Catalytic NDMA Reduction

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US EPA Region IX

1906 – Market from Mason

Outline

- Background
- Research objectives
- Experimental setup
- Results
- Acknowledgements

N-nitrosodimethylamine

Occurrence

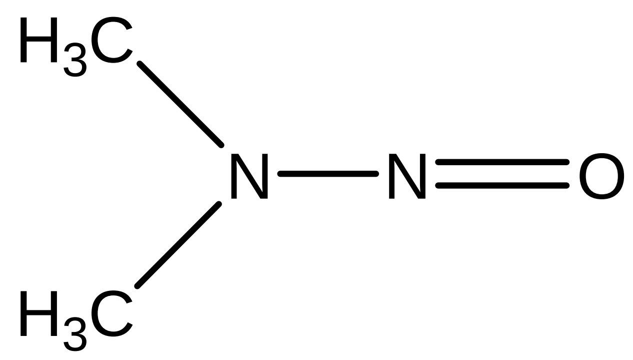
- 1,1-dimethylhydrazine
- Chloramination

Risk

- Liver cancer, neurological damage

10^{-6} risk level 0.7 ng L^{-1}

More potent than THMs



NDMA

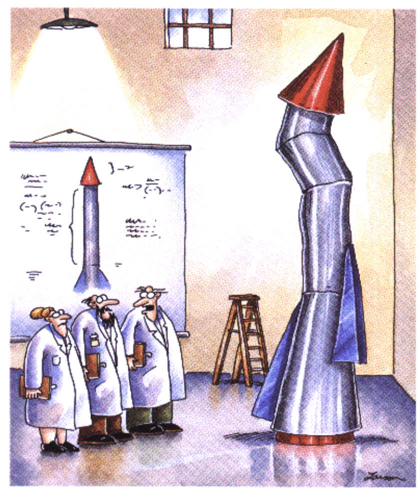
NDMA exposure

Traditional

Dietary

- Beer
- Nitrate-cured meats
- Tobacco smoke

Emerging



"It's time we face reality, my friends. … We're not exactly rocket scientists."

Water contaminant

- 1,1-dimethylhydrazine
- Chloramination

Occurrence

Sacramento (1998)

- 400 µg L^{-1} onsite
- 20 µg L^{-1} nearby

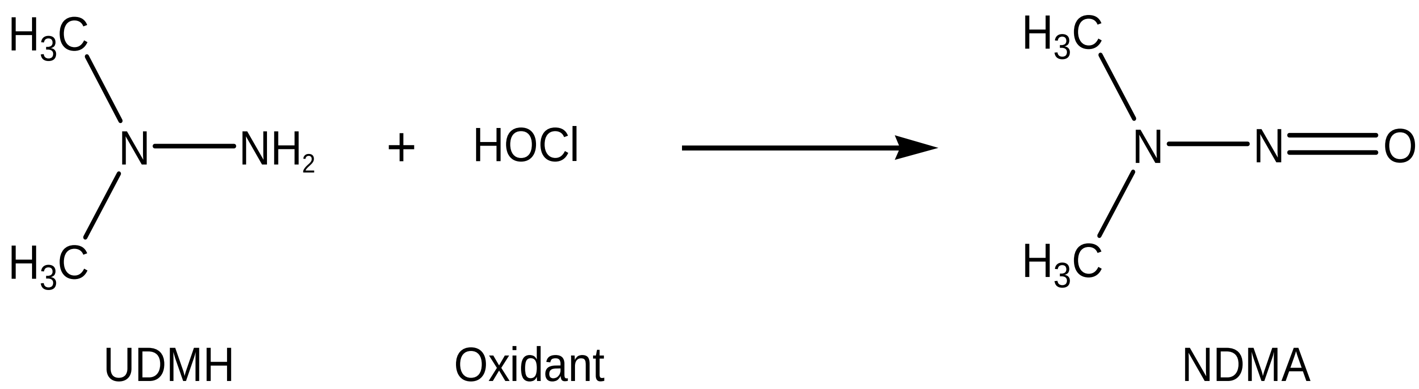
EPA cleanup level 0.7 ng L^{-1} (10^{-6} risk)

