Advanced NO Decomposition Catalysts: Supported, Alkali-doped Cobalt Oxide

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ACKNOWLEDGEMENTS

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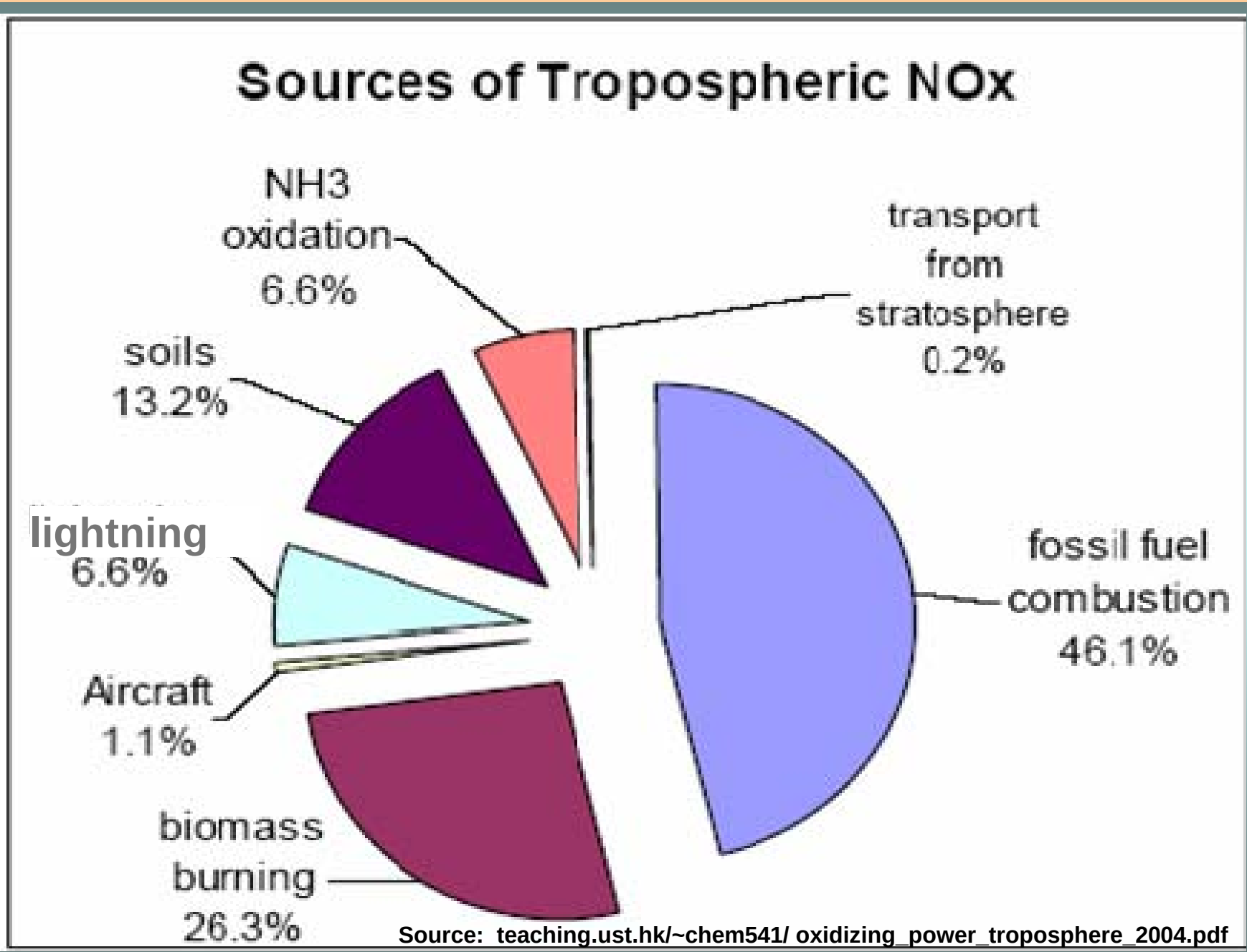
Kenny Komola

Problems Caused by NO_x Emissions

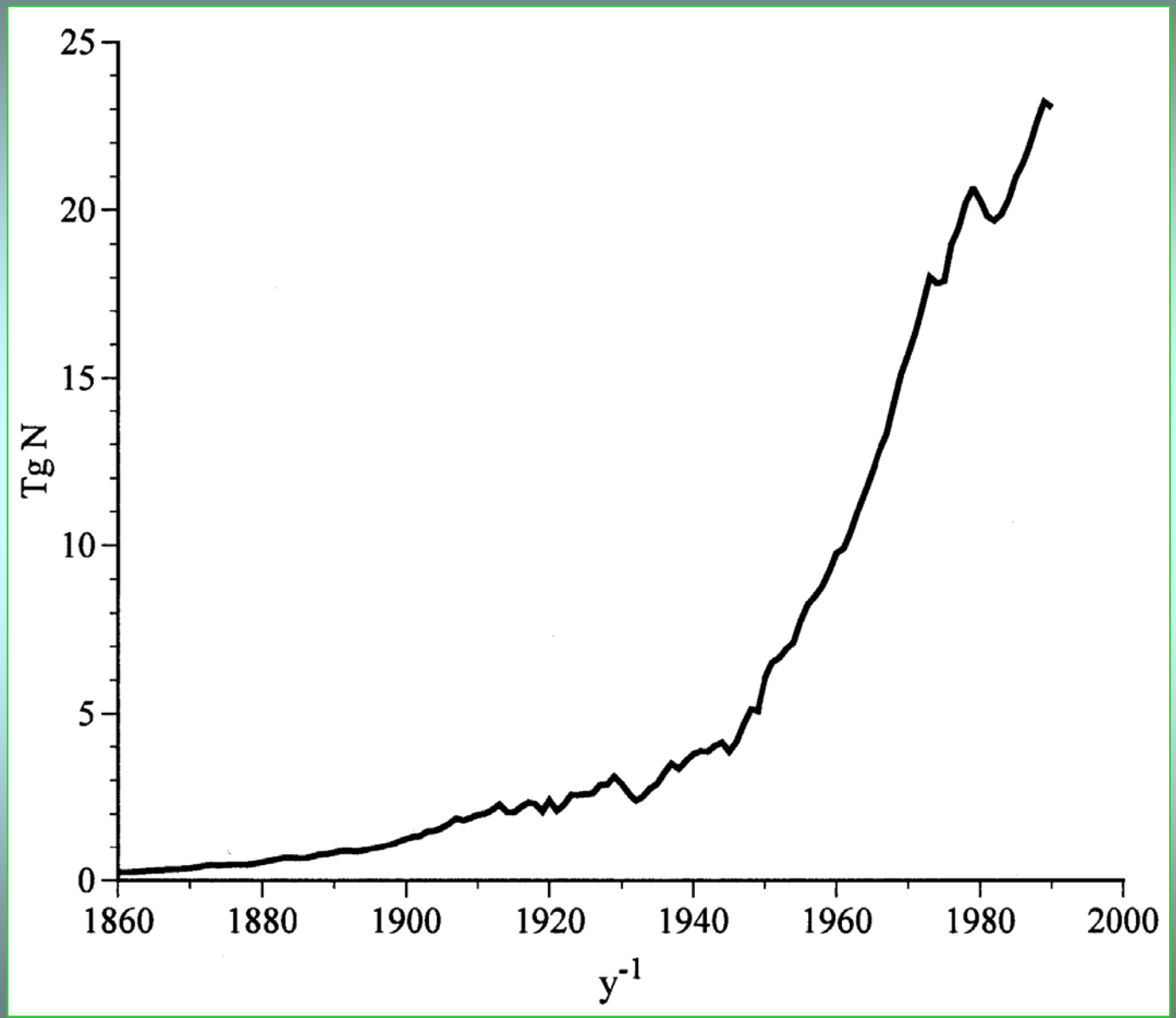
- **Involved in ground-level ozone formation**
- **Particulates and aerosols add to respiratory problems and decrease visibility**
- **Acid rain**
- **Source of nitrogen that deteriorates water quality**
- **Greenhouse gases**

NO_x Sources in the Lower Atmosphere



Source: teaching.ust.hk/~chem541/ oxidizing_power_troposphere_2004.pdf

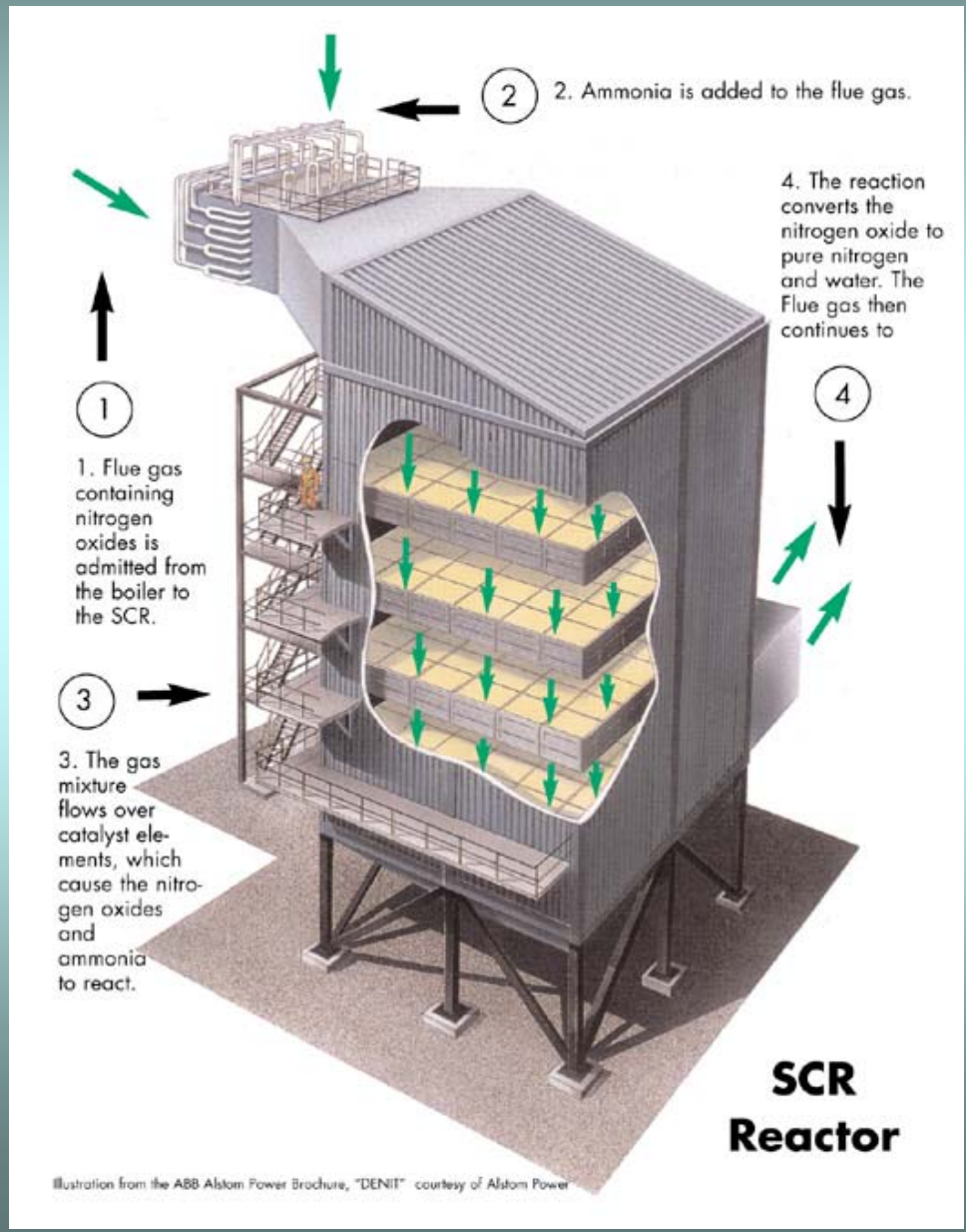
Global Annual NO_x Emissions



Holland & Lamarque, *Nutrient Cycling in Agroecosystems* 48 (1997) 7–24

Current Industrial Approaches to NO_x Control

- **Problem: High T combustion creates NO_x (air pollutant → O_3)**
  - **Primary (combustion) control**
  - **Secondary (e.g., SCR) control**
    - **$NO_x + NH_3 \rightarrow N_2 + H_2O$ on VO_x/TiO_2**
    - **Required rxn T ~350°C**
    - **NH_3 slip (bypassing) is environmental problem**



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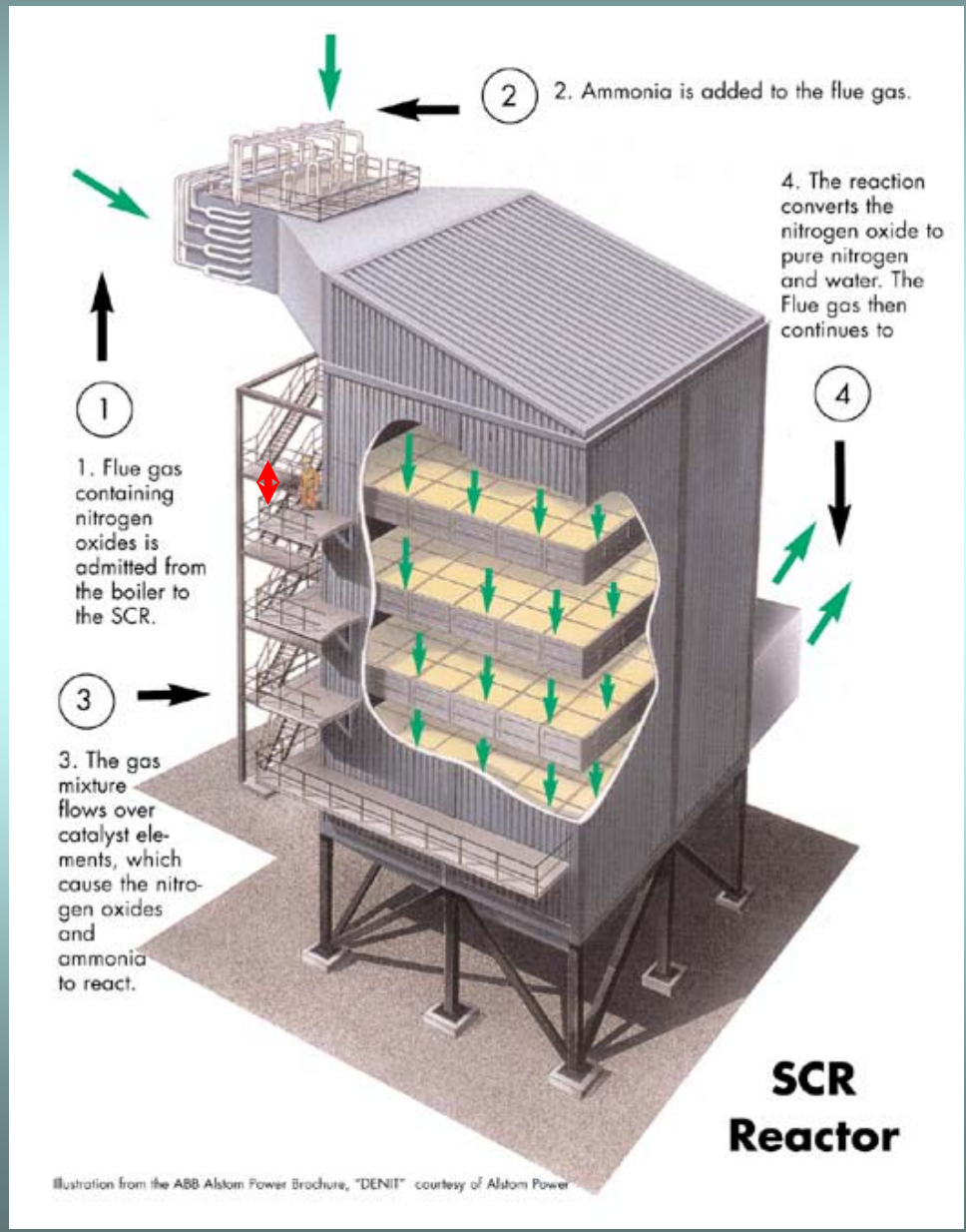

