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Metal-Catalyzed Reduction of *N*-Nitrosodimethylamine with Hydrogen in Water[†]

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There is considerable need for the rapid destruction of *N*-nitrosodimethylamine (NDMA) in water because current alternative treatment methods are relatively inefficient. Powdered metal catalysts in conjunction with hydrogen gas showed notable potential for rapid destruction of *N*-nitrosodimethylamine (NDMA) in water. Palladium, copper-enhanced palladium, and nickel catalysts showed significant efficacy for NDMA reduction, with observed half-lives on the order of hours using 10 mg L⁻¹ catalyst metal. Other catalysts were screened because of their well-documented efficacy for reduction of halogenated hydrocarbons, including zerovalent iron, nickel-enhanced iron, nickel, and manganese. Starting with 100 µg L⁻¹ NDMA, a level observed at multiple field sites, pseudo-first-order kinetics were observed for all catalysts tested. No reaction intermediates were observed in any experiment; the amine group of NDMA was cleaved and reduced to dimethylamine with carbon balance in excess of 97%. Reductive catalysis may prove an efficient technology for mitigating the health risk posed by NDMA; this study provides the foundation for mechanistic and longevity research.

Introduction

N-Nitrosodimethylamine (NDMA) has been recently discovered as a contaminant in drinking and groundwater; due to potential health implications, it is of increasing interest to the public health community and water industry. Historically documented exposure to *N*-nitrosamines is dietary, mostly through beer, nitrate-cured meats, and tobacco smoke (1, 2). Industrial contamination of groundwater with NDMA was first discovered at sites containing hypochlorite-treated 1,1-dimethylhydrazine (3). NDMA has been detected at elevated levels at many wells throughout California and Canada (4, 5), and it was recently discovered that NDMA is formed during chloramination of drinking and biologically treated wastewater (6–8). The United States Environmental Protection Agency (EPA) now classifies NDMA as a probable human carcinogen (9, 10); chronic health effects include liver cancer, lung cancer, non-cancerous liver damage, internal bleeding, and neurological damage (10, 11).

NDMA is difficult to remove using conventional physiochemical treatment methods. With an estimated Henry's Law

constant of 2.63×10^{-4} atm M⁻¹, NDMA is not significantly removed from water by volatilization or air stripping (12–14). NDMA has a log octanol–water partition coefficient (log K_{ow}) of –0.57 and thus is not amenable to granular activated carbon adsorption; soil does not significantly adsorb NDMA (10). Ozone does not directly react with NDMA, and advanced oxidation methods using hydroxyl radicals produced from hydrogen peroxide or ozone using ultraviolet (UV) radiation are limited by radical scavengers and therefore are relatively ineffective (15).

Biological degradation shows potential to eliminate NDMA in aqueous systems but with mixed reports of efficacy. Earlier literature reports half-lives on the order of 12–55 days (16–18) without isolation of the bacterial communities responsible for the removal. More recent studies show greater than 50% removal in 30 days for 15 wastewater effluent samples (19), implicating aerobic bacteria with monooxygenase enzymes likely working cometabolically to sustain growth (20, 21). Relatively long half-lives seemingly limit biological NDMA degradation to groundwater applications where slow transport allows extended contact periods; a more detailed understanding of microbial NDMA reduction is necessary before considering above-ground treatment applications. A significant problem in water reuse applications is that NDMA passes through reverse osmosis (RO) membranes (only approximately 50% removal), necessitating a post-RO treatment step specifically for NDMA in some cases (22).

Currently, the most prevalent NDMA treatment method is direct UV photolysis. However, order of magnitude reduction of NDMA concentration in drinking water requires intensive UV treatment—approximately 1000 mJ cm⁻² (14, 22). Photolysis of NDMA in sunlight has shown approximately 50% removal of NDMA in shallow basins with residence times of approximately 1 day at the Orange County Water District's Water Factory 21 (22, 23). While effective, such methods are expensive and inefficient for large-scale NDMA removal.