Drinking and waste water DBP

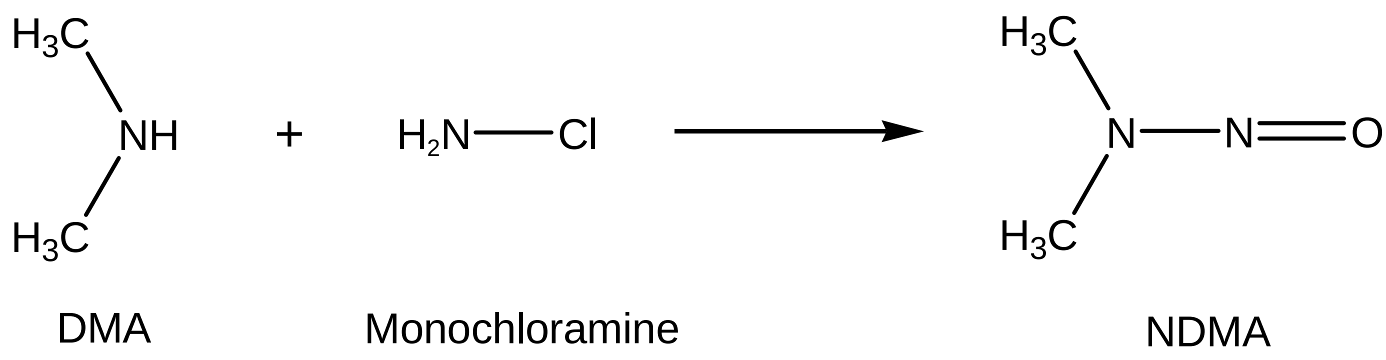
- >10 ng L^{-1}

Formation

Oxidation of 1,1-dimethylhydrazine



Chloramination of drinking and waste water



Remediation technologies

Physical/chemical **INEFFECTIVE**

- GAC, air stripping, O_3, RO
  - $H_{cc} = 2.63 \times 10^{-4}$
  - $K_{ow} = 10^{-0.57}$