Current Industrial Approaches to NO_x Control and Research Opportunity

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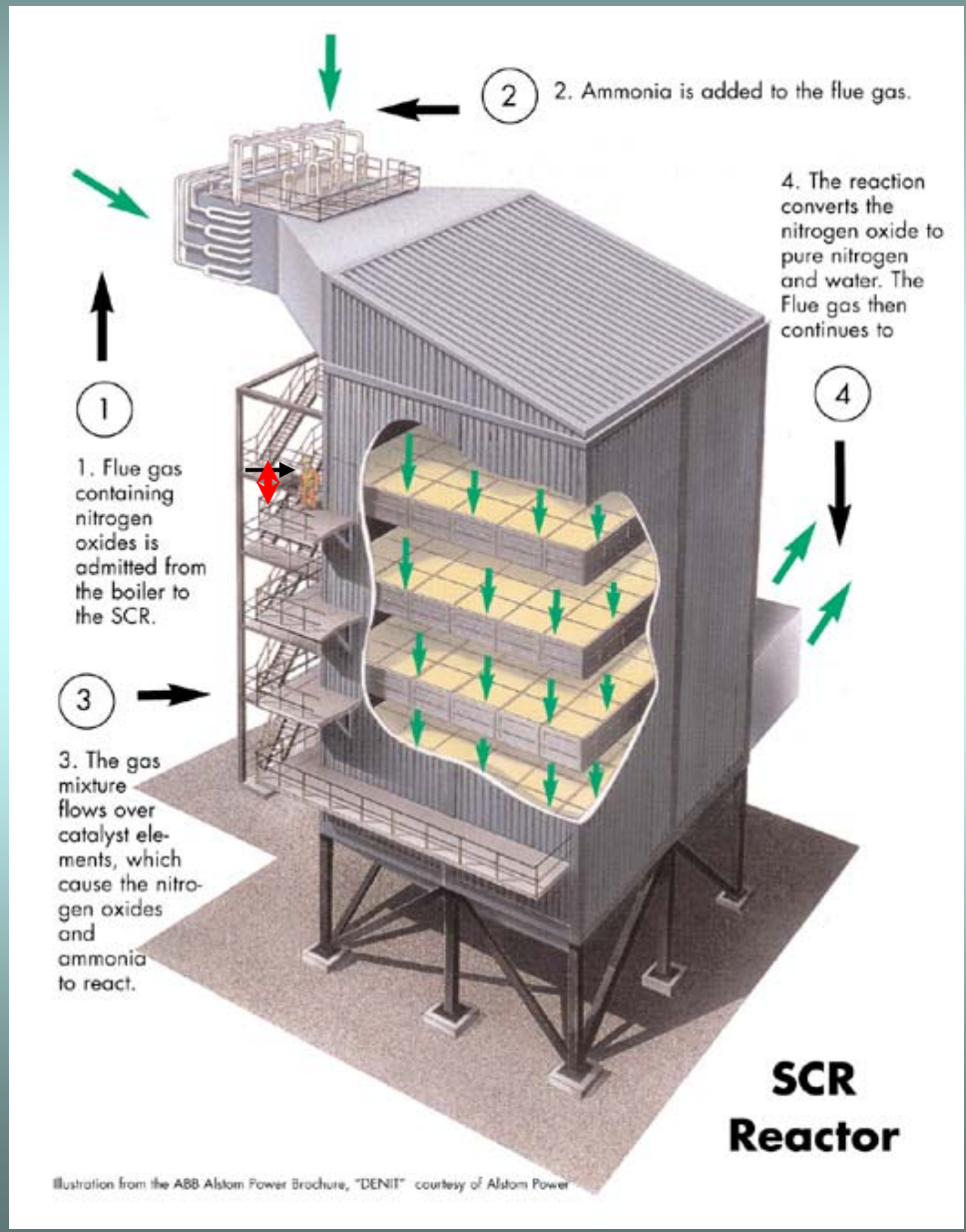
    - $NO_x + NH_3 \rightarrow N_2 + H_2O$ on VO_x/TiO_2
    - Required rxn T ~350°C
    - NH_3 slip (bypassing) is environmental problem
- **Research opportunity: develop more active and efficient catalysts**
  - lower reaction temperature
  - eliminate reductant addition
    - Cu-ZSM-5 active in NO reduction [B. Moden et al., *J. Catal.* 209, 77 (2003)]



Methods and Approach: Catalytic Reaction on Supported Metal Oxides

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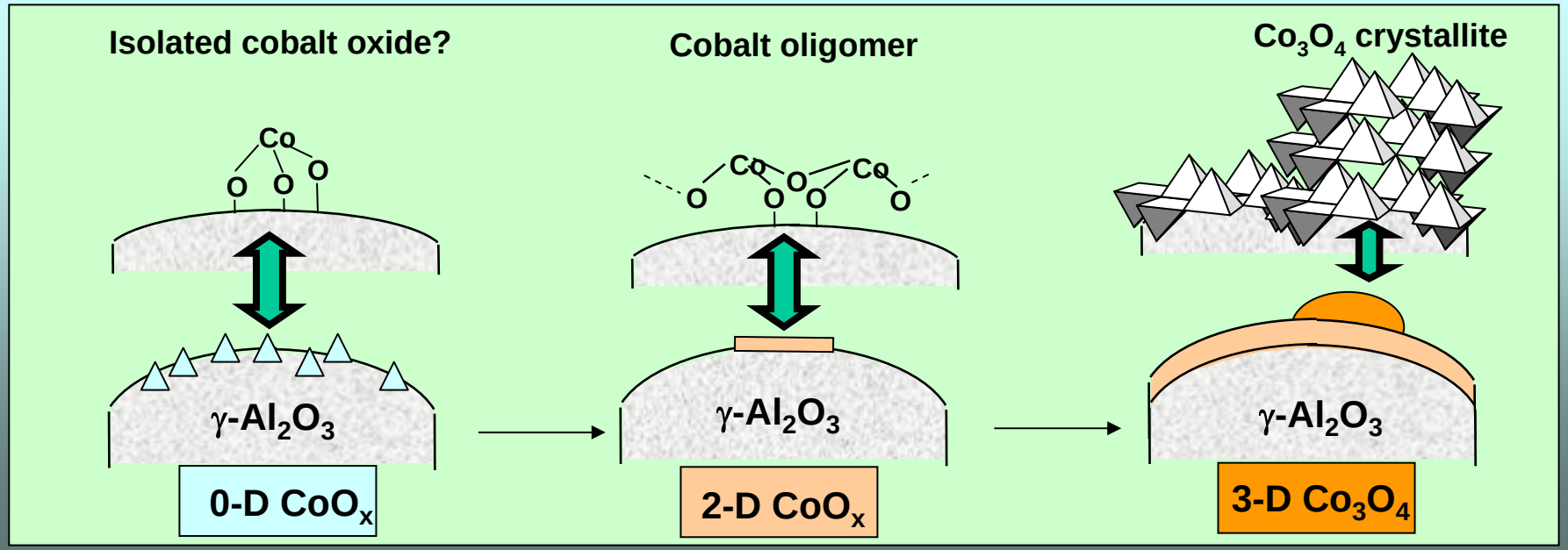

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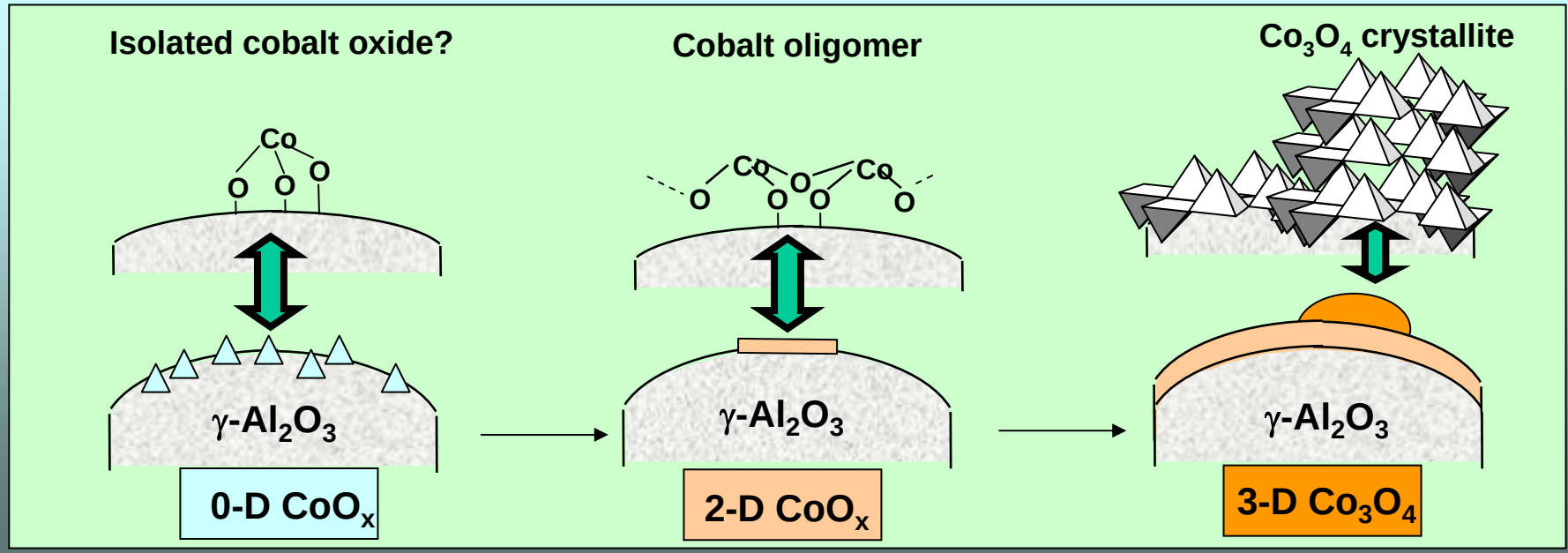

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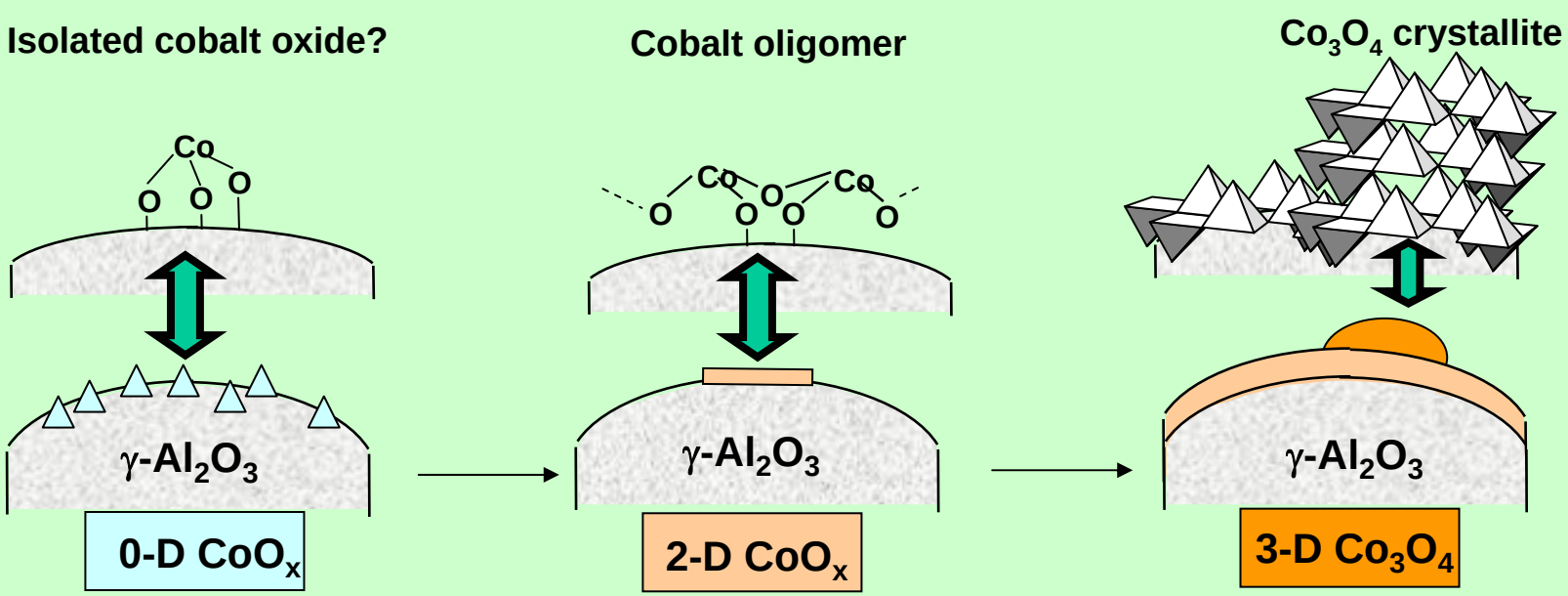
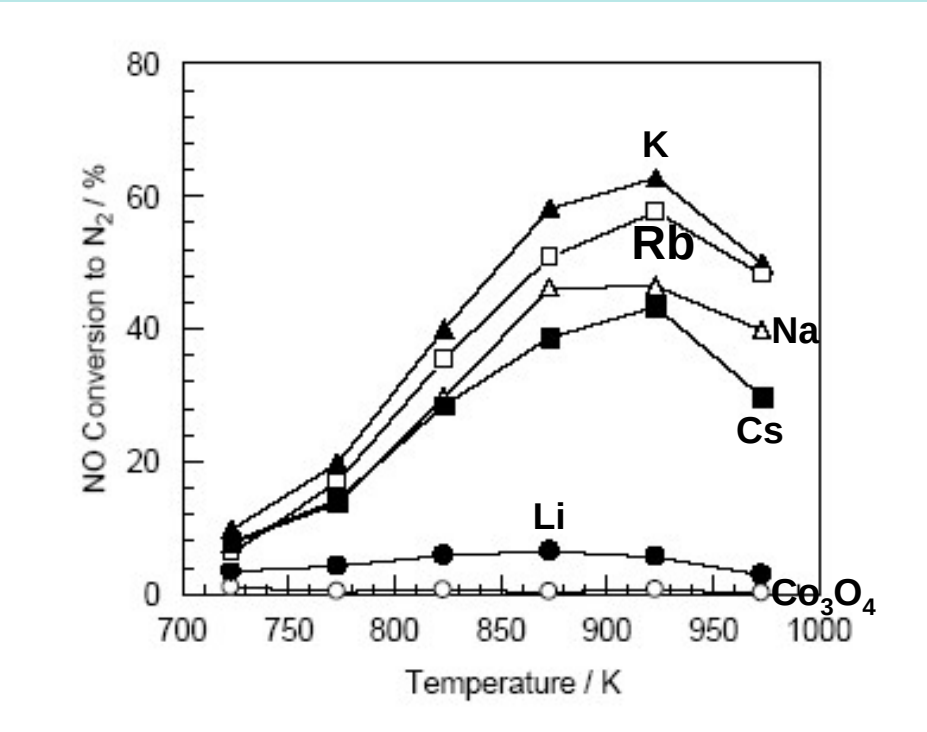
SURFACE FUNCTION: Probe surface properties (e.g., reducibility) and their catalytic implications (by chemical titrations, in situ spectroscopies, ….)



