



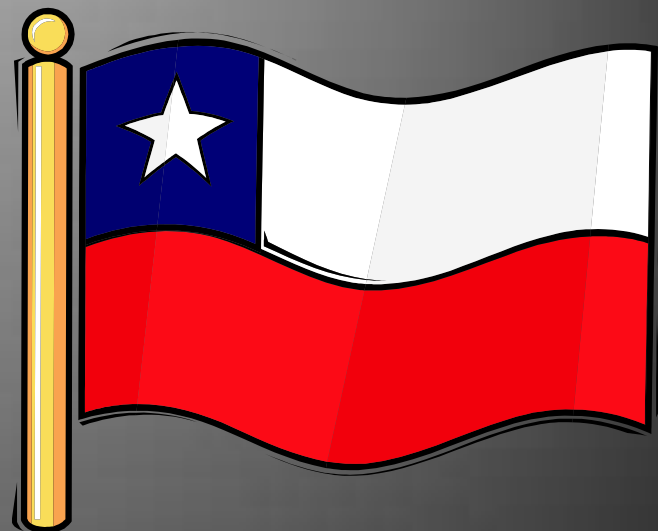
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Characterization of metal catalysts supported on active carbons made from chilean coal

6 months stay for PhD. Thesis @ Kaneko Laboratory, Chiba, Japan
February 2008

Our laboratory (in Chile)

- Carbons & Catalyst Group
 - www.udec.cl/~carbocat
- Professors:
 - Ximena García
 - Alfredo Gordon
 - Romel Jiménez
 - Ljubisa R. Radovic
- Research interests:
 - Catalysts for environmental protection; biomass use; combustion; and, more recently, coal & carbon structure and molecular modeling



Nitric oxide problem

- NO_x emissions: in diesel engines especially
- Important part of air pollution problem, they contribute to:
 - Global warming
 - Acid rain
 - Deteriorated water quality



Solutions for NO_x abatement

Approach	-	+
NO catalytic reduction with CO over TWC	Not effective under oxydizing conditions/ Sulfur poisoning	Simultaneous remotion of CO, NO and HC
SCR with NH ₃	NH ₃ handling and storage / special systems for 'ammonia slip' avoiding	High NO remotion efficiency in O ₂ presence
SCR with HC	Low selectivity / 'HC slip'	High potential of NO remotion / efficient in presence of O ₂
Direct decomposition (perovskites, Cu-ZSM-5, Pt/Al ₂ O ₃)	Low activity/ SO ₂ / O ₂ is difficult to desorb	Harmless, forms N ₂ + O ₂ / does not use reducing agents

Topics in my thesis

- Environmental concern
 - NO reduction
 - NO decomposition
- Coal- and/or biomass-derived catalysts
 - Active carbon
 - Metals supported on active carbon
- Oxygen transfer
 - Role of metal species in improving the efficiency of oxygen-transfer-controlled reactions

Possible roles of (active) carbon

- Structural support
 - High surface area, optimal PSD
- Reducing agent
 - $C_f + 2NO \rightarrow N_2 + CO_2$
 - $C_f + NO \rightarrow C-N + CO$
- Catalyst!
 - $2C_f + 2NO \rightarrow N_2 + O_2 + 2C_f$

NO decomposition (1981)

TABLE 1.—CATALYTIC DECOMPOSITION OF NO OVER CuNaY-69 AT VARIOUS CONTACT TIMES^a

contact time ^b /g (cat) s cm ⁻³ (gas)	catalyst weight /g	flow rate /cm ³ (s.t.p.) min ⁻¹	500 °C conversion (%)		
			of NO	to N ₂	to O ₂
0.6	0.36	35.4	16.5	8.8	trace
1.3	0.79	35.2	27.8	15.9	trace
4.0	2.33	34.0	58.0	29.0	0.5
7.8	3.22	25.0	88.5	42.0	5.0
10.9	3.56	19.6	99.0	49.2	8.3

CONCLUSIONS

Cu^{II} ion-exchanged Y-type zeolites exhibit high catalytic activities for the decomposition of NO without deterioration. This indicates new horizons for the removal of NO without using reducing agents.

Iwamoto, M., S. Yokoo, K. Sakai and S. Kagawa (1981). "Catalytic decomposition of nitric oxide over copper(II)-exchanged, Y-type zeolites." *J. Chem. Soc., Faraday Trans. 1*(77): 1629 - 1638.