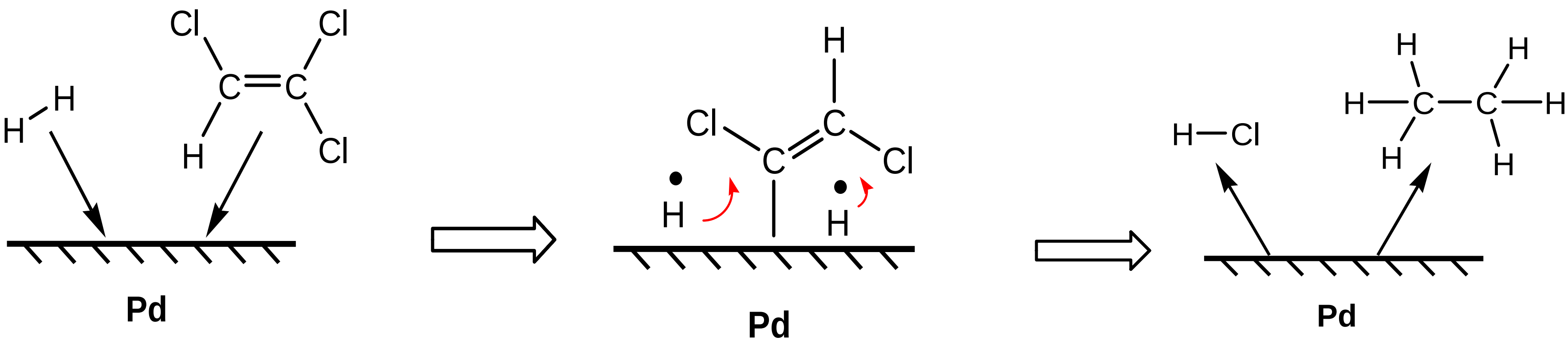
Biological **VERY SLOW**

- Half-life 12-55 d

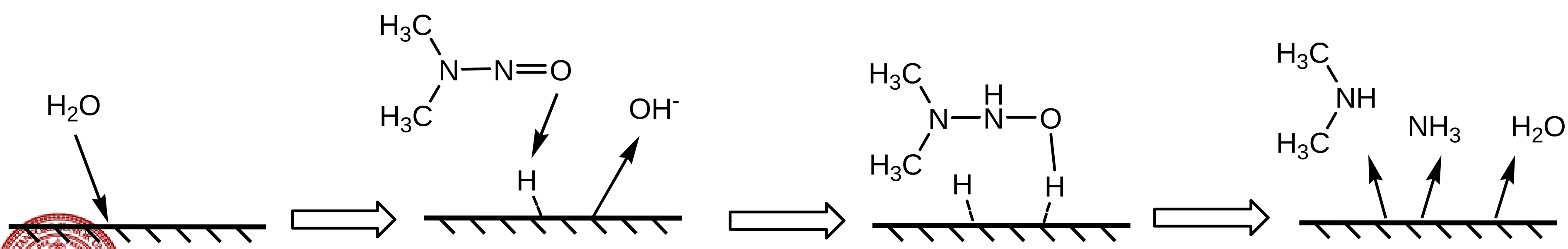
UV most prevalent

Reductive catalysis

Chlorinated species (e.g. TCE)



NDMA with Fe(0) and Fe-Ni



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Motivation and goals