Supported Metal Oxide Catalysts for Direct NO_x Decomposition

Haneda et al. showed that unsupported Co_3O_4 with added alkali are effective direct NO decomposition catalysts



[Haneda et al., Appl. Catal. B 46 (2003) 473]

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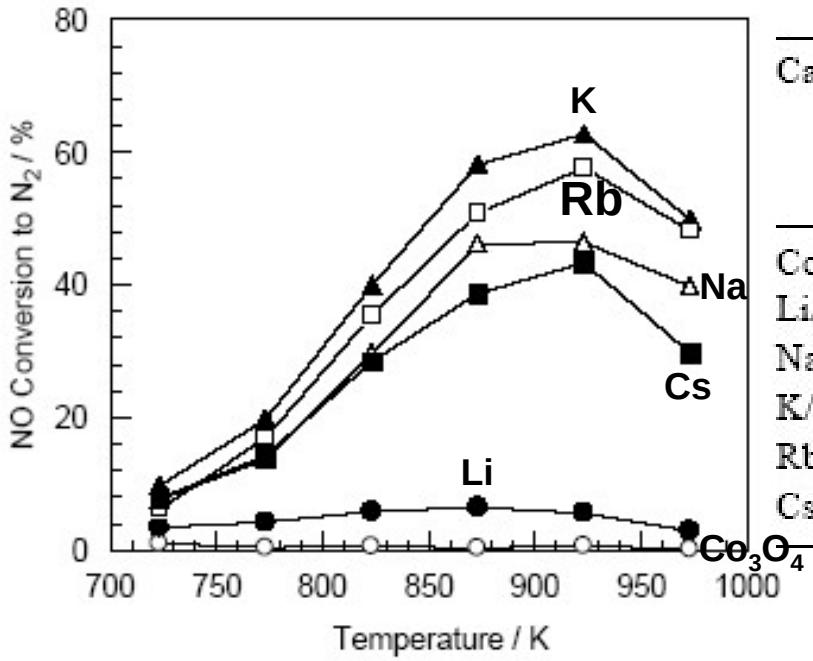

Catalyst	BET surface area ($m^2\ g^{-1}$)	Activity[a] at 873 K	
		mol N_2 $min^{-1}\ g^{-1}$	mol N_2 $min^{-1}\ m^{-2}$
Co_3O_4	9.0	1.35×10^{-8}	1.50×10^{-9}
Li/Co_3O_4	8.3	4.04×10^{-7}	4.87×10^{-8}
Na/Co_3O_4	23	1.72×10^{-6}	6.90×10^{-8}
K/Co_3O_4	34	2.17×10^{-6}	6.39×10^{-8}
Rb/Co_3O_4	38	1.91×10^{-6}	6.60×10^{-8}
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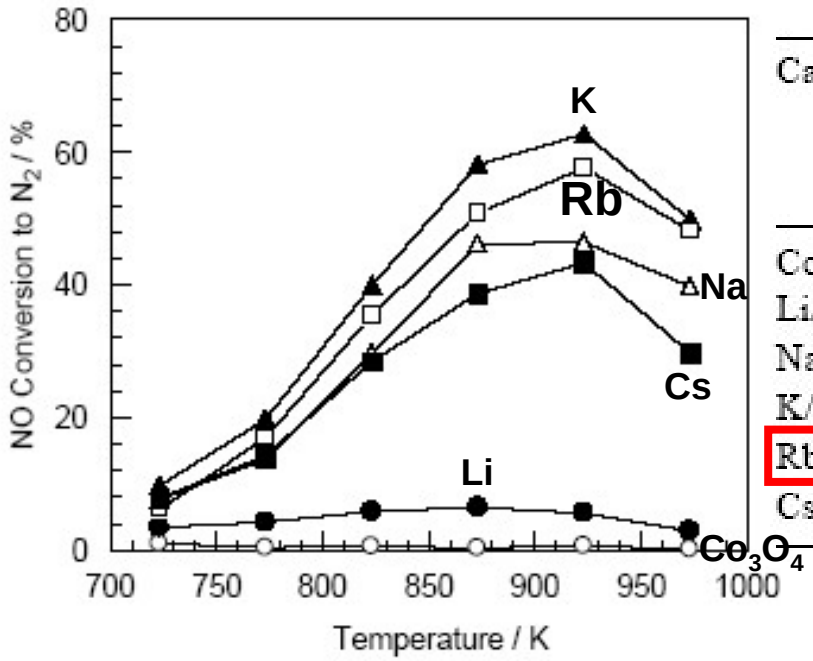

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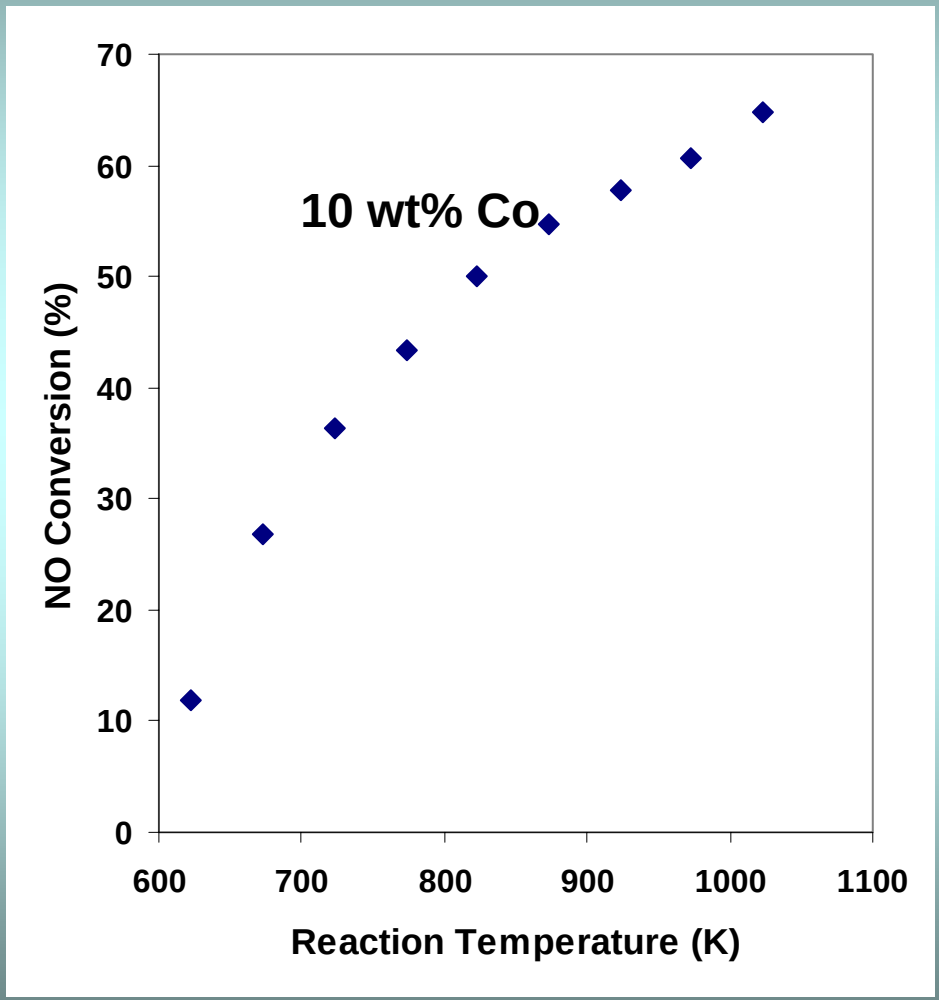
10 wt% CoO_x catalyst with 0.035 Rb atom/Co atom, supported on γ-Al_2O_3, appears ~6 times more active per gram [923 K]

Supported Alkali Promoted Cobalt Oxide Performs More Efficiently than the Unsupported Material



[0.035 atom ratio Rb:Co, 0.04 g catalyst, 0.5 ml/s 1000 ppm NO in N_2]

~6 times as active per gram of catalyst

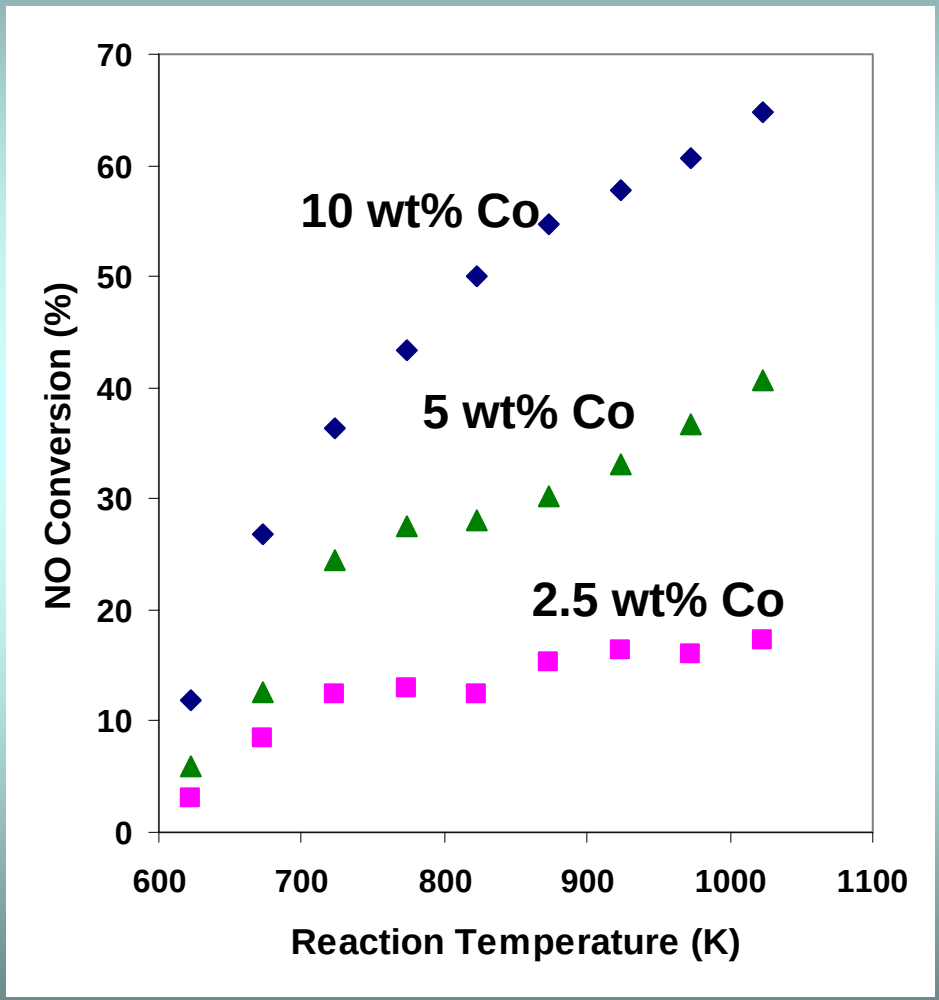
~60 times as active per gram of cobalt

~2 times as active on a surface area basis

Rates:

- **2.0×10^{-5} mol NO/(min g)**
- **2.6×10^{-7} mol NO/(min m^2)**
- **1.0×10^{-3} mol NO/(min mol Co)**

NO Conversion Rates Apparently Increase with Increasing Co Surface Density



[0.035 atom ratio Rb:Co, 0.04 g catalyst, 0.5 ml/s 1000 ppm NO in N_2]