Reductive catalysis is an innovative technology for the destruction of halogenated hydrocarbons in groundwater that has also been explored for removal of nitrate and nitrite (24–29). Noble metal catalysts, especially palladium, are effective for the destruction of halogenated and polyaromatic hydrocarbons; for many species, complete dehalogenation occurs with half-lives on the order of minutes (24). Matrix effects have been observed to reduce catalytic activity, and sulfide species are known to poison palladium catalysts (30, 31). Sulfide poisoning of palladium is reversible, however, and catalyst activity can be restored through oxidative processes (30, 32). Regeneration of bimetallic copper-enhanced palladium is difficult due to poor recovery of copper activity; a recent study showed that palladium activity is easily recovered through a hypochlorite rinse, but copper is not regenerated effectively (31). This limits bimetallic catalysis to water matrices without sulfide and requires control of biological fouling through deliberate system design.

Catalytic reduction of NDMA has been studied using zerovalent iron catalysts, yielding dimethylamine (DMA) and ammonium as products (33, 34). Pseudo-first-order reaction rates were observed, but kinetics were much slower than those for halogenated hydrocarbons; using zerovalent iron, NDMA had an observed half-life of 13 h (33) compared with 0.67 h for trichloroethylene (25). Nickel-enhanced iron showed much faster reduction, but kinetics varied over time (33). These long half-lives necessitate large reactor beds in above-ground applications to provide sufficient contact time for NDMA destruction, thus iron catalysts are not well-suited for drinking or wastewater streams.

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TABLE 1. Catalyst Physical Properties

property	Pd	Pd–Cu	Ni	Fe	Fe–Ni	Cu	Mn
BET surface area (m ² g ⁻¹)	153.3	140.8	1.5	0.5	0.3	0.5	ND ^b
pore volume (cm ³ g ⁻¹)	0.77	0.45	0.01	0.001	0.003	0.002	0.001
pore size distribution (nm)	39 ± 9	18 ± 6	22 ± 8	26 ± 10	34 ± 7	33 ± 13	22 ± 10
metal content ^a (% w w ⁻¹)	1	1, 0.3	99.99	99	58, 42	99	99
metal dispersion (%)	45	45					

^a Manufacturer data. ^b ND = not determined.

Bimetallic catalysts, an emerging subset of metal catalysts, combine two metals with different surface activities to favorably influence reaction kinetics. While monometallic palladium is effective in reducing nitrite to dinitrogen and ammonium in the presence of hydrogen, it cannot perform the initial reduction of nitrate to nitrite. Addition of a small copper loading to palladium catalyst can reduce nitrate to nitrite, which can then be completely reduced at the palladium surface (27, 35, 36). Palladium is an excellent catalyst for activating dihydrogen to atomic hydrogen (37), while copper can perform single-electron transfers to nitro groups. Combining these strengths in one catalyst should be useful in enhancing efficacy for nitrosamine destruction in a one-step process.

In general, iron is less active for reduction of trace organic contaminants than precious metal catalysts when weight-normalized. For example, trichloroethylene (TCE) dechlorination with zerovalent iron proceeded with a half-life of 40 min (25); addition of 0.25% by weight palladium reduced the half-life to 1.7 min (38). The drastic efficacy improvement via palladium addition is similar for many other halogenated compounds. The same has been shown to some degree with NDMA: nickel-enhanced iron had much higher affinity for NDMA reduction than zerovalent iron (33). For these reasons, it is expected that NDMA reduction will proceed much more rapidly using palladium and other precious metal catalysts than previously studied zerovalent iron.

The objectives of this study were to (1) determine the activity of various metal catalysts for NDMA reduction; (2) explore the impact of copper enhancement of supported palladium catalyst; and (3) quantify reaction intermediates and products. The catalysts selected for study were palladium, copper-enhanced palladium, nickel, zerovalent iron, nickel-enhanced iron, and manganese; all catalysts were commercially available. Palladium, copper-enhanced palladium, and nickel were selected for analysis of intermediate and product formation due to favorable kinetics and application feasibility.