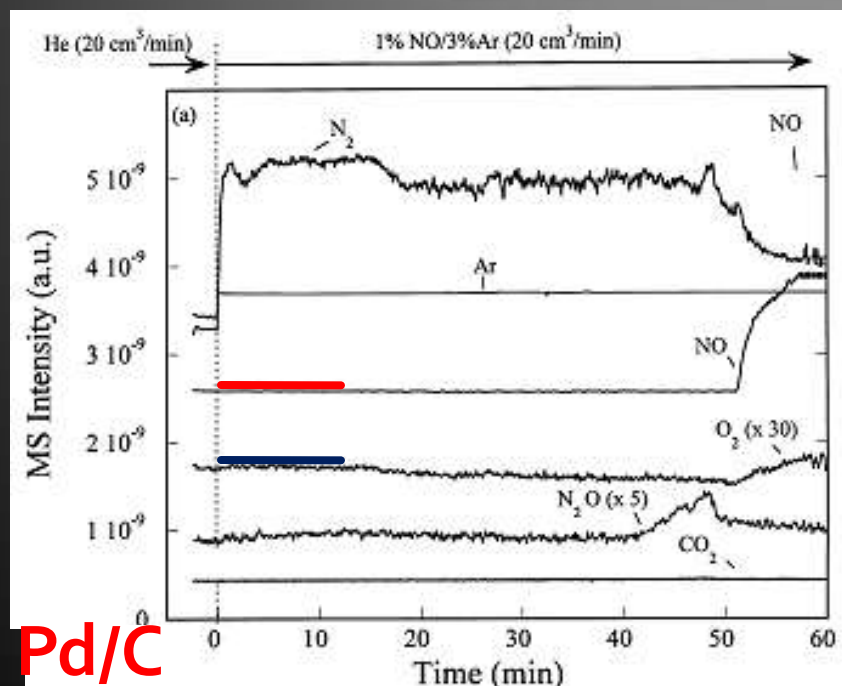
NO decomposition (2000)

In situ infrared study of catalytic decomposition of NO on carbon-supported Rh and Pd catalysts

K. Almusaiteer, R. Krishnamurthy, S.S.C. Chuang *

Department of Chemical Engineering, The University of Akron, Akron, OH 44325-3906, USA

400 °C



Pd/C

decomposition have revealed that the low activity of the catalysts is due to their inability to desorb oxygen produced from NO dissociation [8,10]. Oxygen

ferred from Table 2 that the carbon-supported catalysts have the ability to uptake more oxygen than alumina-supported catalysts. Comparison of the

or Pd) remains on the surface [10,23,24]. Unless the catalyst has the ability to desorb oxygen, S-O from reaction (1) will accumulate on the surface and blocks the sites for NO dissociation resulting in the increase in the surface coverage of the IR-observable species (active and spectator adsorbate).

bine for desorption as molecular oxygen. The difference in Pd/C and Pd/Al₂O₃ in oxygen desorption could be due to dispersion of metal particles (Table 2) or metal-support interaction. Lack of detailed structural surface information does not allow elucidation of the role of metal-support interaction in the oxygen desorption.


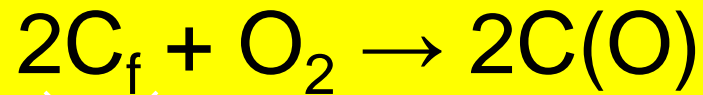
Almusaiteer, K., R. Krishnamurthy and S. S. C. Chuang, In situ infrared study of catalytic decomposition of NO on carbon-supported Rh and Pd catalysts, *Journal of Catalysis*, 1999, 191, 291-299.

Hypothesis

- Practical
 - Cheap and abundant raw materials can be converted in highly efficient catalyst if the preparation conditions are carefully chosen
- Fundamental
 - Catalyst efficiency in NO reduction or decomposition can be improved by optimizing oxygen transfer
 - The easier this transfer is, the lower the reaction T and the more probable that oxygen surface recombination results in $C_f + O_2$

Oxygen transfer mechanism of carbon reactions (1)

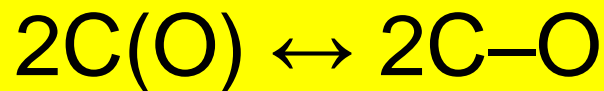
(i) Dissociation of O₂ (or CO₂ or NO or H₂O) on carbon “reactive sites”



Reactive sites : ‘unsaturated’ carbon atoms, typically located at the edges of crystallites...