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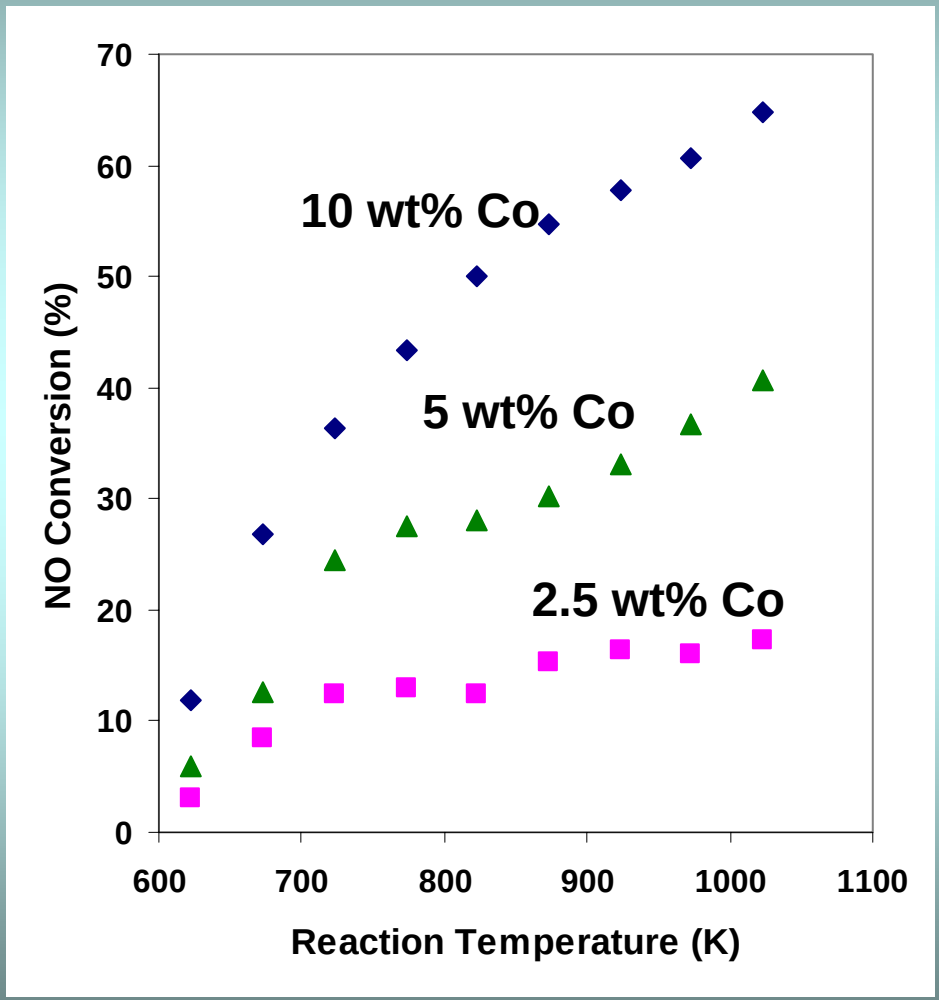
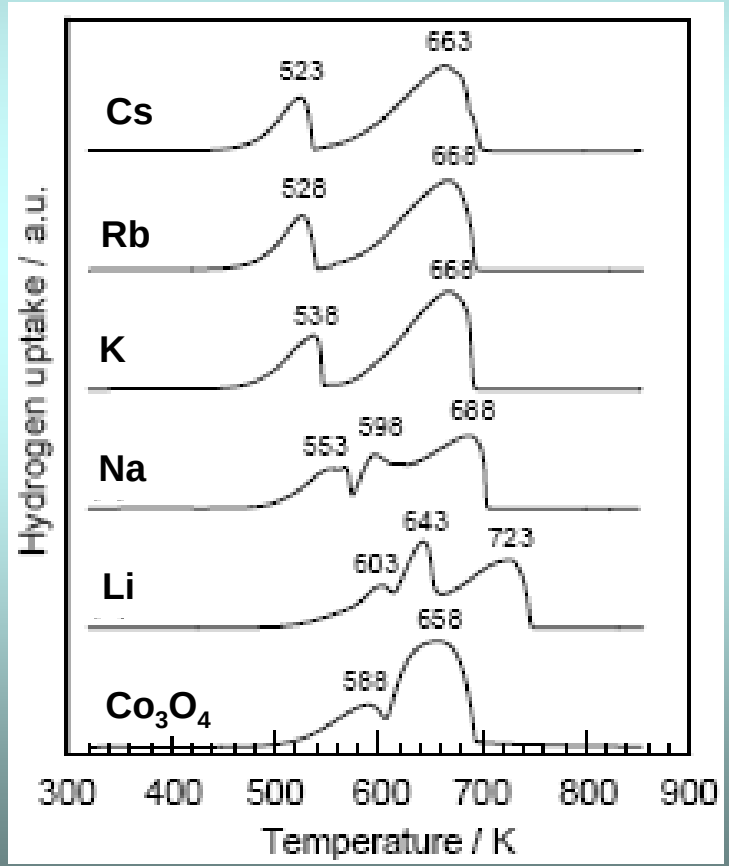


[0.035 atom ratio Rb:Co, 0.04 g catalyst, 0.5 ml/s 1000 ppm NO in N_2]

Correlates with reducibility?



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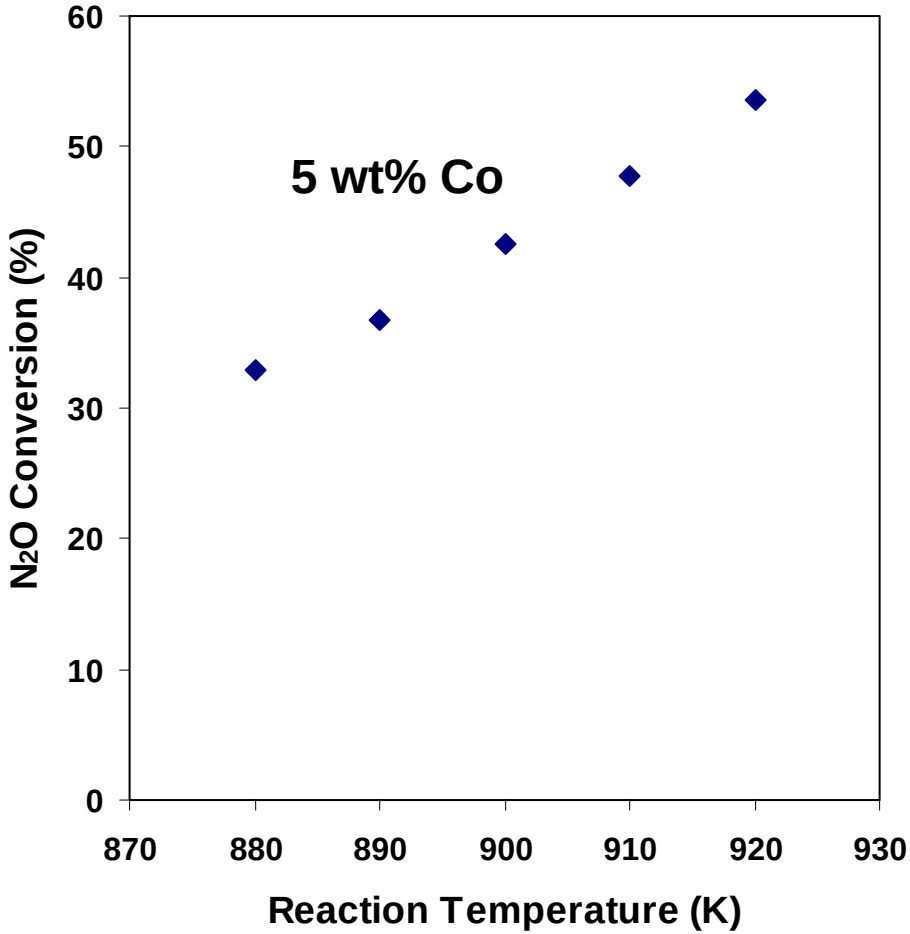
N_2O Conversion Similar to NO Conversion



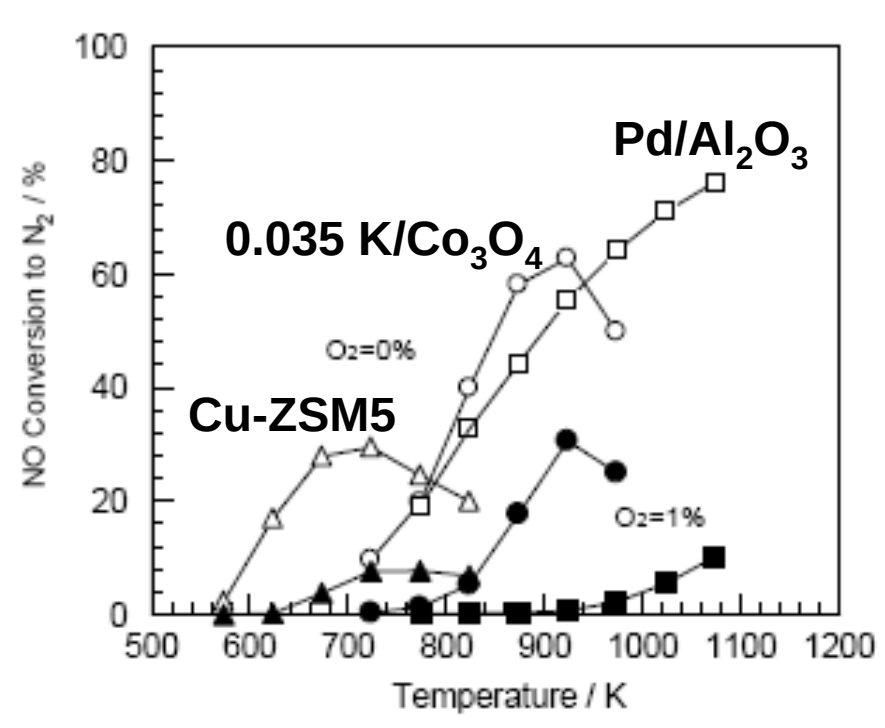
Haneda et al. note they observed no N_2O formation

Our data suggest the reason is high N_2O conversion activity

Must verify if similar trend of increasing N_2O decomposition rate with increasing Co surface density holds

[5 wt% Co, 0.035 atom ratio Rb:Co, 0.04 g catalyst, 0.5 ml/s 1000 ppm N_2O in He]

Alkali-Cobalt Oxide Is Active in the Presence of O_2



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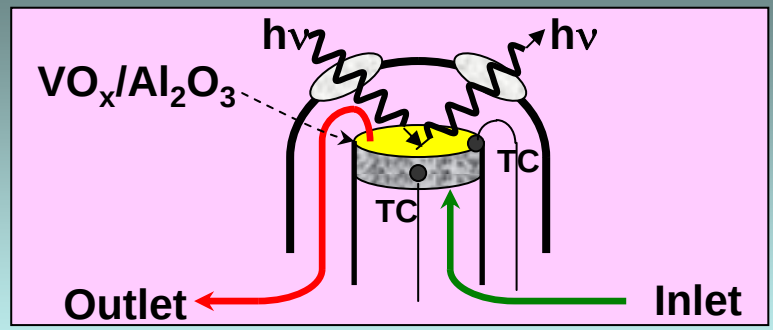
Although losing ~half its activity, alkali-cobalt oxide catalysts remain active in the presence of O_2

Respond much better than either Cu-ZSM5 or Pd

UV-VISIBLE SPECTRA ABSORPTION EDGE ENERGY: Domain Size of Co_3O_4-like Surface Structures Increases with Increasing Cobalt Surface Density



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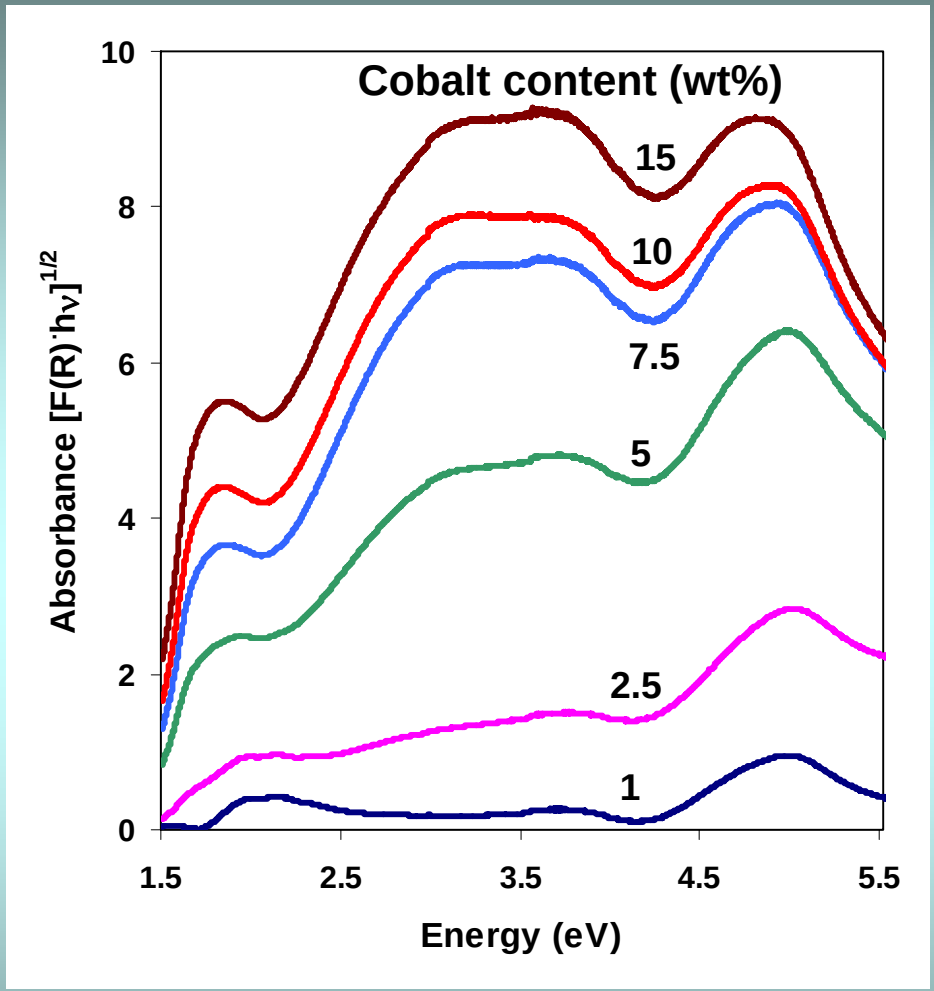

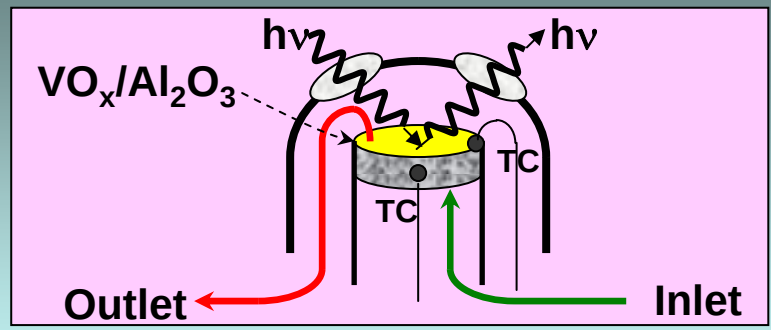

0.035 Rb:Co atom ratio

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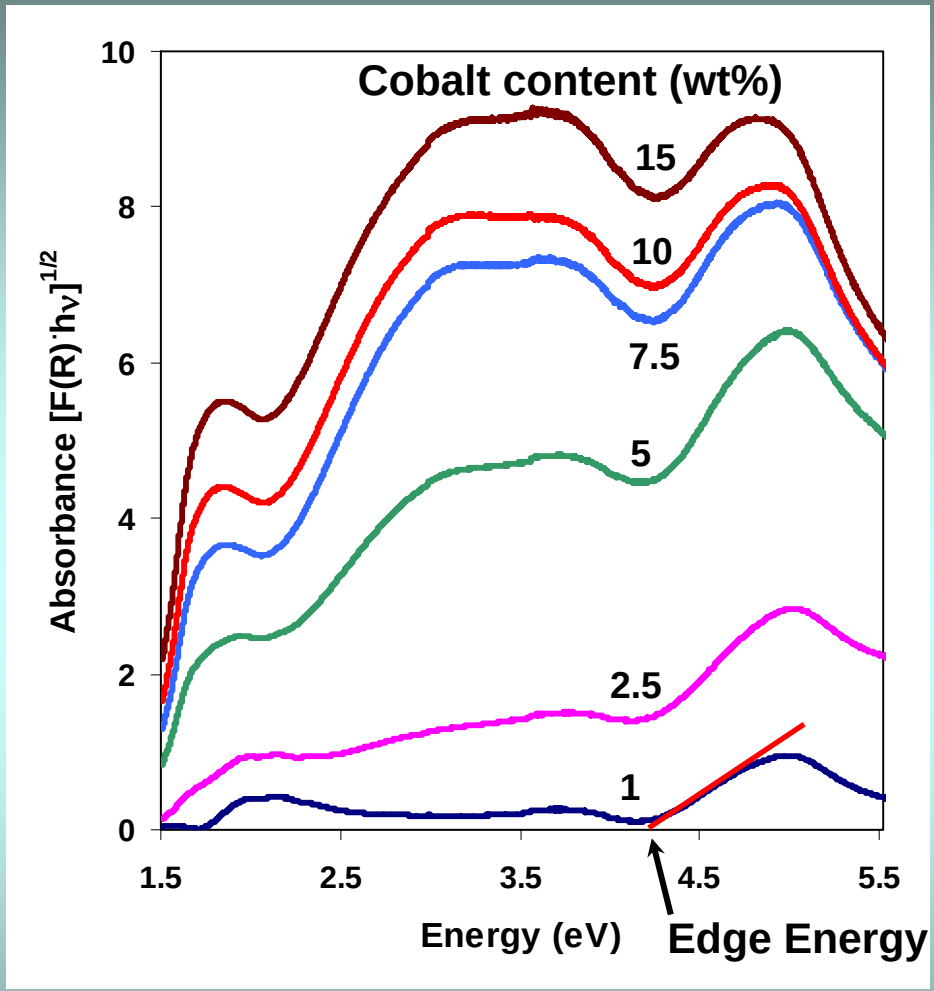