Need efficient NDMA removal technology

(1) Screen potential catalysts

(2) Intermediate/product distribution

(3) Explore effect of secondary metal addition

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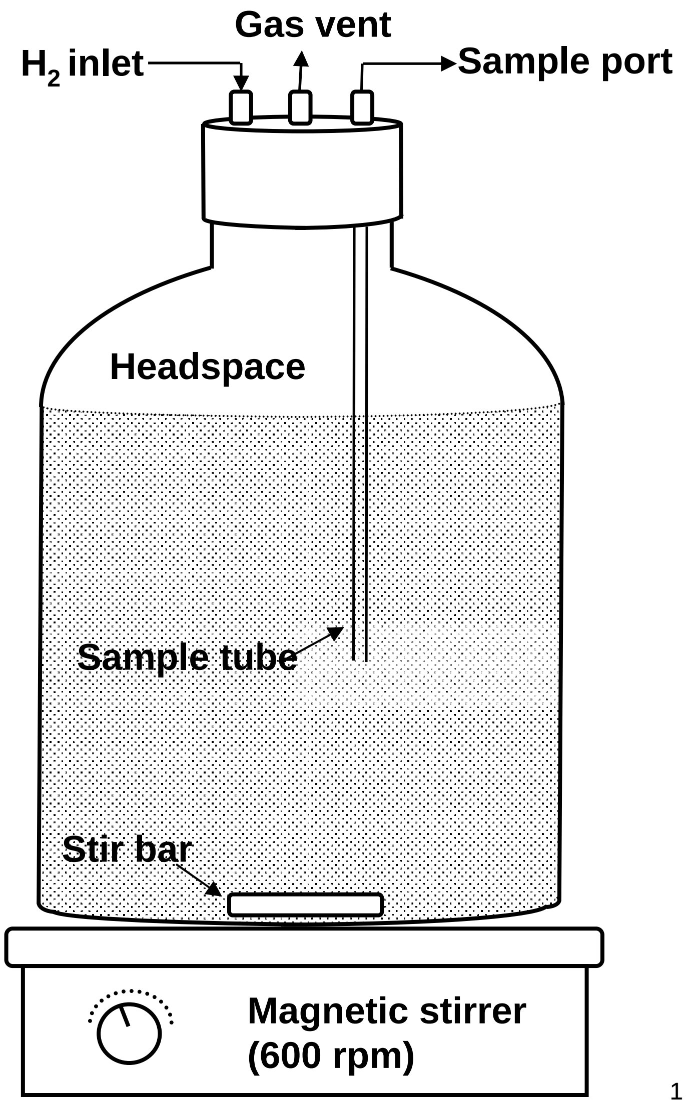
Batch reactor

