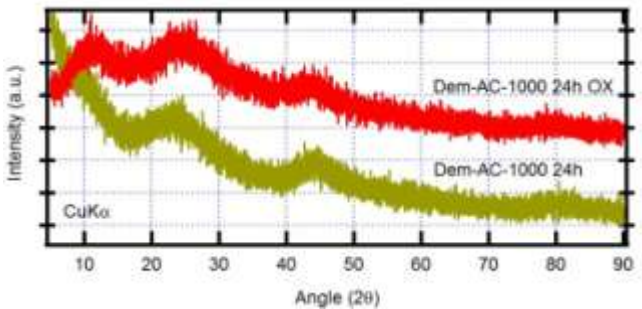
XRD: Co-impregnated samples

Co content ~8% wt.



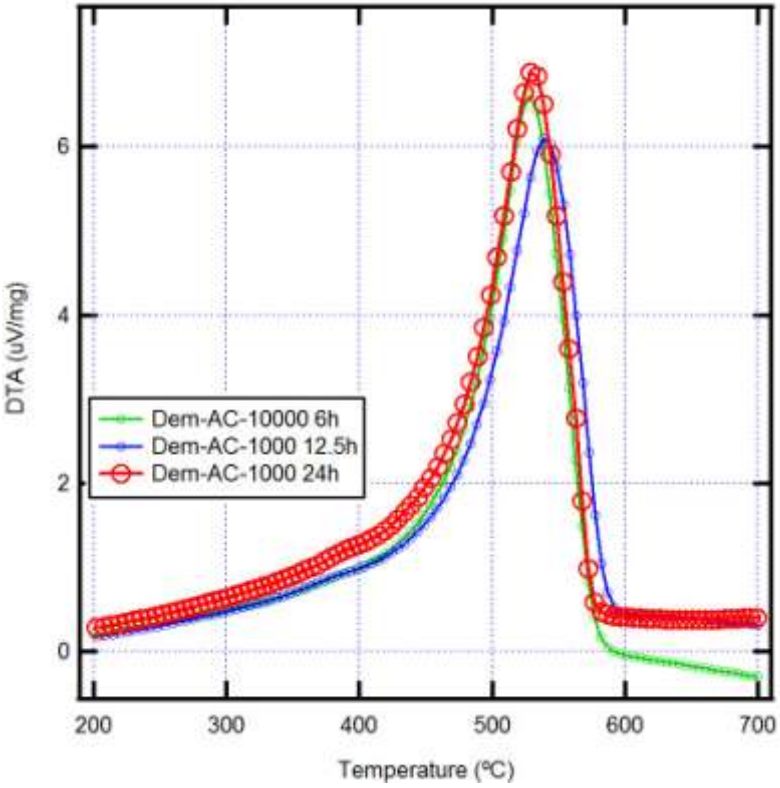
Co content ~0.2% wt.



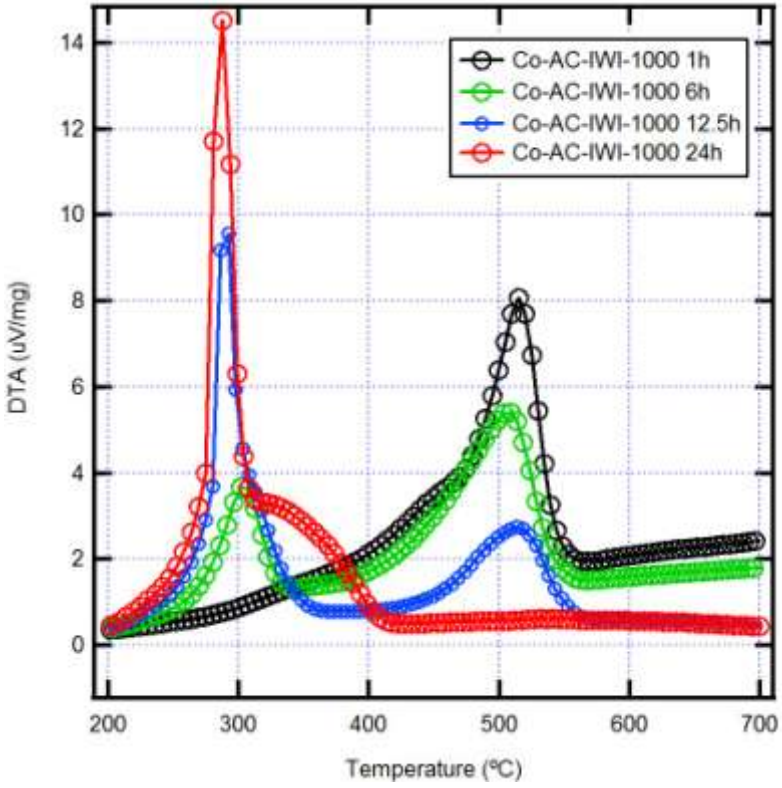


What happens (with the reactivity) when the catalyst is added?