Oxygen transfer mechanism of carbon reactions (2)

(ii) Surface migration of oxygen



*Surface
intermediates*

*Surface
'spectators'
(complexes)*

Oxygen transfer mechanism of carbon reactions (3)

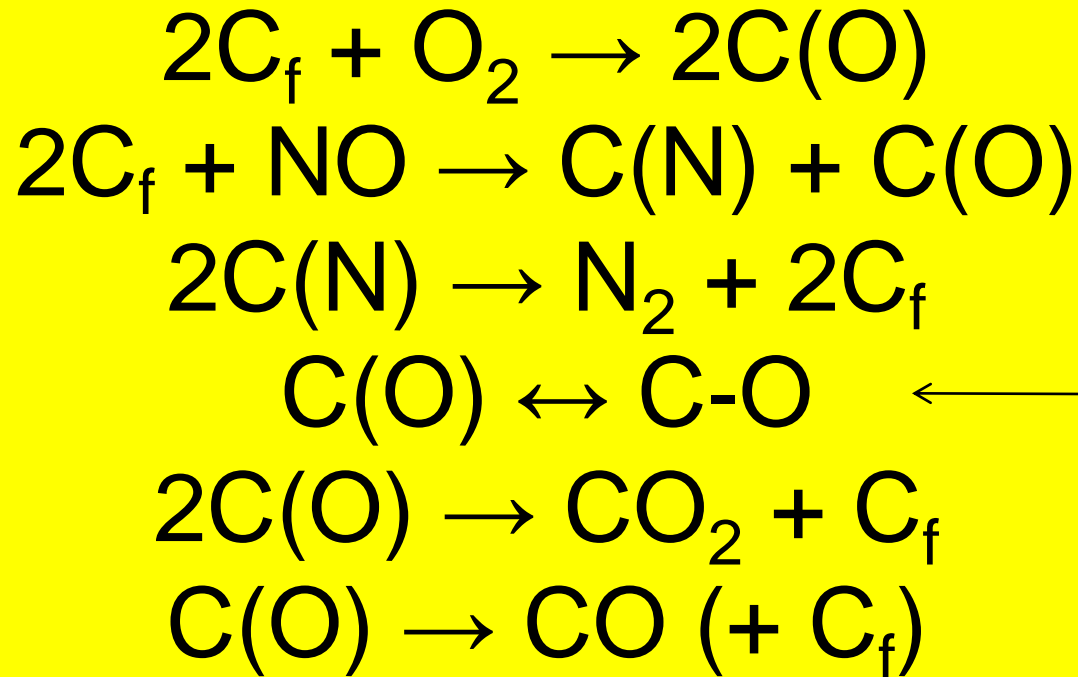
(iii) Desorption of CO and/or CO₂



$$m=2 (!?) \quad n=1 (?!)$$

Note: CO/CO₂ = f(T, [C(O)], [C-O], carbon structure)

Removal of NO_x: (oxygen transfer mechanism)