Setup reactor
- Mass catalyst
- Add water

Equilibration
- 90 min
- 23˚C

Sampling
- 0.22 µm syringe filter
- 4˚C storage



Analysis

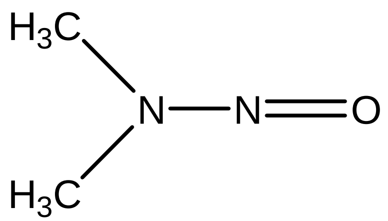
LC-MS/MS

Lopez-Mesas et al.

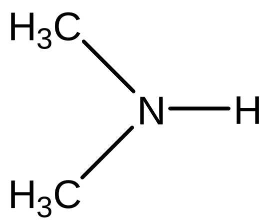
NDMA-d_6 as I.S.

0.5 µg L^{-1} detection

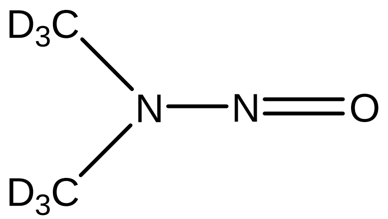
(a) NDMA



(b) DMA



(c) NDMA-d_6



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Task #1

Catalyst screening

Which catalysts are most effective for NDMA reduction?

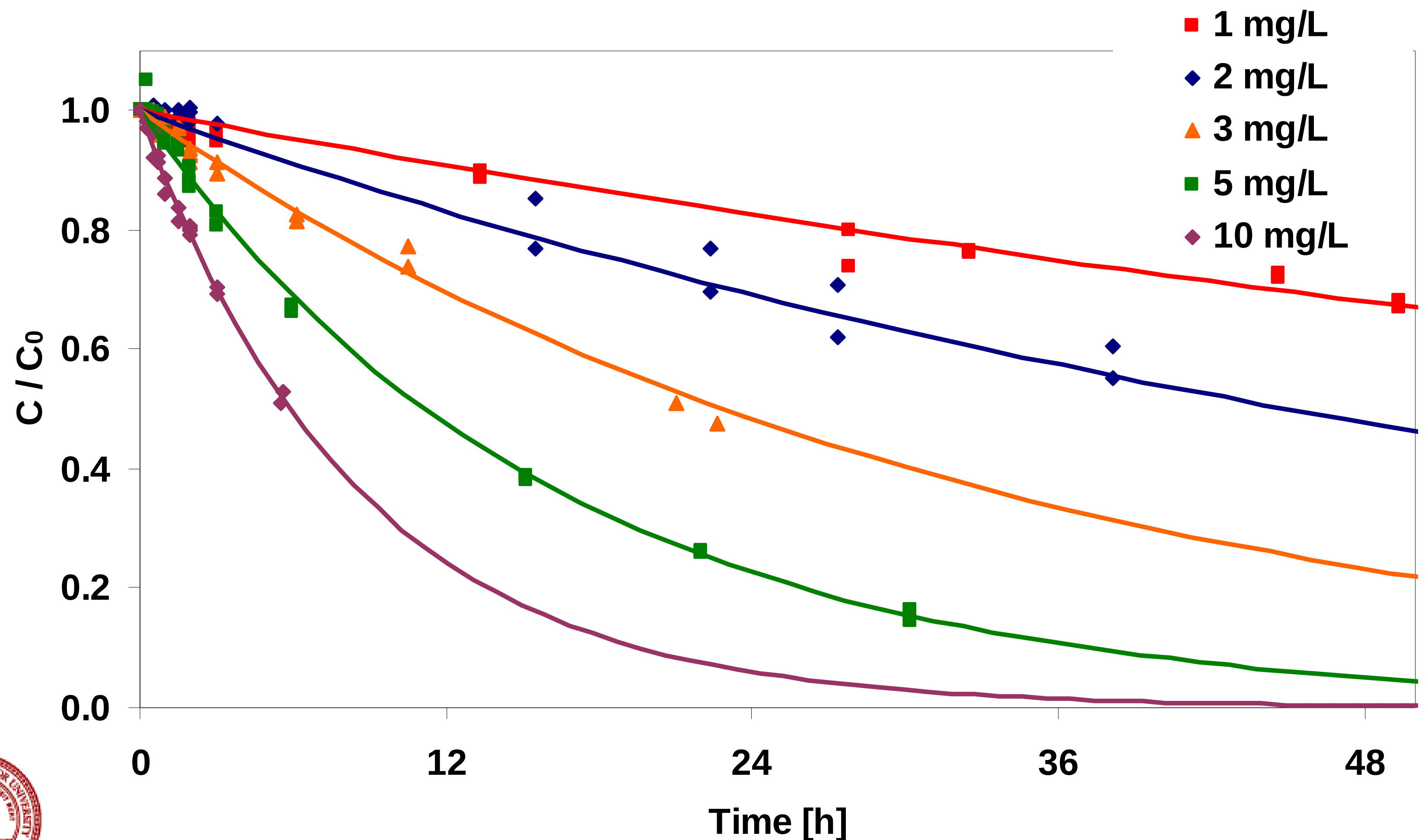
Catalysts screened

Powdered catalysts

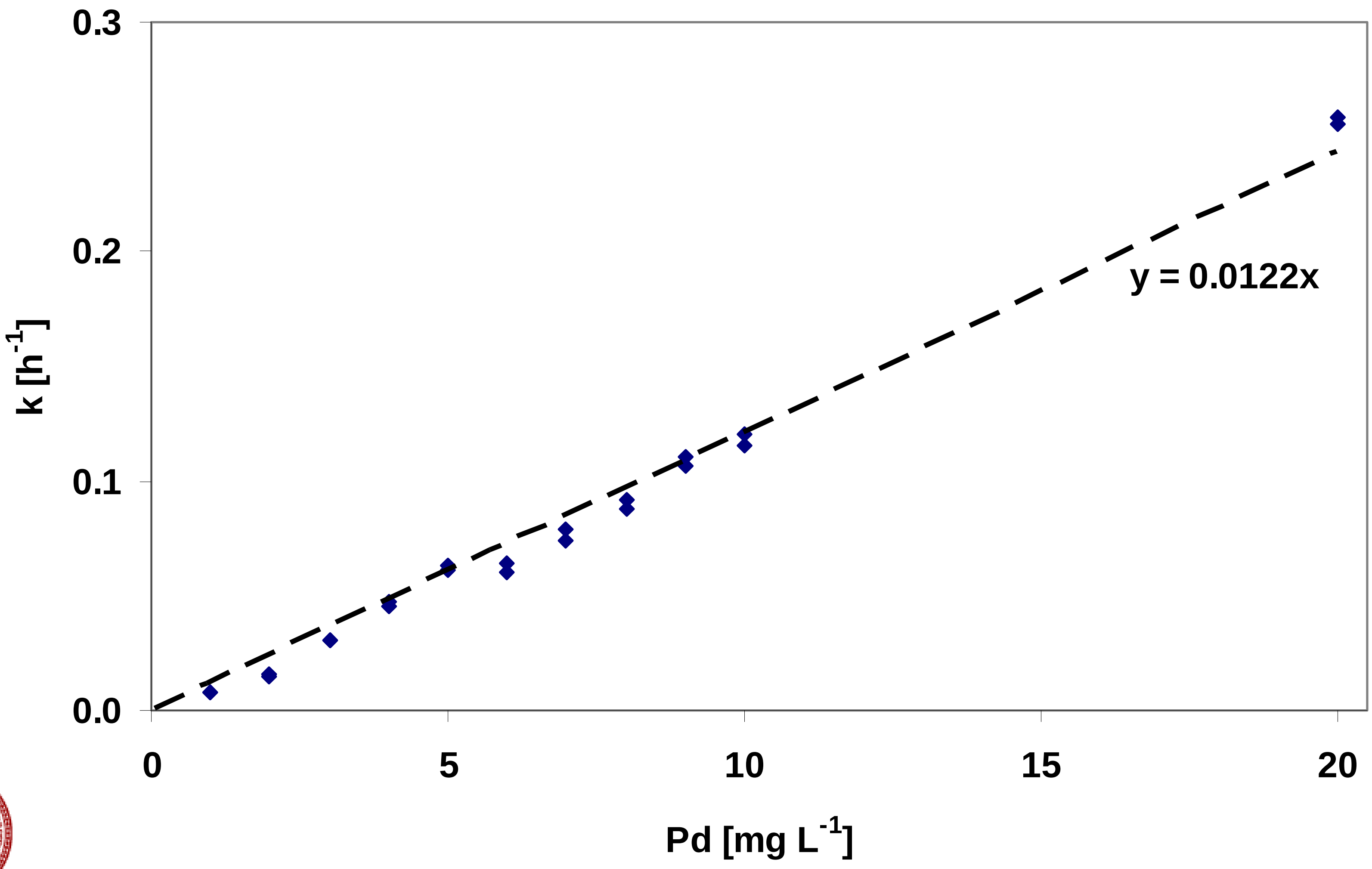
Fe	(99+%)
Fe-Ni	(42% Ni)
Pd on γ-Al_2O_3	(1% Pd)
Pd-Cu on γ-Al_2O_3	(1% Pd, 0.3% Cu)
Ni(99+%)	