Materials and Methods

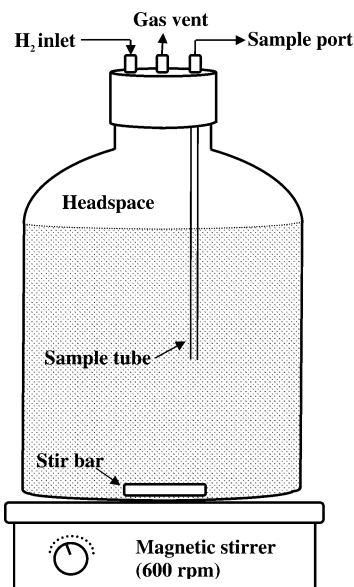
Chemicals. All experiments were conducted using 18.2 MΩ cm⁻¹ Milli-Q water generated by a Synergy 185 Millipore with Simpapak2 purifying system (Millipore; Billerica, MA). NDMA and deuterated NDMA (NDMA-d₆) were purchased as analytical grade solutions in methanol (Supelco; Bellefonte, PA). Hydrogen gas (H₂, 99.995%) was supplied by Praxair (Danbury, Connecticut). DMA was purchased as a salt (Sigma-Aldrich; St. Louis, MO). All chemicals were used as received without further purification.

Catalysts. 99.99% nickel (Ni), 99+% copper (Cu), 99+% manganese (Mn), and prereduced 1% palladium by weight on γ-Al₂O₃ (Pd) powders were purchased from Sigma Aldrich. 99+% zerovalent iron (Fe), nickel-enhanced iron (42% Ni by weight, Fe–Ni), and prereduced 1% palladium 0.3% copper on γ-Al₂O₃ (Pd–Cu) powders were purchased from Alfa Aesar (Ward Hill, MA). Mn is not a true catalyst as it is expected to oxidize in water, but for simplicity in this paper all metal reaction surfaces are referred to as catalysts. No special precautions were taken to avoid catalyst exposure to air prior

TABLE 2. Reactor Operating Conditions for Kinetic Studies

temperature (K)	294 ± 1
headspace hydrogen pressure (psig)	8
[H ₂](aq) ^a (μM)	800
volume (L)	2.2
aqueous/vapor (L/L)	2.0/0.2
pH ^b	5.6
mixing speed (rpm)	600
C _{me} ^c (mg L ⁻¹)	1–20
[NDMA] ₀ (μg L ⁻¹)	100

^a [H₂](aq) estimated using Henry's constant (7×10^4 atm). ^b pH remained at 5.6 for Pd, Pd–Cu, and Ni; slight increase (to 5.8) observed for Fe, Fe–Ni, and Mn. ^c Metal concentration refers to the amount of active metal in the system.

**FIGURE 1. Headspace reactor. Total reactor volume is 2.2 L with 2.0 L aqueous and 0.2 L headspace.**

to batch experiments. Catalyst physical properties are given in Table 1. BET surface area, pore volume, and pore size distribution were measured using a Coulter SA 3100 surface area and pore size analyzer (Beckman Coulter; Fullerton, CA). Manufacturer-specified metal weight contents were assumed to be accurate.

Reactors. NDMA reduction experiments were performed in 2.2 L Pyrex bottles (Fisher Scientific; Pittsburgh, PA) with 2.0 L water and 0.2 L hydrogen headspace maintained at 8 psig (except those involving Fe, Fe–Ni, and Mn, which obtain atomic hydrogen from water). Each reactor was equipped with a 3-port cap to allow sampling, hydrogen pressurization (except Fe, Fe–Ni, Mn), and headspace sparging; mixing was driven by an isotemp magnetic stirrer at 600 rpm (Fisher Scientific). Reactor operating conditions are summarized in Table 2; a system schematic is shown in Figure 1.

The experimental procedure was as follows: each reactor was filled with 2.0 L water and the appropriate amount of

catalyst. The reactor was then sparged with hydrogen gas for 15 min while mixing at 600 rpm to remove dissolved oxygen (reactive species) and provide an excess of hydrogen. After sparging, the catalyst/water combination was allowed to equilibrate with 8 psig hydrogen headspace for 90 min to ensure hydrogen saturation (est. 800 μM). A concentrated aqueous solution of NDMA was added to yield an initial concentration of 100 $\mu\text{g L}^{-1}$. Samples (1 mL) were withdrawn from the reactor at each time point and filtered through 0.22 μm syringe filters (Millipore) to remove catalyst particles. NDMA- d_6 was added as an internal standard (30 $\mu\text{g L}^{-1}$), and samples were stored at 4 $^{\circ}\text{C}$ in amber sample vials equipped with Teflon-lined septa until analysis. NDMA and DMA standards were prepared from dilutions of known concentrations at the time of sampling and stored with the samples.