Key hypothesis

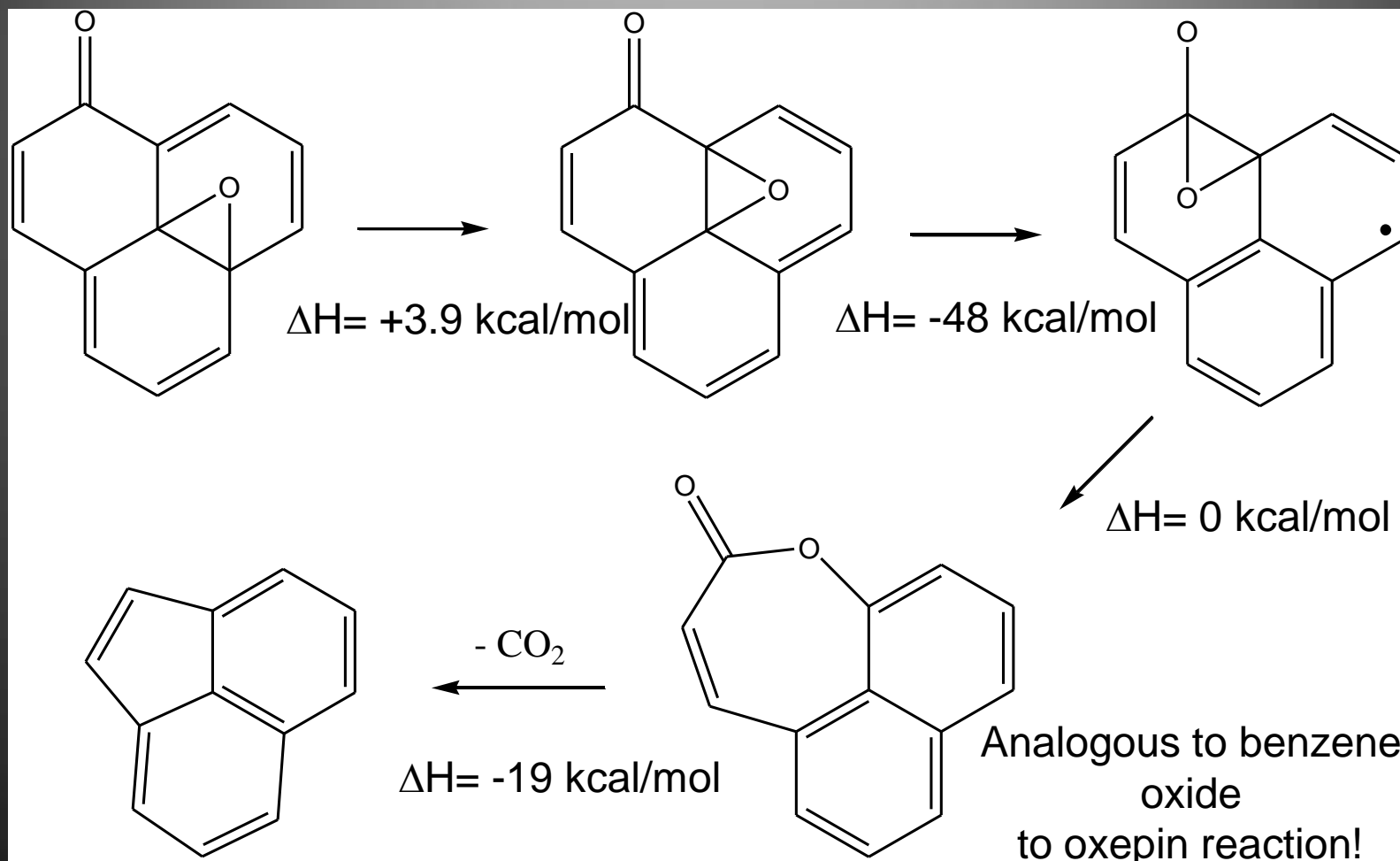
As oxygen surface coverage increases, CO → CO₂ (→ O₂?!)

(And as catalyst dispersion and catalyst/carbon contact improve, oxygen can accumulate on the carbon surface... This will be pursued and tested using TPD!)