H_2 as e^- donor (except Fe catalysts)

1% Pd on γ-Al_2O_3



1% Pd on γ-Al_2O_3



Observed second-order rates

Catalyst	Second-order rate [a] $[L\ g_{Me}^{-1}\ h^{-1}]$	Half-life [b] [h]
Pd	11.5 ± 0.9	6.0 ± 0.4
Pd-Cu	66.5 ± 7.4	1.0 ± 0.1
Ni	8.3 ± 2.9	8.4 ± 2.2
Fe	0.13 ± 0.09	533 ± 218
Fe-Ni	0.65 ± 0.01	107 ± 2
Mn	0.07 ± 0.02	990 ± 220
Cu	0	-
γ-Al_2O_3	0	-

[a] Pseudo first-order rates are normalized by active metal content (n > 8).

[b] Calculated half-lives assuming 10 $mg_{Me}\ L^{-1}$ active metal.

Promising catalysts

Pd $t_{1/2} = 6.0$ h

Well-studied

Pd-Cu $t_{1/2} = 1.0$ h

Kinetics

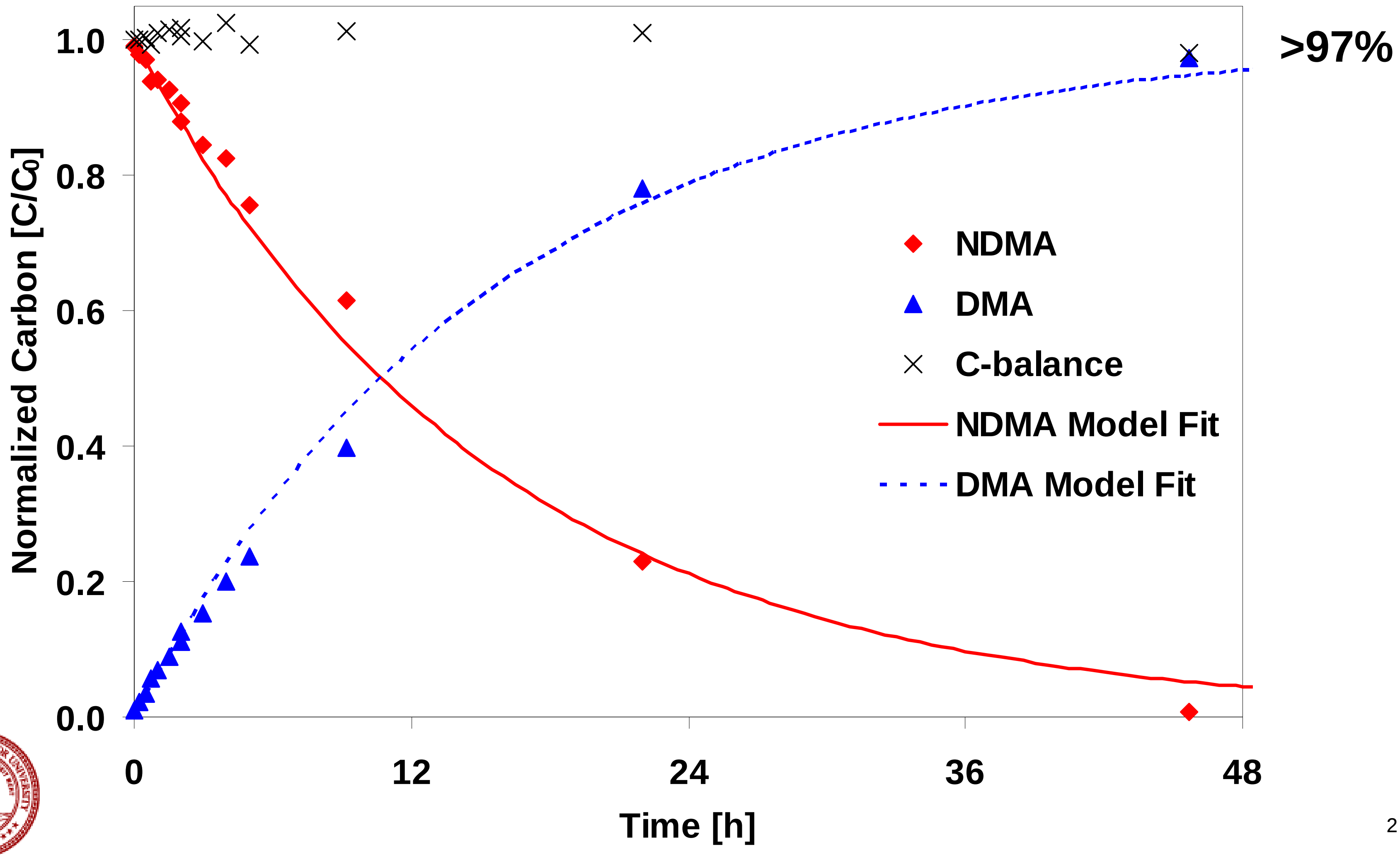
Copper regeneration?