Oxygen reduction:
Demineralized



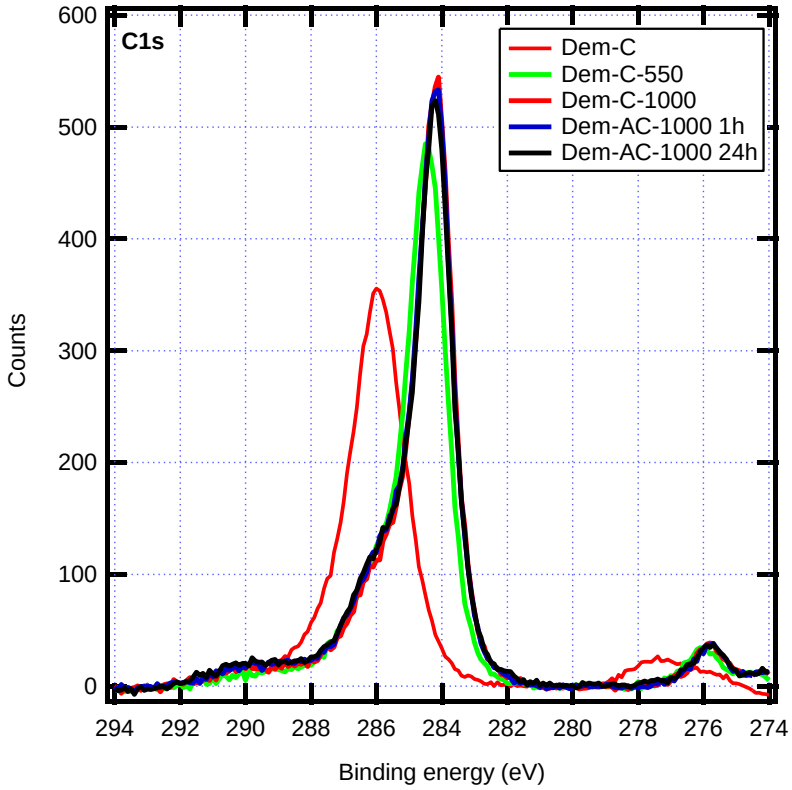
Oxygen reduction:
Cobalt IWI

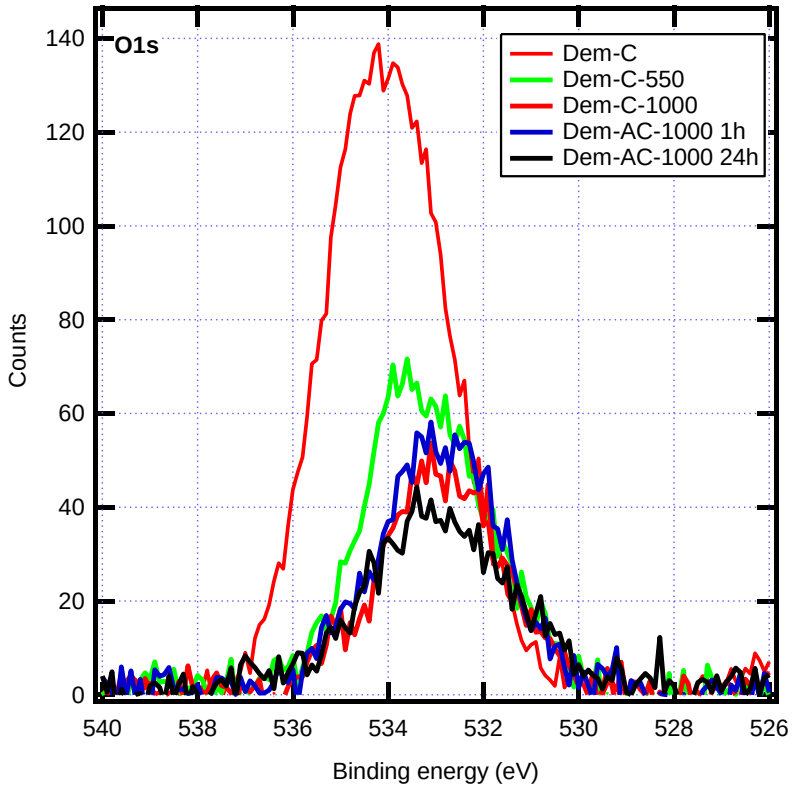


2 peaks! → Different carbons?? → おもしろいね！

Is this difference chemical or structural?

XPS results: supports





After HTT: C1s 286.0 eV → 284.2 eV…… charge effect?

No difference in surface chemistry of heat-treated samples!?