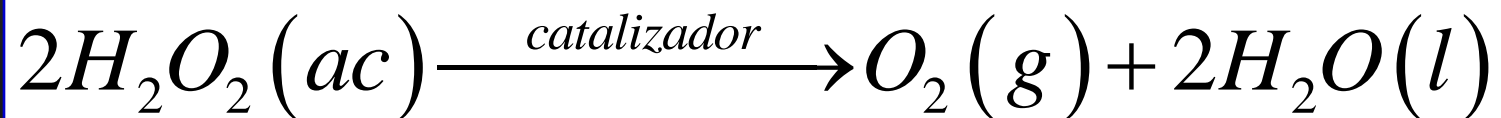
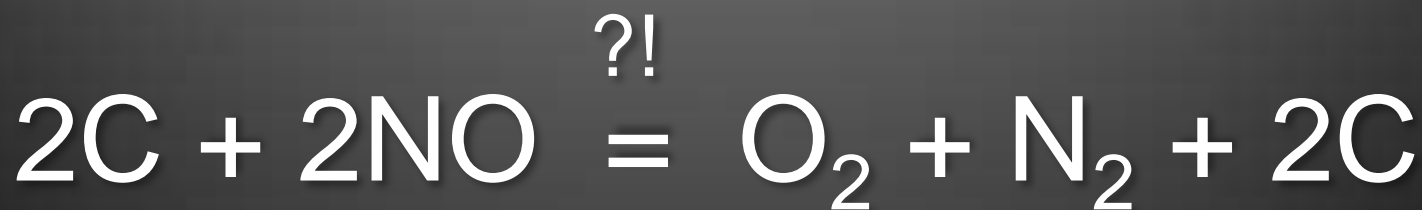
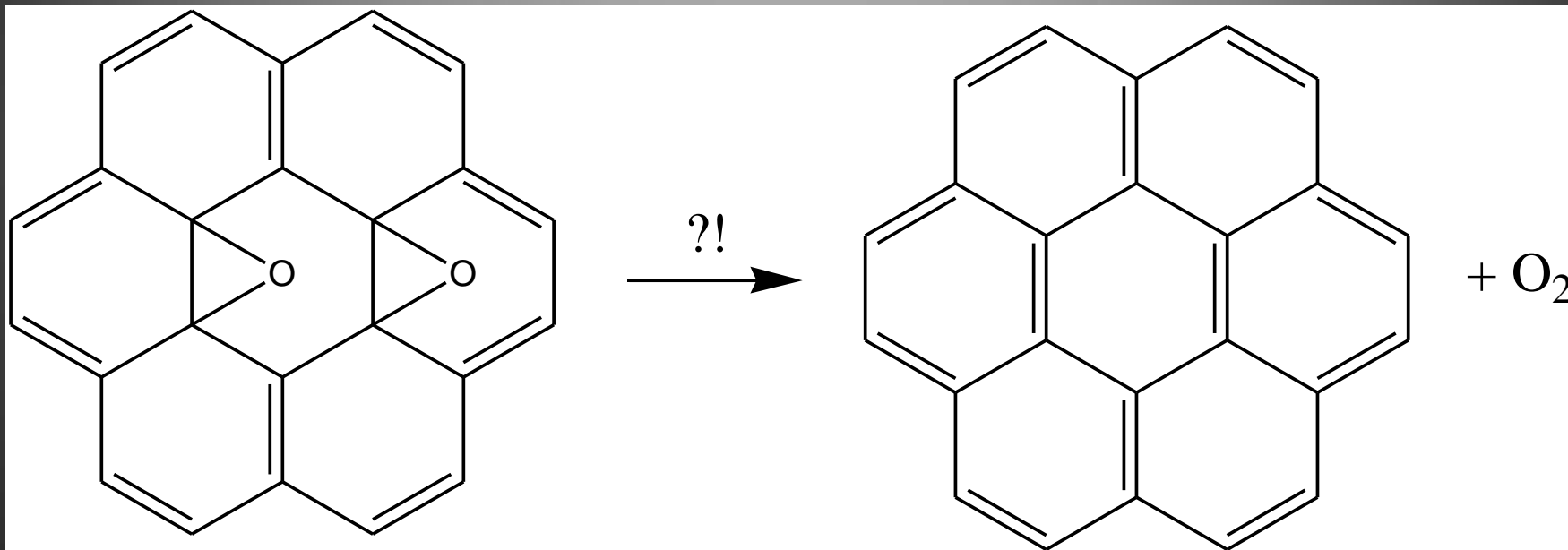
Oxygen transfer mechanism is also dominant in **catalytic** gasification reactions!



Hypothetical route to CO_2 formation (with participation of basal-plane, epoxy-type oxygen)



Hypothetical route to O_2 formation
(with participation of basal-plane, epoxy-type oxygen)



Objectives

- Make cheap, efficient and easy-to-prepare catalysts for NO reduction or decomposition
- Investigate the effect of preparation conditions on catalytic activity

Preparation

- AR-C (As received coal, grinded and sieved)
- Dem-C (Acid demineralization)
- Dem-C-*** (Pyrolyzed, 550-700-850-1000°C)
- Dem-AC-*** ** (CO₂ activation, 825°C)

- Metal addition (Co, Cu and K)
 - Incipient wetness impregnation (IWI) ← Nitrate decomposition HTT
 - Ion exchange (IE) ← HNO₃ oxidation
 - Phthalocyanines