Task #2

Reaction intermediates and products

- Pd
- Pd-Cu

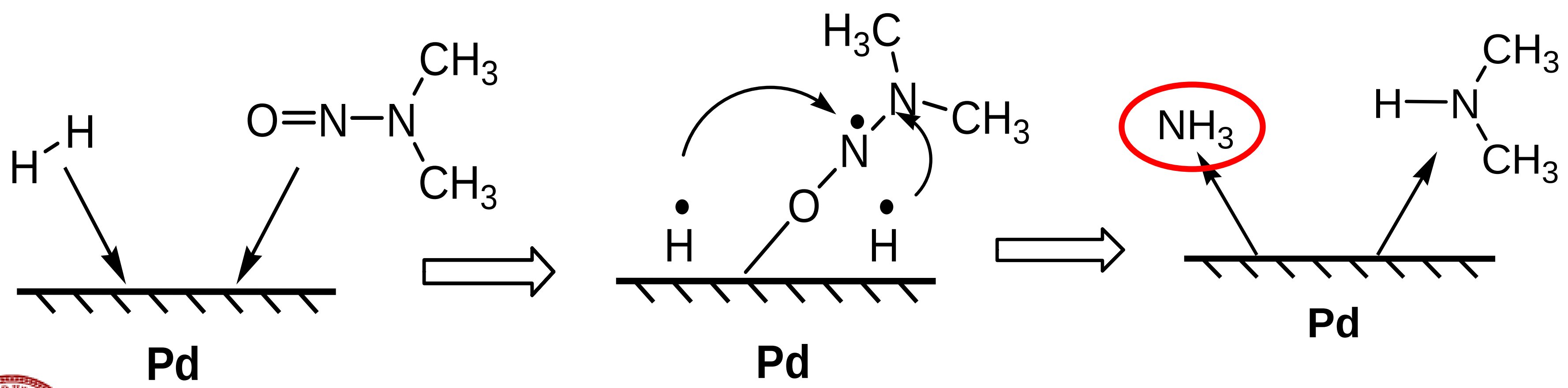
1% Pd on γ-Al_2O_3



Reaction mechanism

No intermediates observed

- Surface-adsorbed reduction
- NH_3 not detected



Find nitroso product

NH_3

- Acid trap (need pH >10)
- Headspace sampling

Other products

- IC analysis (NO_3^-,NO_2^-)

C-balance > 97%

Task #3

Effect of secondary metal addition

Cu-enhanced Pd

Cu-enhanced Pd

Cu alone

- No NDMA disappearance

Pd-Cu

- 6x better than Pd alone

Does Cu rapidly activate NDMA?

Bimetallic catalysis

Pd-Cu for nitrate reduction

Pd $NO_2^- \rightarrow N_2 + NH_3$

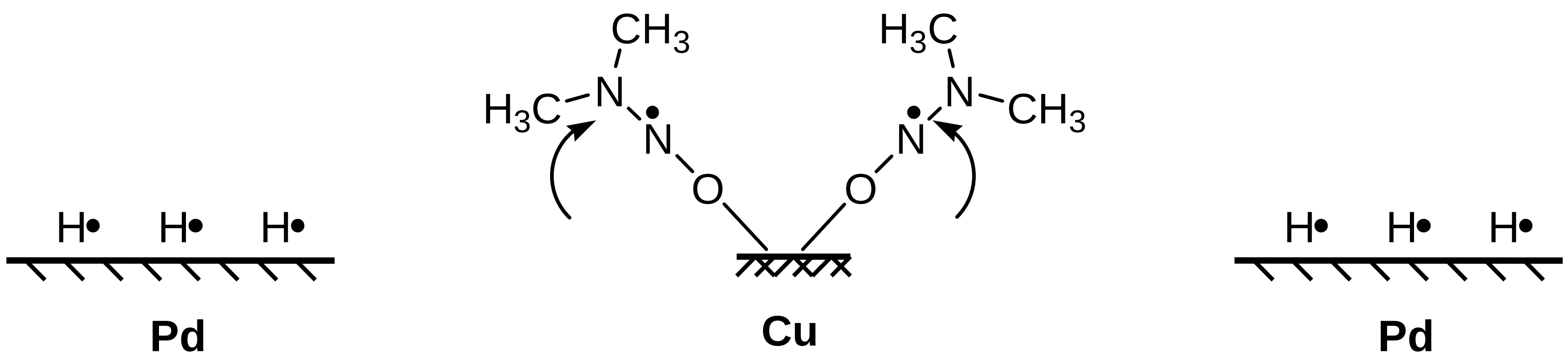
Cu $NO_3^- \rightarrow NO_2^-$

Pd cannot make single e^- transfer

Proposed mechanism

Recall second-order rates

Pd	11.5 L g_{Pd}^{-1} h^{-1}
Pd-Cu	66.5 L g_{Pd}^{-1} h^{-1}



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Collaboration

Martin Reinhard	(Stanford)
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Questions?