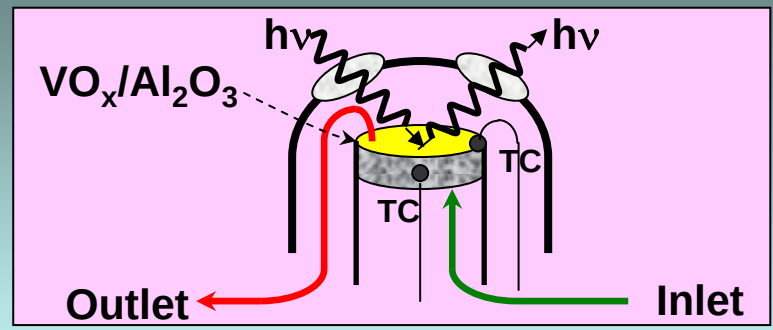

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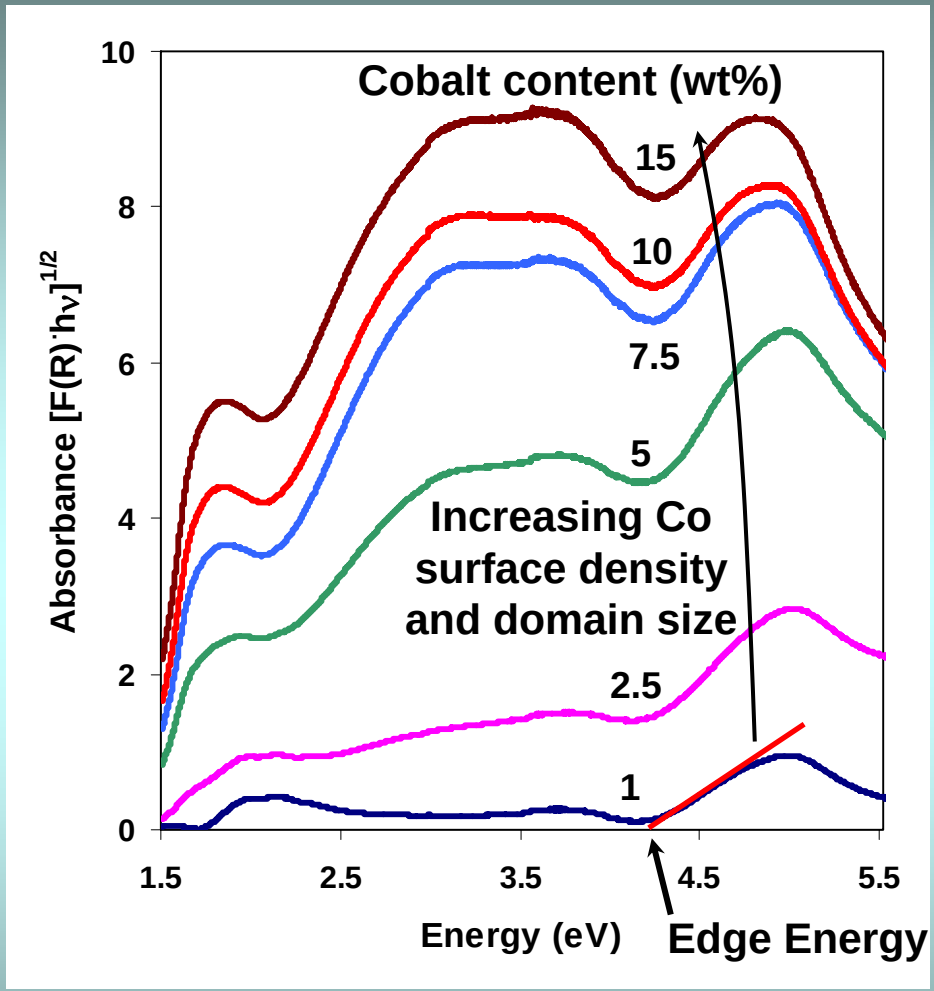

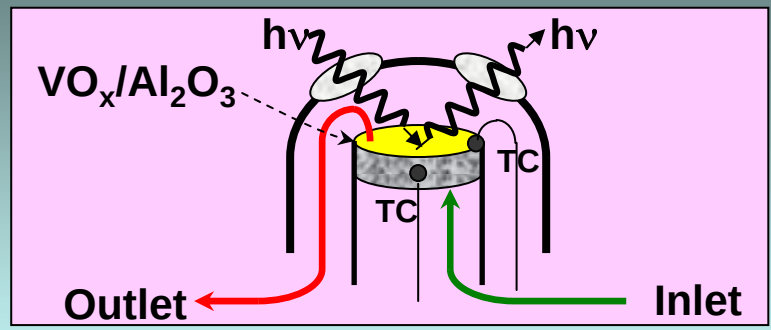

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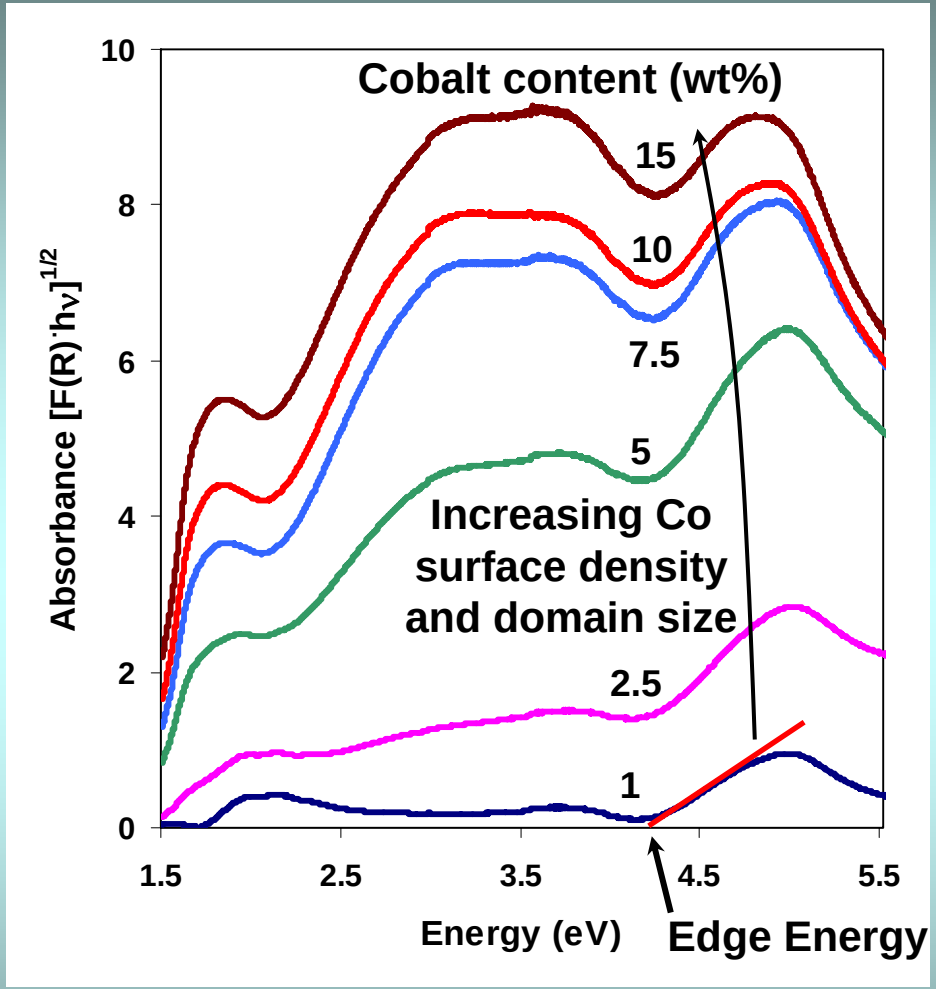

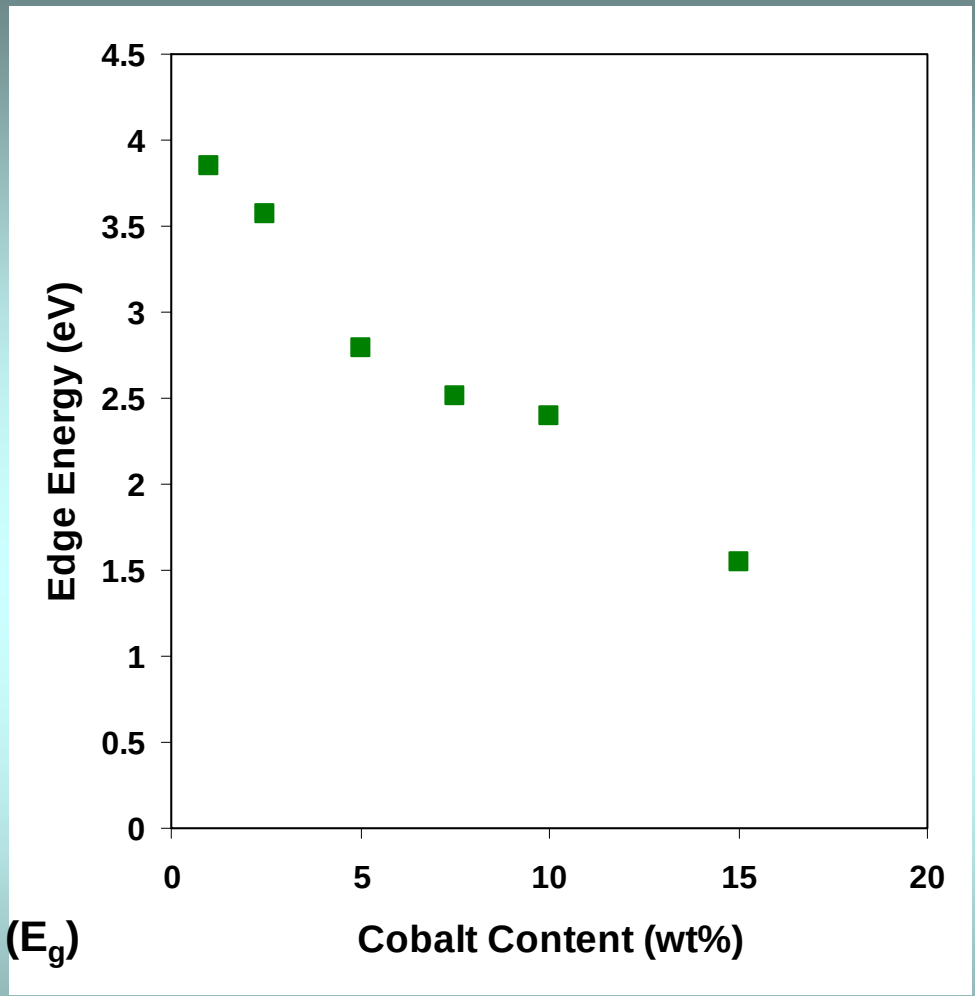

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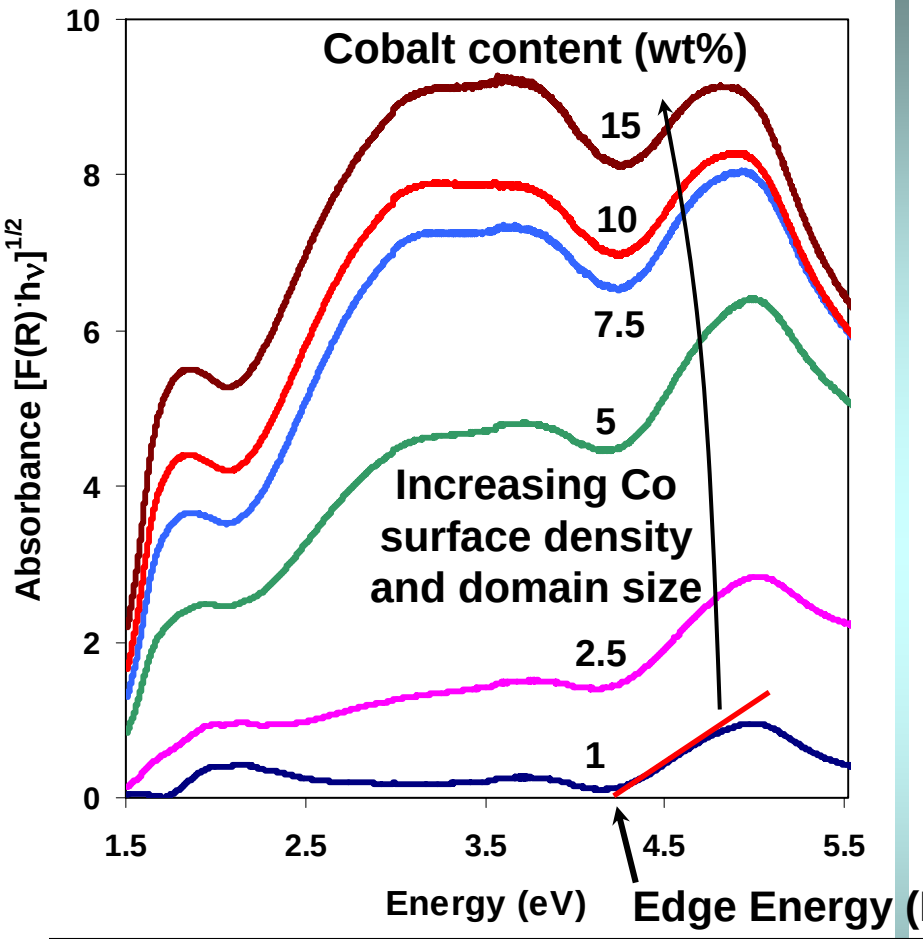