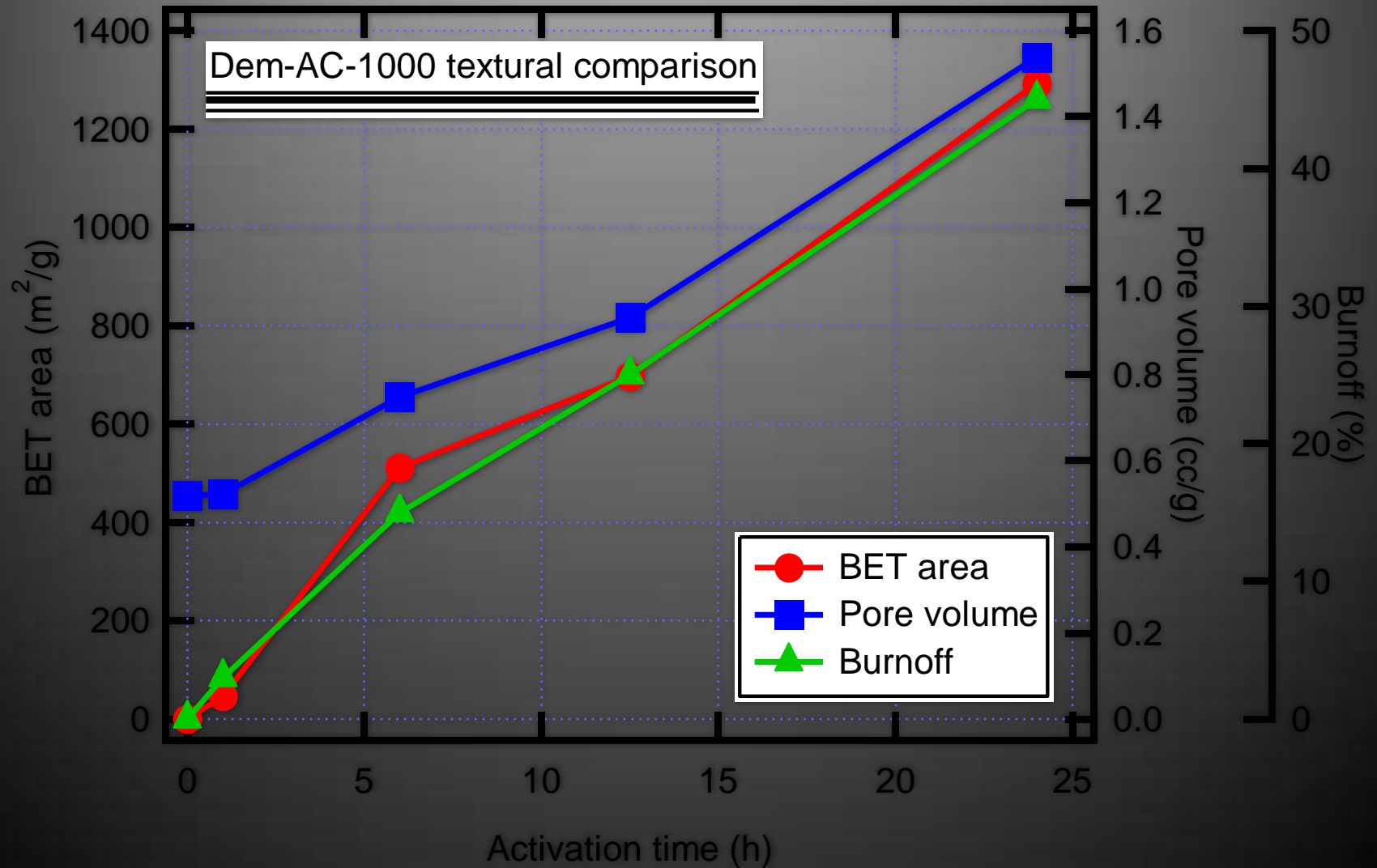
Catalysts prepared

Not impregnated	Incipient wetness impregn.	Ion exchanged
AR-C	Co-AC-IWI-1000 1h	Co-AC-IE-1000 1h OX
Dem-C	Co-AC-IWI-1000 6h	Co-AC-IE-1000 6h OX
Dem-C-550	Co-AC-IWI-1000 12.5h	Co-AC-IE-1000 12.5h OX
Dem-C-700	Co-AC-IWI-1000 24h	Co-AC-IE-1000 24h OX
Dem-C-850	Cu-AC-IWI-1000 1h	Cu-AC-IE-1000 1h OX
Dem-C-1000	Cu-AC-IWI-1000 6h	Cu-AC-IE-1000 6h OX
Dem-AC-1000 1h (and OX)	Cu-AC-IWI-1000 12.5h	Cu-AC-IE-1000 12.5h OX
Dem-AC-1000 6h (and OX)	Cu-AC-IWI-1000 24h	Cu-AC-IE-1000 24h OX
Dem-AC-1000 12.5h (and OX)	K-AC-IWI-1000 1h	K-AC-IE-1000 1h OX
Dem-AC-1000 24h (and OX)	K-AC-IWI-1000 6h	K-AC-IE-1000 6h OX
	K-AC-IWI-1000 12.5h	K-AC-IE-1000 12.5h OX
	K-AC-IWI-1000 24h	K-AC-IE-1000 24h OX