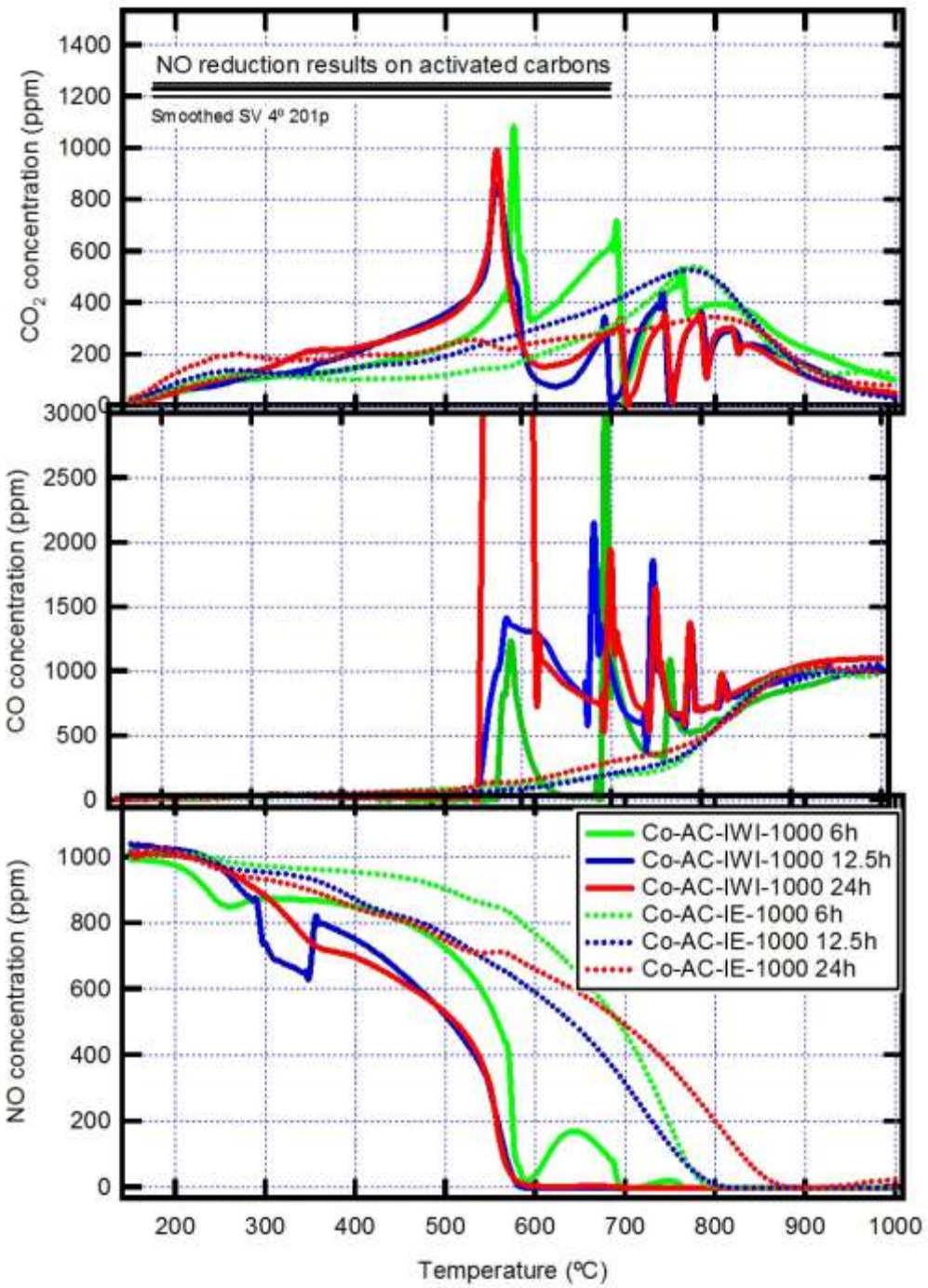
XPS: surface elemental composition

Sample	C%	N%	O%	Metal%
Dem-C	82.4	1.0	16.6	-
Dem-C-550	91.4	1.0	7.7	-
Dem-C-1000	94.0	0.6	5.4	-
Co-IWI-1000 6h	58.4	0.6	30.0	11.0
Co-IWI-1000 24h	72.3	0.9	20.8	6.0
Co-IE-1000 6h	79.5	0.8	18.3	1.4
Co-IE-1000 24h	85.8	1.1	13.0	0.1

- Metal concentration is lower in the sample with more porosity → confirmation of pore penetration
- Almost no presence of metal on 24h IE sample!

NO reduction results (Chile)

- Even small amounts of metal have a large effect on (catalytic) activity
- Relatively complex TPR plots!?



Interesting issues

- Explanation of coal reactivity and surface area relationship
- Effect of metal loading
- Effect of metal/support contact on ease of oxygen transfer
- …

Future experiments

- Analysis of data
  - Raman
  - XPS
- Adsorption on catalysts
- Try to acquire ‘good’ FTIR data
- Slow (less SNR) XRD for analysis of (10) peak
- TEM
  - Is there a particle size (catalyst dispersion) dependence on available support surface?

THE END

The thing that doesn't fit is the thing that's most interesting, the part that doesn't go according to what you expected

Richard P. Feynman - 1981