Reaction product studies were completed using the same reactor setup as the kinetic studies above. The initial NDMA concentration was increased to 1 mg L^{-1} in order to provide better intermediate and product resolutions. Preliminary studies were completed to screen for reaction intermediates and products by direct sample infusion to the MS source plate to scan for molecular masses in solution. Once the products were characterized, sampling and analysis proceeded according to the same method for kinetic studies.

Analytical Methods. NDMA and DMA were detected using an API 3000 high-pressure liquid chromatograph with tandem mass spectrometers (LC-MS/MS, Applied Biosystems; Foster City, CA) using the method of Lopez-Mesas et al. (in preparation); this method was modified to include DMA transitions using the same analytical procedure and conditions as explained below. A C-18 column (5 μm particles, 50 \times 2.1 mm, Higgins Analytical; Mountain View, CA) was used to separate peaks in the LC before injection into the MS/MS.

Briefly, for NDMA and DMA analyses, 50 μL samples were injected into the LC with an initial mobile phase of 90:10 water with 2 mM ammonium acetate:methanol at a flow rate of 150 $\mu\text{L min}^{-1}$. The mobile phase (1) increased linearly to 40% methanol over 6 min; (2) increased linearly to 100% methanol over 2 min; and (3) remained at 100% methanol for 4 min to prevent sample carry-over. NDMA and DMA eluted at 2 min with sharp transition peaks, each about 1 min in duration. The MS/MS was operated in positive ionization mode; molecular ions were observed as proton adducts. The 75/43 transition was used for quantification of NDMA. NDMA- d_6 was used as the internal standard, and the 81/46 transition was used for quantification. The method developed by Lopez-Mesas et al. was modified by adding DMA quantification during the same run for NDMA. DMA was quantified using the 46 amu peak, and NDMA- d_6 was used as the internal standard for DMA.

Ammonium was measured using a photometric probe (Hach Analytical; Loveland, Colorado). This method involves mixing an ammonium cyanurate reagent with a 10 mL aqueous sample until dissolved, followed by inserting the sample vial into the detection cell for photometric analysis. The reagent powder buffers the aqueous solution to pH > 10 so that ammonia dominates the equilibrium ($\text{p}K_{\text{a}} = 9.3$). The manufacturer-specified detection limit using this method is 0.01 mg L^{-1} $\text{NH}_3\text{-N}$.

Evaluation of Reaction Kinetics. Catalyst activity was evaluated using pseudo-first-order rate constants normalized with respect to (1) metal concentration and (2) metal surface area

$$-\frac{1}{C_{\text{me}}} \frac{dC_{\text{NDMA}}}{dt} = k'_{\text{obs}} C_{\text{NDMA}} \quad (1)$$

$$-\frac{1}{SA_{\text{me}}} \frac{dC_{\text{NDMA}}}{dt} = k'_{\text{obs}} C_{\text{NDMA}} \quad (2)$$

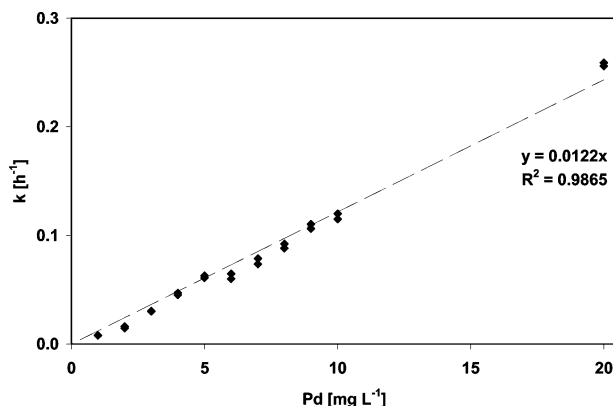


FIGURE 2. Observed pseudo-first-order rate constant for NDMA reduction as a function of Pd weight in the system (1% Pd on $\gamma\text{-Al}_2\text{O}_3$ catalyst, 200-mesh powder). Results of this analysis and identical ones for all catalysts are shown in Table 3.