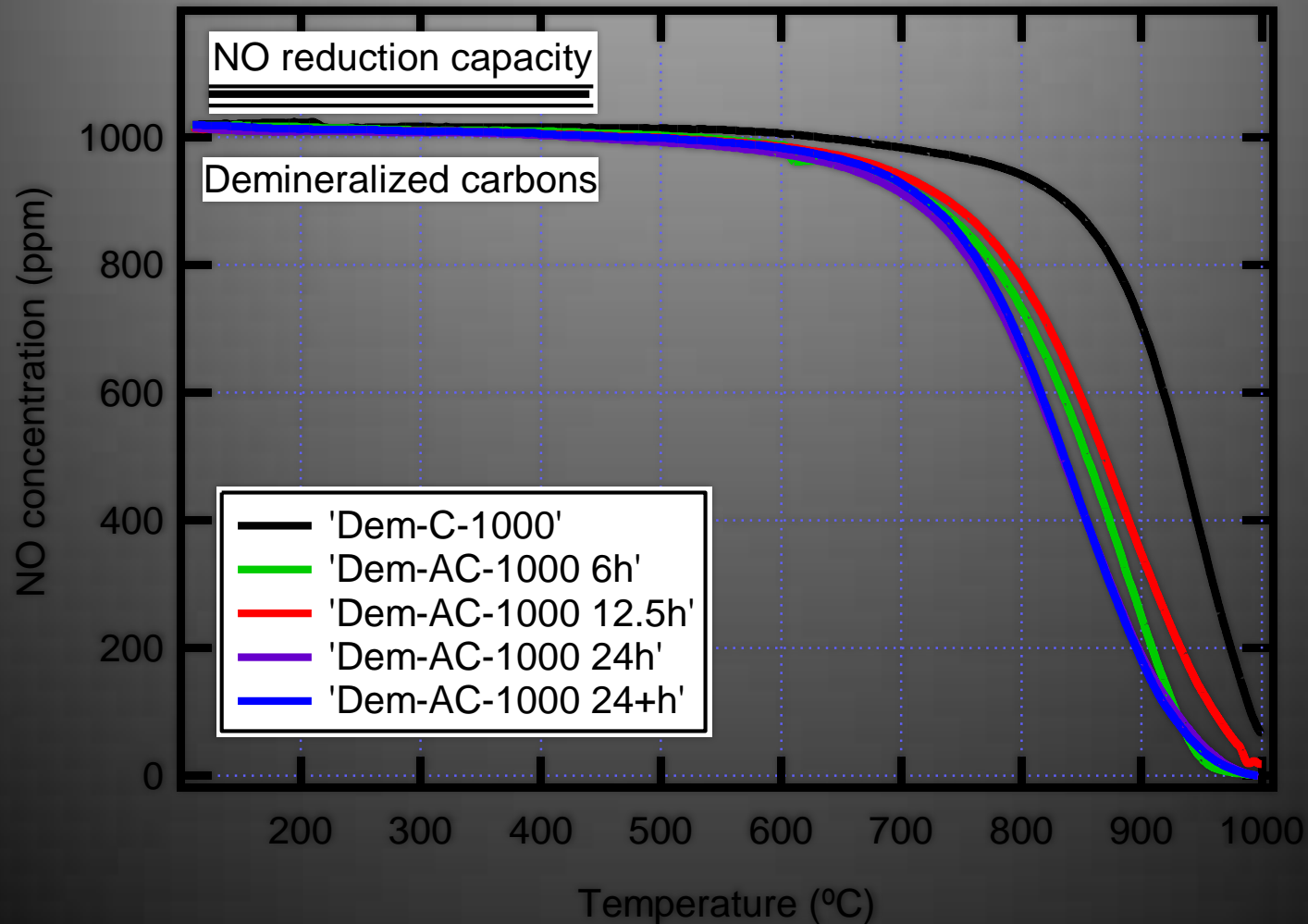
Analyses done

- For supports:
 - Water pore volume (needed for IWI)
 - PZC
 - N₂ adsorption
 - CO and CO₂ desorption
- For catalysts:
 - NO catalytic activity (NO, CO and CO₂ analyzer)
 - O₂ catalytic activity (MS analyzer)

