Catalytic NDMA Reduction

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1906 – Market from Mason





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 exposure

Traditional



Dietary Beer Nitrate-cured meats Tobacco smoke



Water contaminant 1,1-dimethylhydrazine Chloramination

Emerging





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





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





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Catalyst screening

Which catalysts are most effective for NDMA reduction?



Catalysts screened

Powdered catalysts

Fe(99+%)Fe-Ni(42% Ni)Pd on γ -Al₂O₃(1% Pd)Pd-Cu on γ -Al₂O₃(1% Pd, 0.3% Cu)Ni(99+%)

H₂ as e⁻ donor (except Fe catalysts)



1% Pd on γ -Al₂O₃



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1% Pd on γ -Al₂O₃



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Observed second-order rates

Catalyst	Second-order rate ^a	Half-life ^b
	[L g _{Me} ⁻¹ h ⁻¹]	[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 ₂ O ₃	0	-

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

Calculated half-lives assuming 10 mg_{Me} L⁻¹ active metal.

Promising catalysts

Pd Well-studied

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

Pd-Cu

Kinetics Copper regeneration? $t_{1/2} = 1.0 h$





Reaction intermediates and products Pd Pd-Cu



1% Pd on γ -Al₂O₃



Reaction mechanism

No intermediates observed Surface-adsorbed reduction NH₃ not detected





Find nitroso product

NH₃ Acid trap (need pH >10) Headspace sampling

Other products IC analysis (NO₃⁻,NO₂⁻)

C-balance > 97%





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





H• H•

Pd

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Questions?