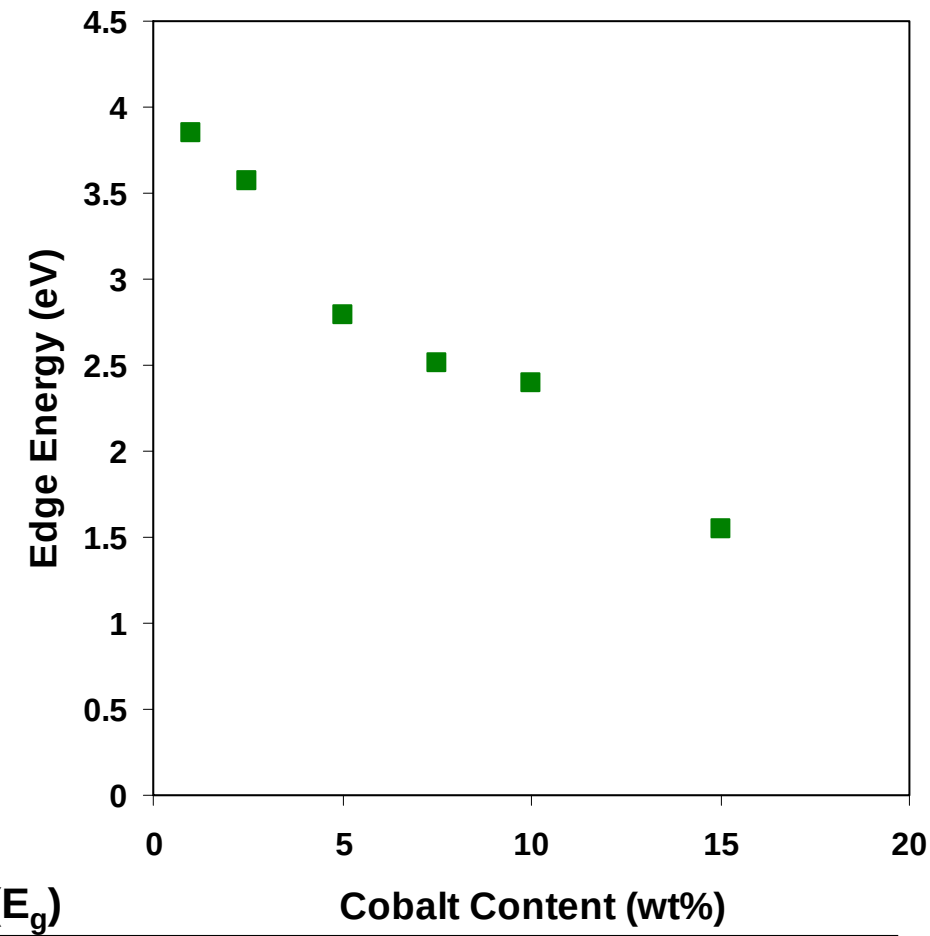

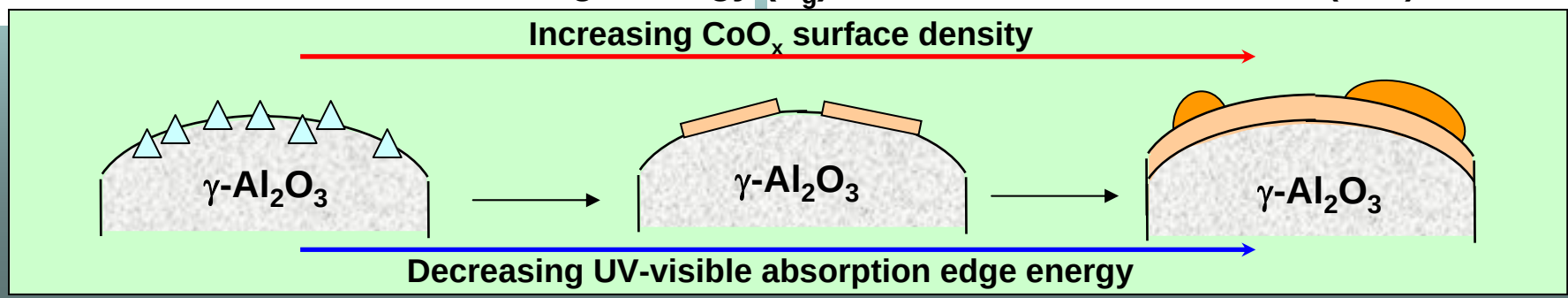

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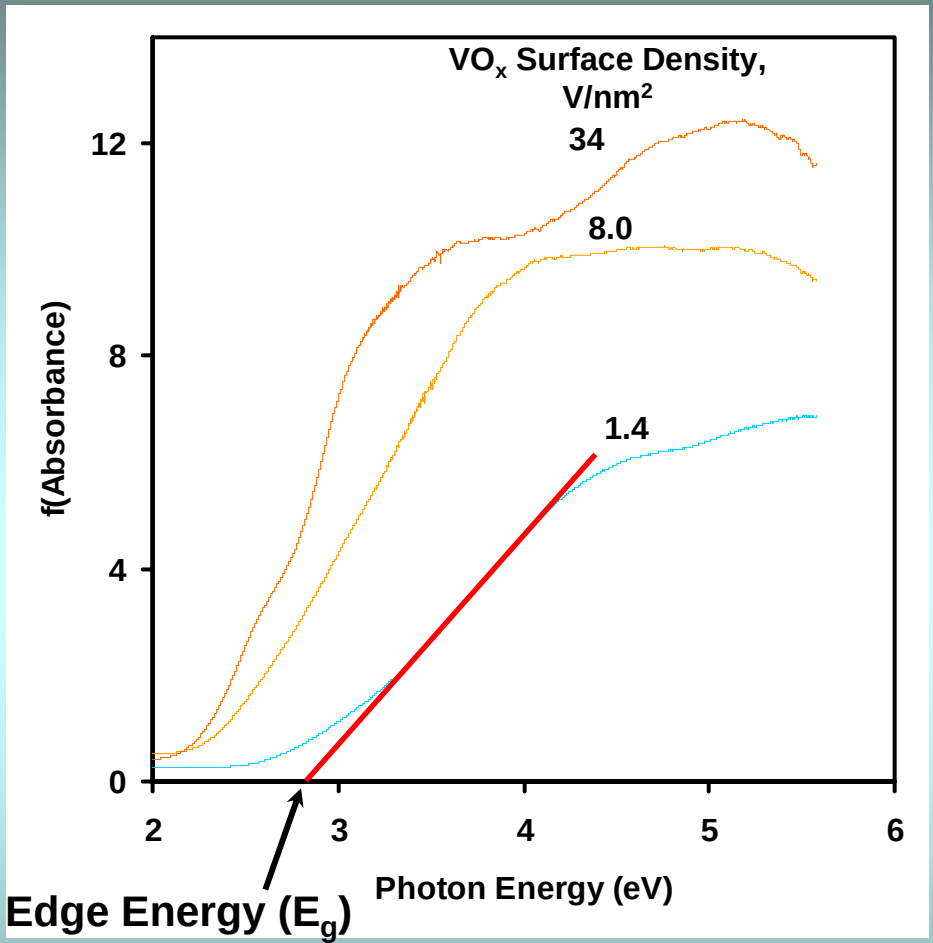

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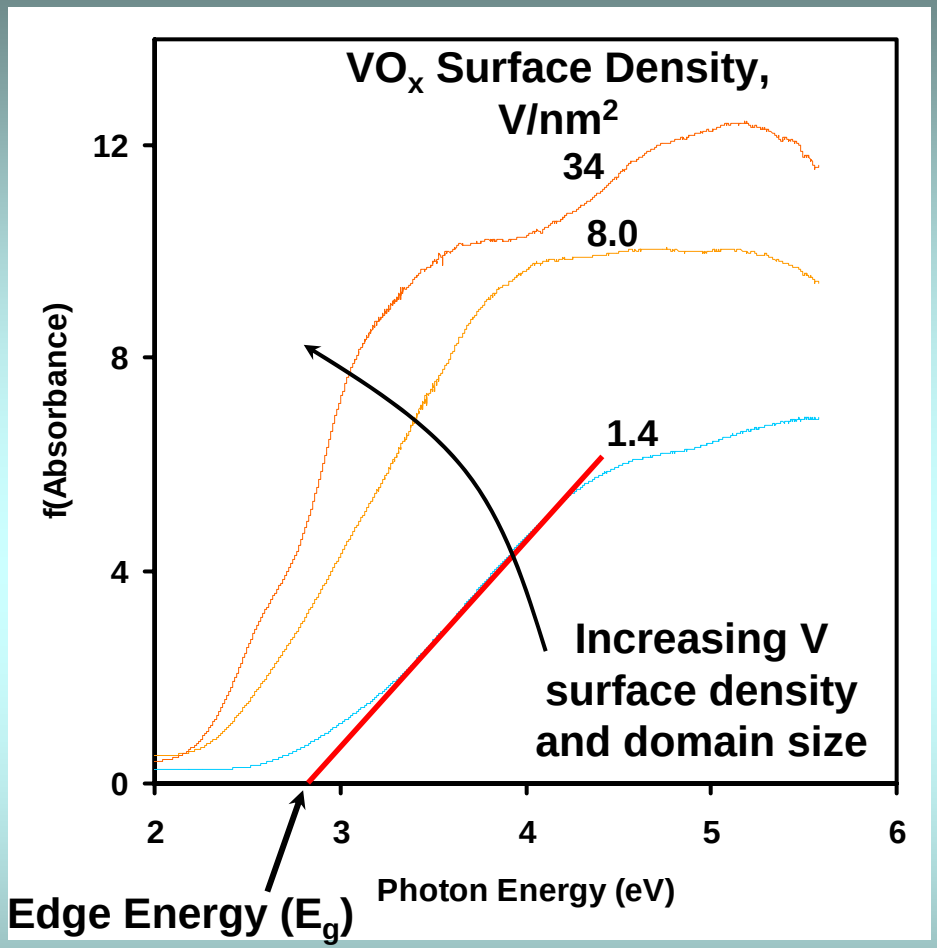