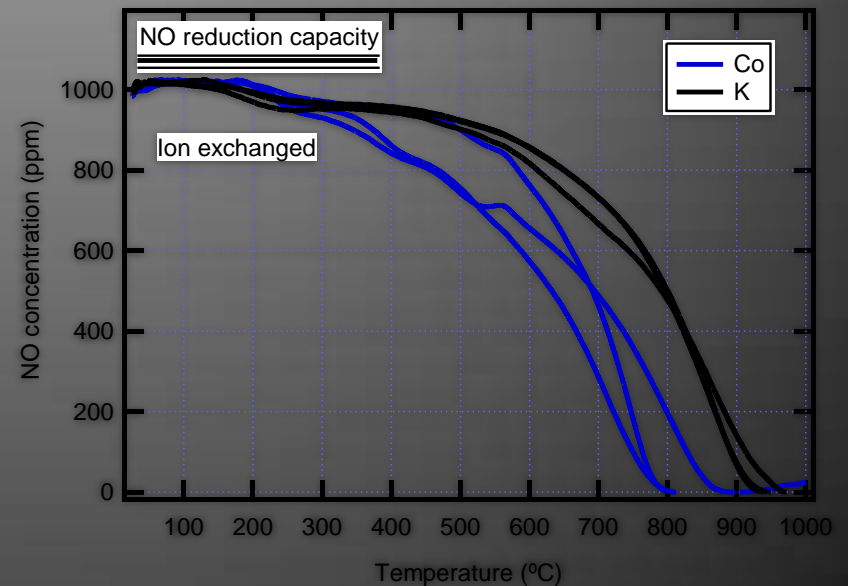
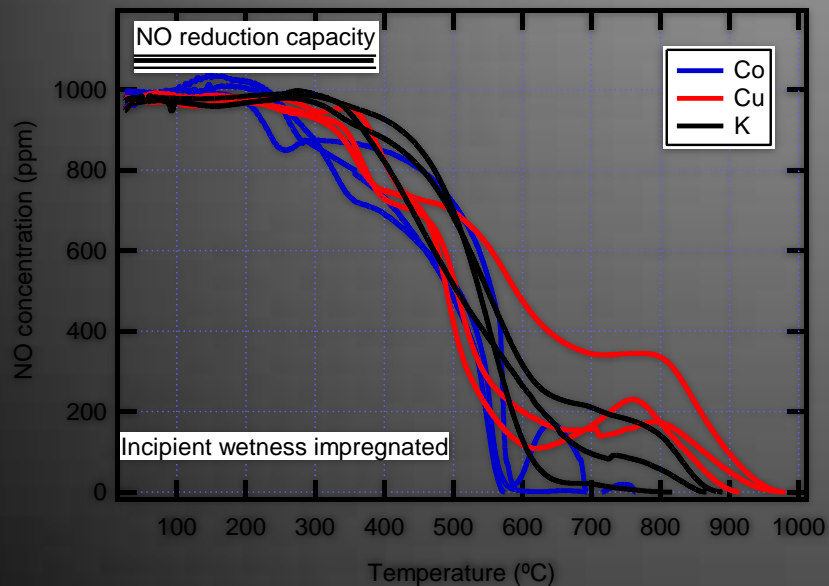
CO₂ activation results



NO reduction (demineralized)



NO reduction (with metals)



Behavior observed to date (1)

- For textural properties:
 - Burnoff α activation time (OK)
 - Adsorption capacity α burnoff (OK)
 - Water penetration α burnoff (OK)
- For demineralized carbons and NO reduction:
 - Activity is higher after activation
 - Activity is not increased when S.A. increases

Behavior observed to date (2)

- For IWI metal added (NO reduction activity):
 - Low conversion: $\text{Co} > \text{Cu} > \text{K}$
 - High conversion: $\text{Co} > \text{K} > \text{Cu}$
 - More surface area is better
- For IE metal added (NO reduction activity):
 - Very low conversion: $\text{K} > \text{Co}$
 - The rest: $\text{Co} > \text{K}$
 - Only at low conversion, more surface is better

Pending issues

- Effect of CO₂ activation on functional groups
 - Types of sites created (quinone?)
 - Size of pores developed
- Effect of oxidation on activated carbons
 - Amount of carboxylic groups created
 - Amount of metal exchanged sites
- Effect of metal addition
 - Changes in PSD
 - Interactions C-Me (carbon matrix and metal)
 - Metal dispersion

Practical challenges

1. Minimize carbon consumption
2. Maximize the extent of NO chemisorption by selecting the catalyst with the highest affinity towards NO
3. Maximize the rate of oxygen transfer by maximizing the catalyst/carbon contact area

Illán-Gómez, M.J., A. Linares-Solano, L. R. Radovic and C. Salinas-Martínez de Lecea (1996). "NO reduction over activated carbons. 7. Some mechanistic aspects of uncatalyzed and catalyzed reaction" Energy & Fuels. (10): 158 - 168.

Experiments to do @ Chiba

- Spectroscopy of surface chemistry
 - XPS, FTIR, DRIFTS
- Metal content & dispersion
 - XPS, XRD, TEM
- Carbon structure
 - XPS, XRD, SEM, N₂ ads, Raman
- Electronic properties
 - SQUID, ESR, χ

END

Thank you for your time!