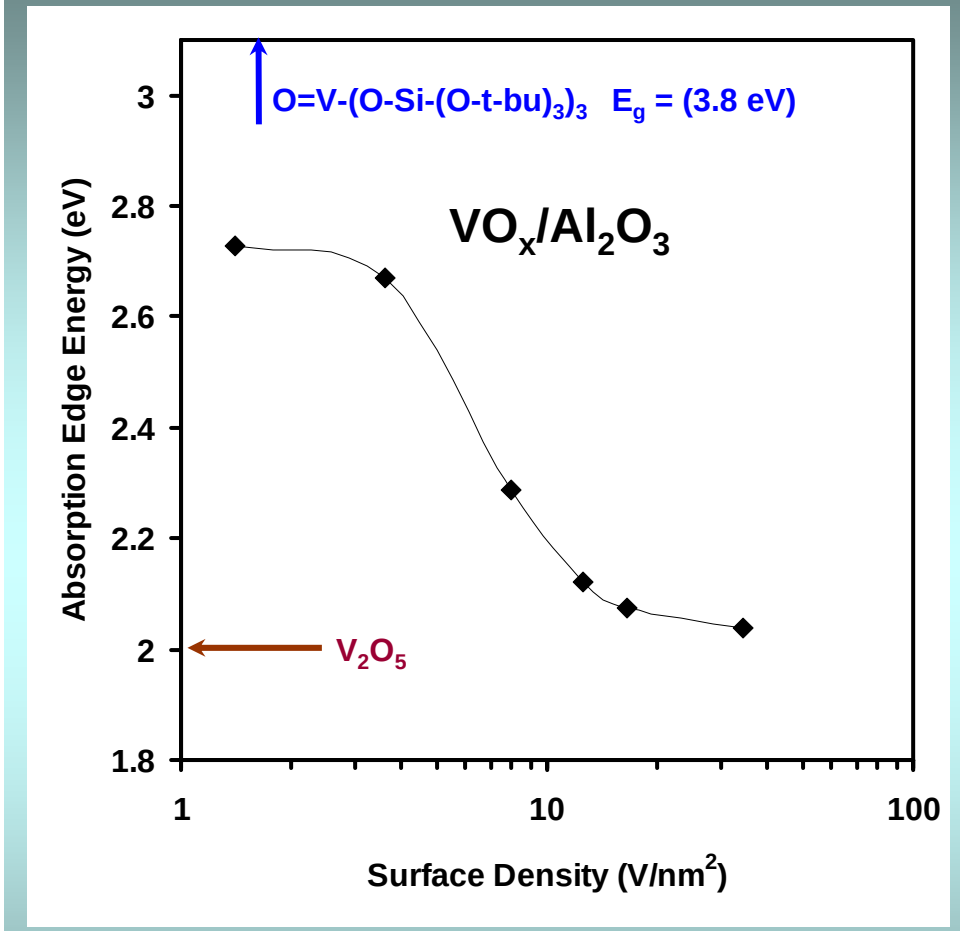

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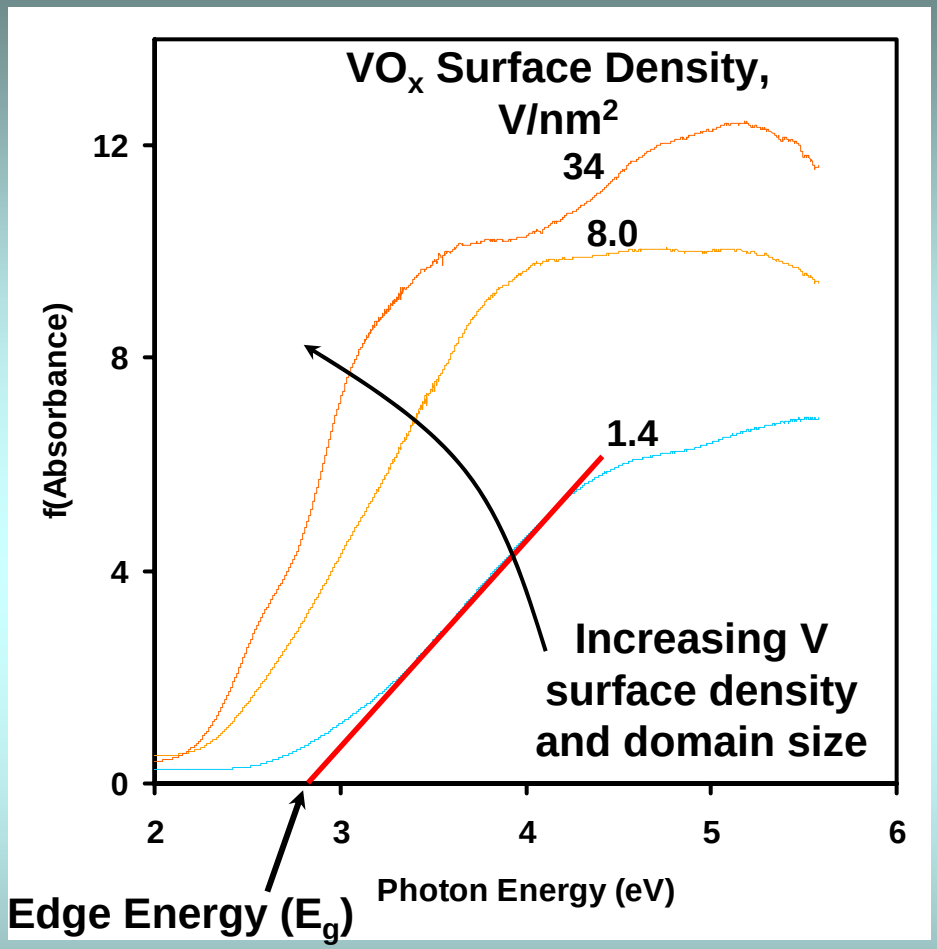
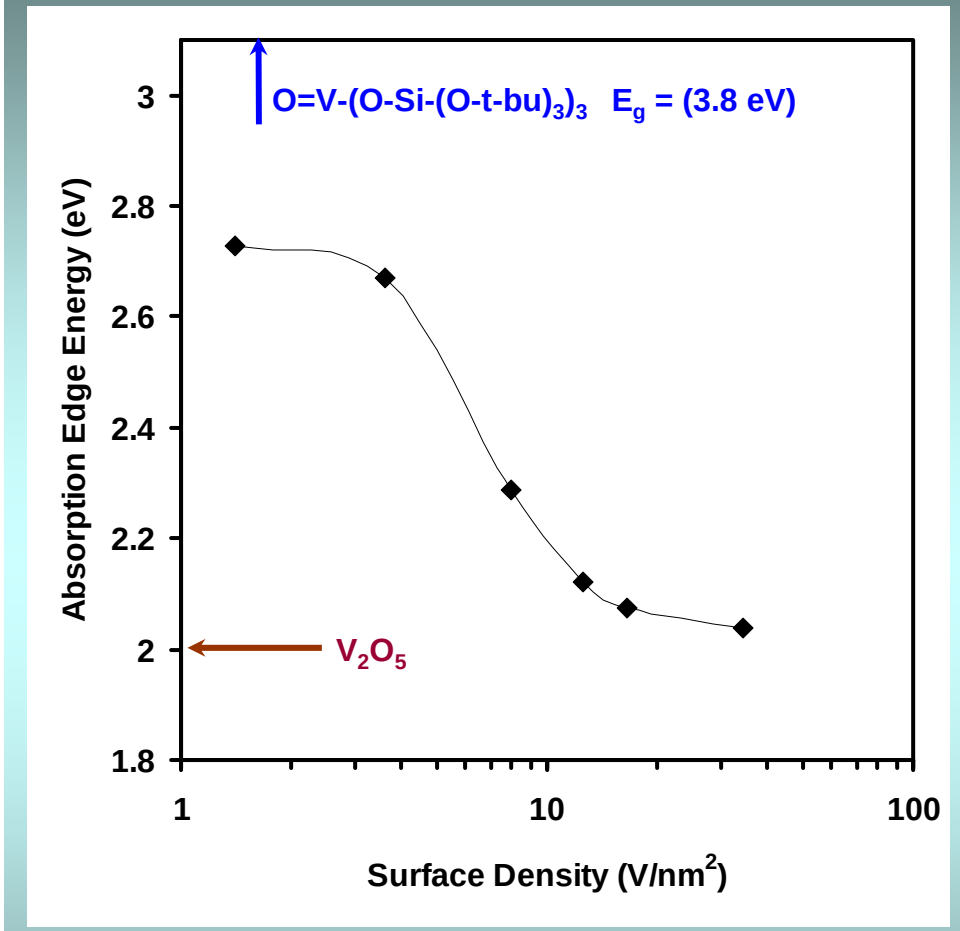
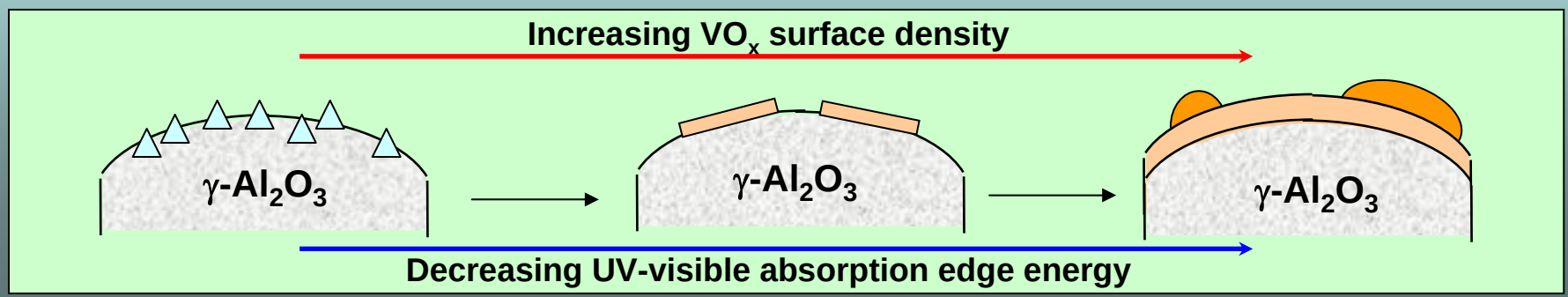
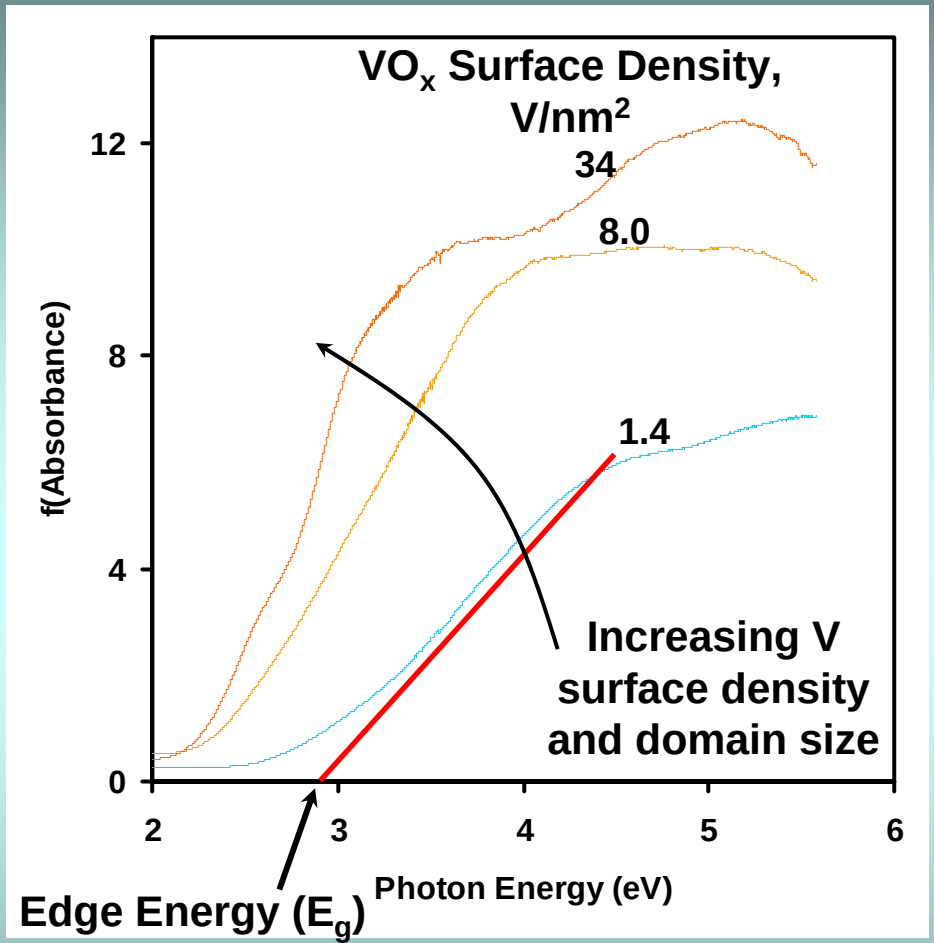
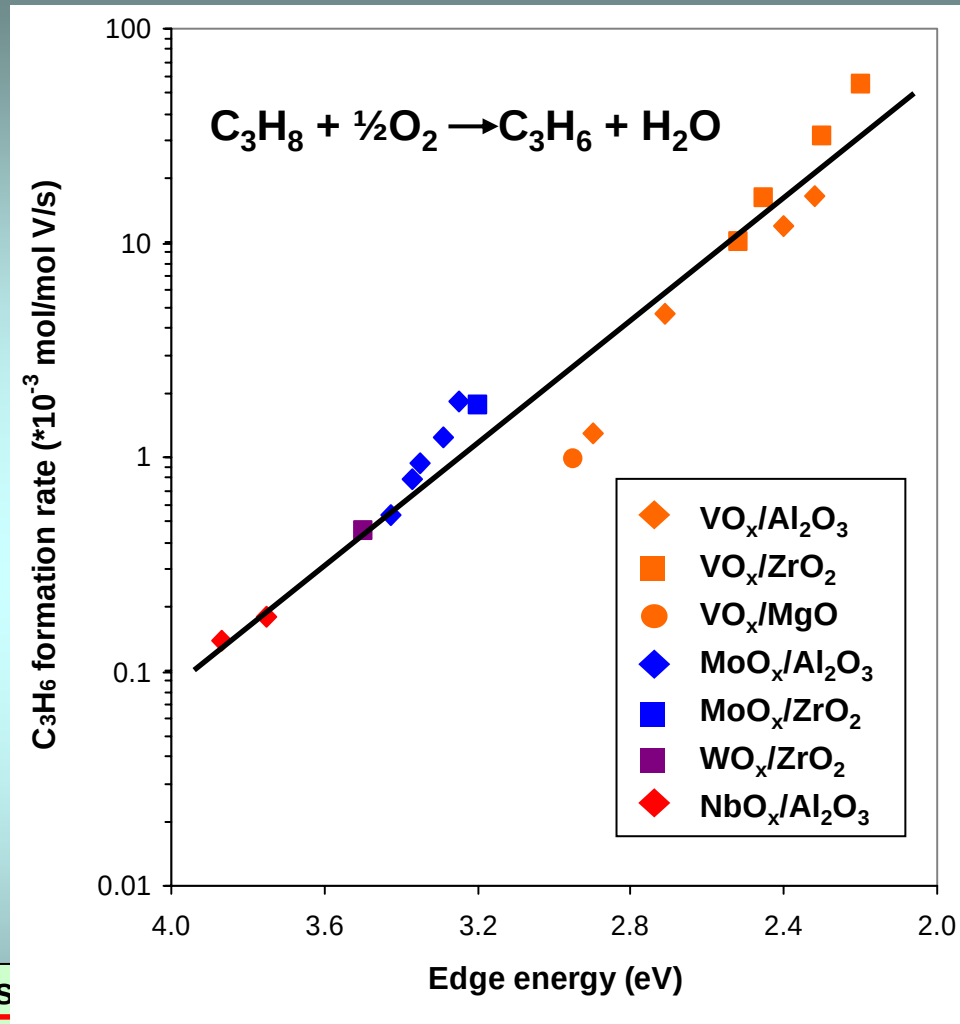


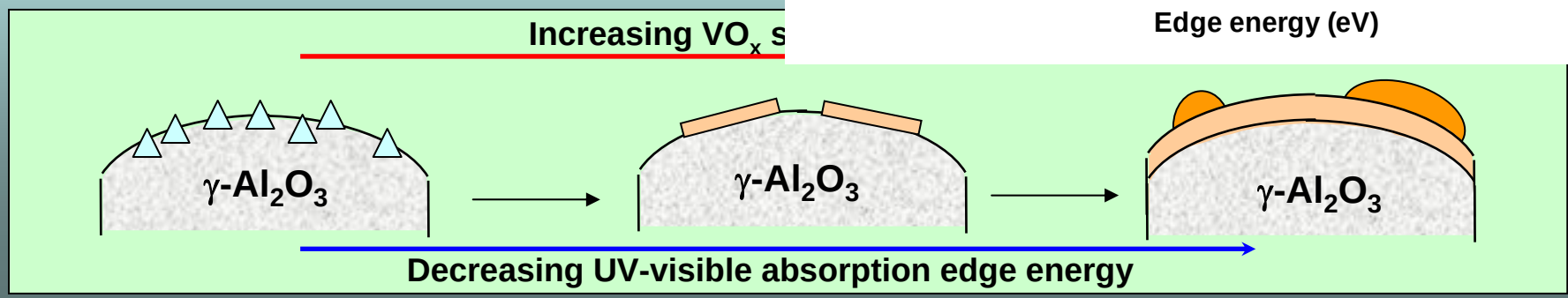




UV-VISIBLE SPECTRA ABSORPTION EDGE ENERGY: Correlates with Propane Oxidative Dehydrogenation Rate







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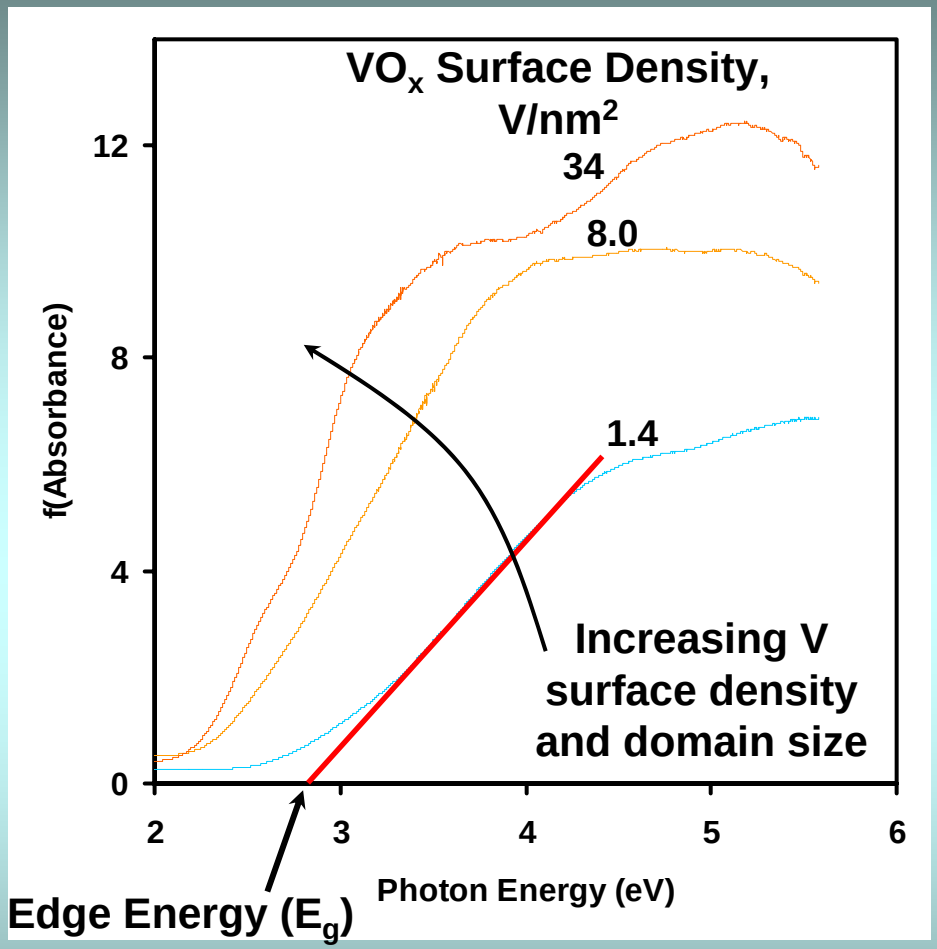
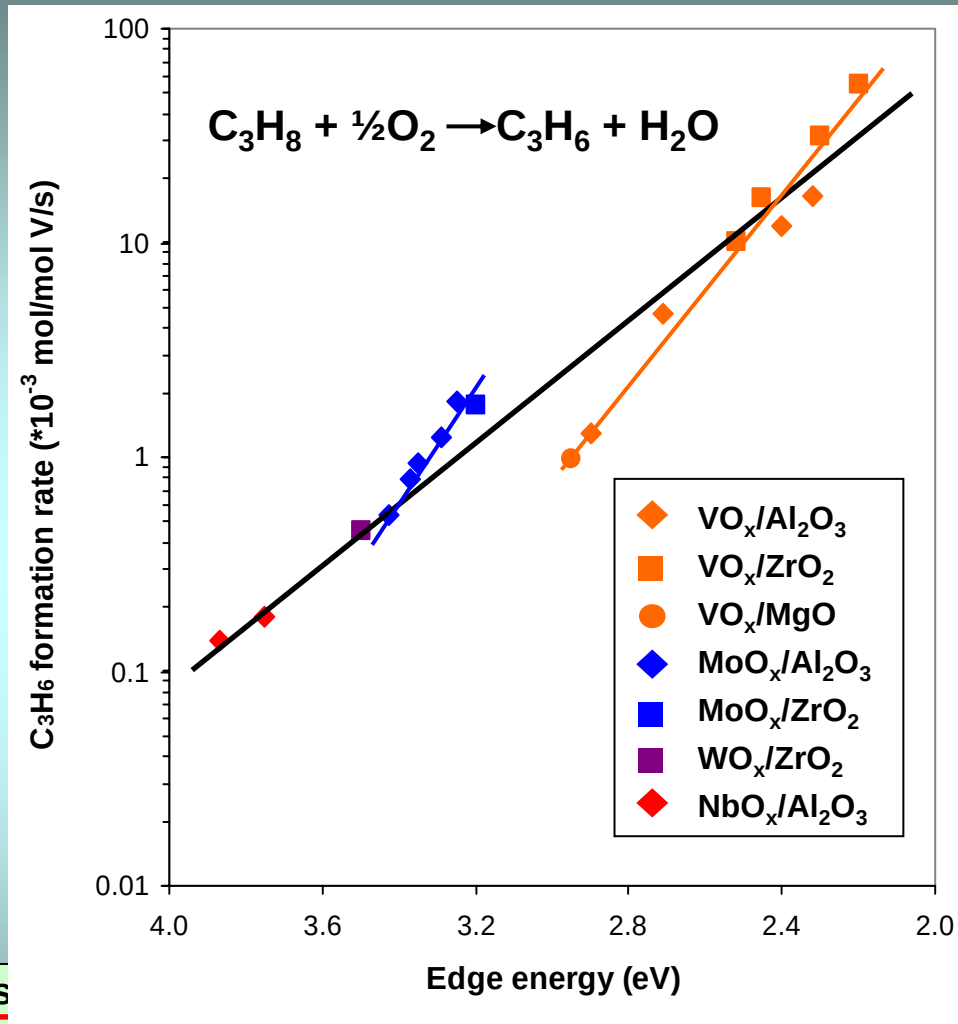
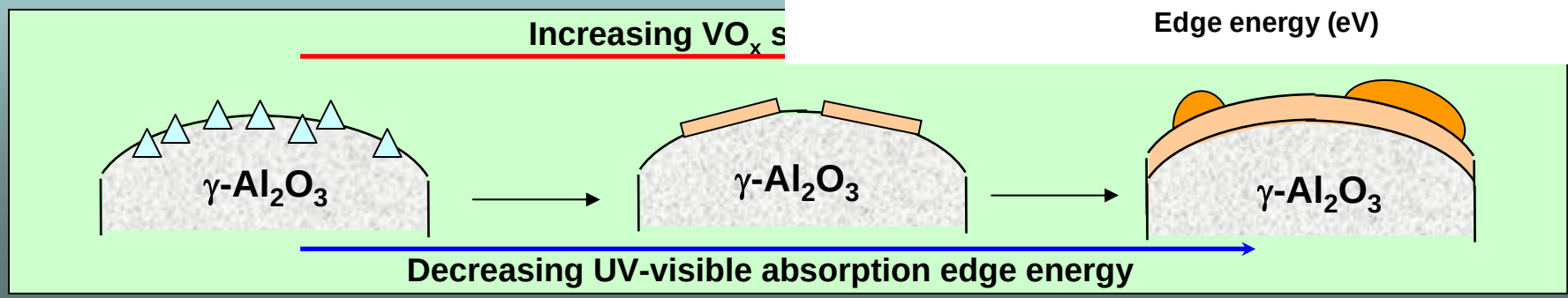
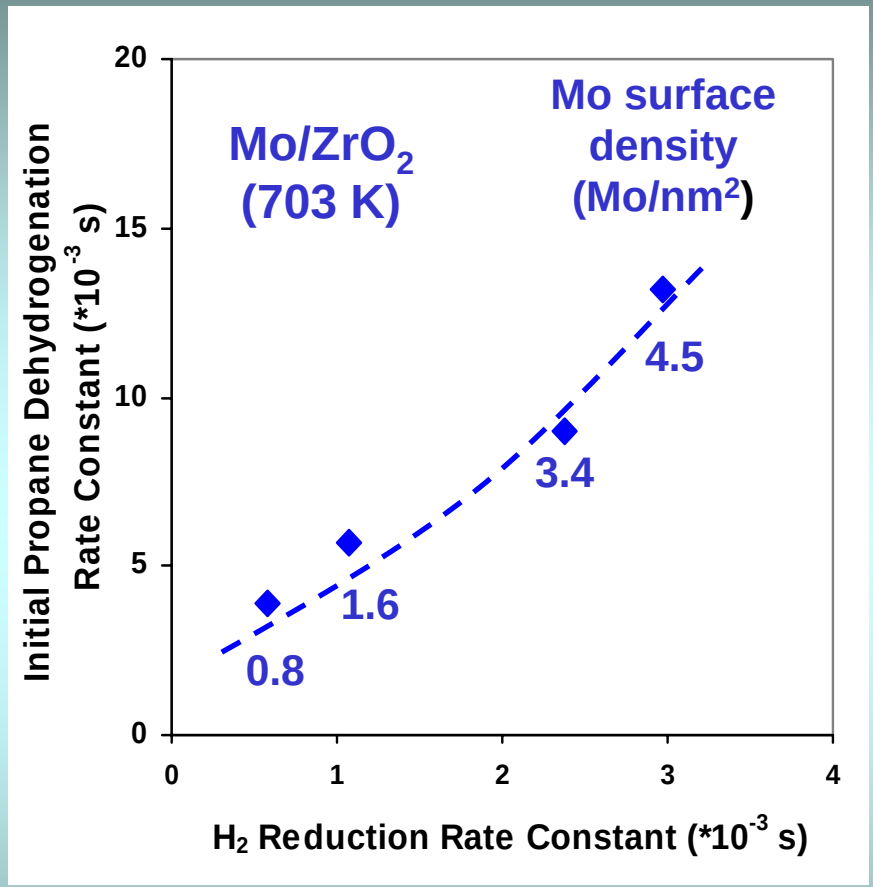
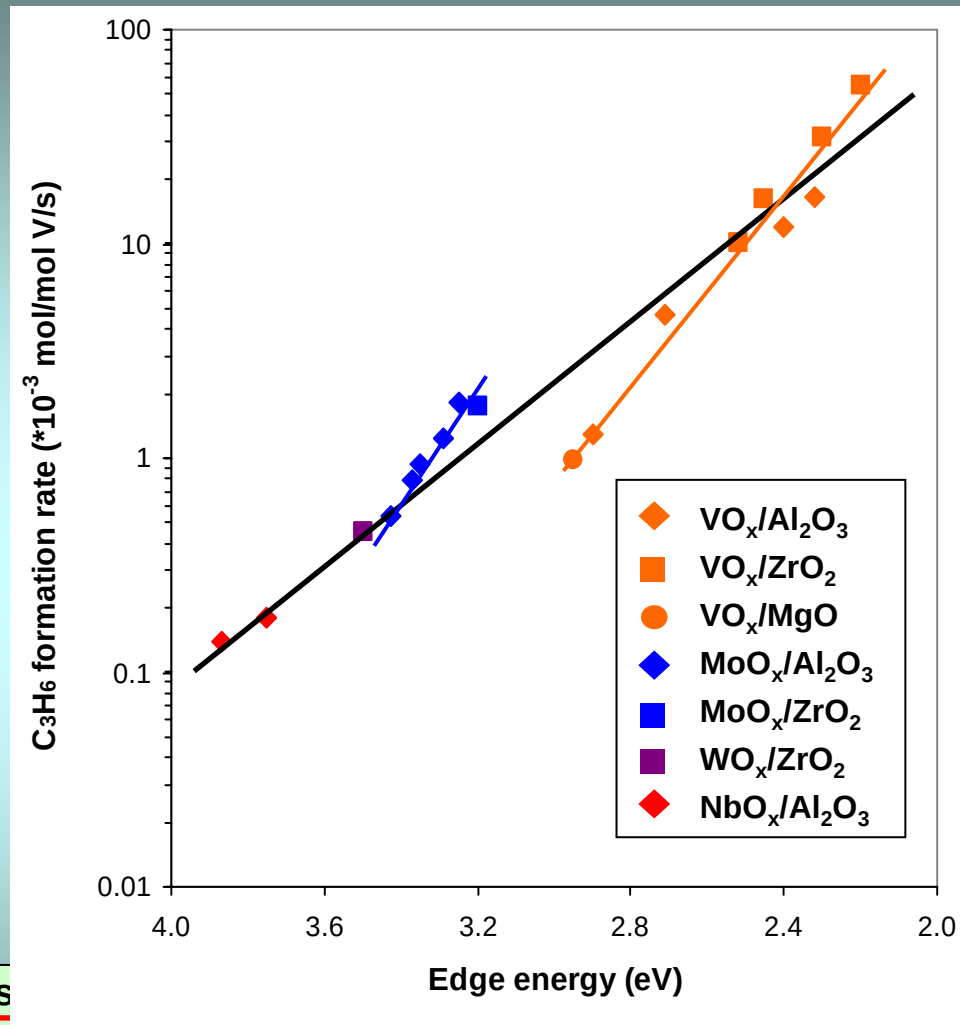


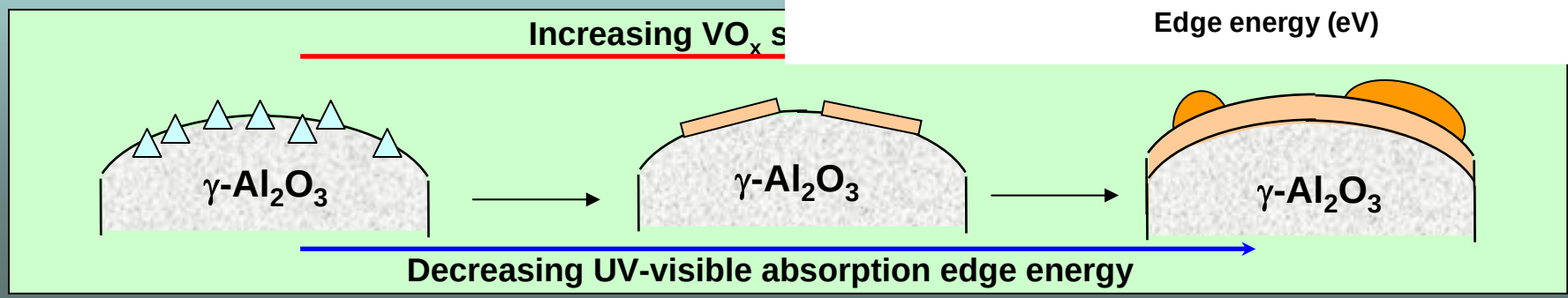




UV-VISIBLE SPECTRA ABSORPTION EDGE ENERGY: Correlates with Propane Oxidative Dehydrogenation Rate and Catalyst Reducibility

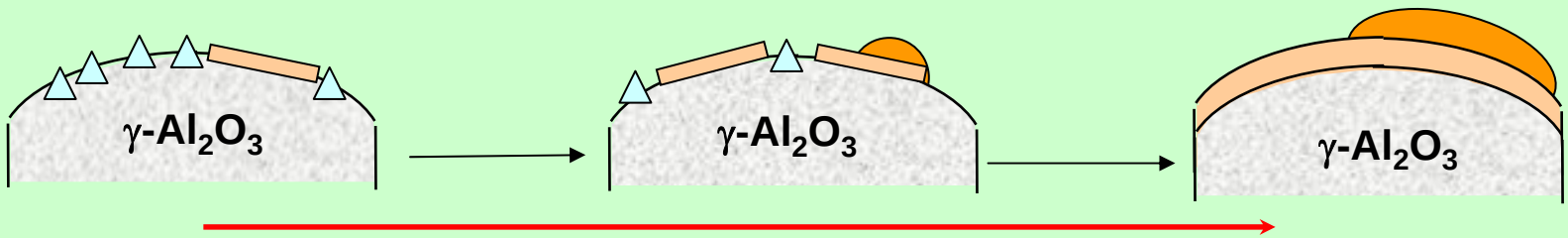






Supported Alkali-Cobalt Oxide Catalysts for NO_x Decomposition: Accomplishments, Summary, and Conclusions

- **Flow microreactor constructed**
- **Series of supported catalysts synthesized**
  - **Appear to be effective NO and NO_2 decomposition catalysts**
  - **Active metal oxide dispersion and mechanistic insight may be accessible through in situ UV-visible studies**



Structural evolution with increasing cobalt surface density and resultant trends:

- **Decreasing UV-visible edge energy**
- **Increasing NO decomposition rate?**

Ongoing Work/Future Work/Questions

- Complete kinetic evaluations
- Complete characterization
  - BET surface area
  - UV-visible spectra
  - Raman spectroscopy
  - Temperature programmed reduction and NO desorption
- In situ UV-vis
- Mechanism determination
- Performance in presence of oxygen and actual flue gas conditions
- Catalyst stability and life

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