where C_{NDMA} and C_{me} represent the NDMA and catalyst metal concentrations, respectively; and k'_{obs} is the observed pseudo-first-order reaction rate constant, normalized by active metal concentration (C_{me}) or metal surface area per liter (SA_{me}) for weight and surface area normalization, respectively. The metal loading was varied for each catalyst to verify that the reaction rate is directly proportional to the amount of catalyst added (for both metal weight and metal surface area). To account for varying metal weights between experiments, the observed pseudo-first-order rate constants were normalized by metal weight or surface area so that the reported rates are second-order with units of [$\text{L g}_{\text{me}}^{-1} \text{h}^{-1}$] and [$\text{L m}_{\text{me}}^{-2} \text{h}^{-1}$], respectively. For bimetallic Pd–Cu catalyst, the pseudo-first-order rate was normalized by Pd weight/surface area to compare with monometallic Pd and since the reaction does not occur on monometallic Cu. Hydrogen was not included in the rate expression because the activation energy for dihydrogen chemisorption onto noble metals is close to zero; rates of adsorption and desorption of dihydrogen onto catalyst active sites were sufficiently high to neglect (36).

For reaction product studies, NDMA disappearance was modeled using the same pseudo-first-order kinetic model described above, and DMA formation was modeled commensurate with NDMA disappearance assuming 100% carbon balance.

Results and Discussion

Kinetics of Surface Reaction. Kinetic data were determined by the disappearance of NDMA from solution. The initial NDMA concentration of 100 $\mu\text{g L}^{-1}$ was well above the LC-MS/MS detection limit (1 $\mu\text{g L}^{-1}$) and below levels measured in contaminated groundwater zones (39). Pseudo-first-order rates were fit using the first four half-lives, and each catalyst was tested at multiple concentrations to validate direct dependency of reaction rate on metal weight/surface area. Figure 2 shows the resulting observed pseudo-first-order rate constants for supported 1% Pd catalyst; similar results were recorded for all catalysts tested (summarized in Table 3).

Two normalization metrics were used to evaluate catalyst efficacy for NDMA reduction in water: catalyst metal weight and catalyst metal surface area. Normalizing the pseudo-first-order rates by catalyst metal weight in the system provides a consistent metric that is directly applicable to field implementation because operators can calculate the quantity of catalyst necessary to reduce a given NDMA concentration to required levels. Monometallic catalysts were weight-normalized by the total metal weight in each experiment. For bimetallic Pd–Cu, the reaction rates were normalized by Pd content to provide direct comparison with monometallic Pd; for bimetallic Fe–Ni, the rates were

TABLE 3. Pseudo-First-Order NDMA Reduction Kinetics

catalyst	catalyst composition	metal weight loading normalized	metal surface area normalized	half-life ^c [h]
		pseudo-first-order rate ^a [L g _{me} ⁻¹ h ⁻¹]	pseudo-first-order rate ^b [L m _{me} ⁻² h ⁻¹]	
Pd	1% Pd	11.5 ± 0.9	0.17 ± 0.01	6.0 ± 0.4
Pd-Cu	1% Pd-0.3% Cu	66.5 ± 7.4	1.05 ± 0.12	1.0 ± 0.1
Ni	99% Ni	8.3 ± 2.9	5.53 ± 1.93	8.4 ± 2.2
Fe	99% Fe	0.13 ± 0.09	0.26 ± 0.18	533 ± 218
Fe-Ni	42% Ni-58% Fe	0.65 ± 0.01	2.17 ± 0.03	107 ± 2
Mn	99% Mn	0.07 ± 0.02		990 ± 220
Cu	99.99% Cu	0		
Al ₂ O ₃	99.99% Al ₂ O ₃	0		

^a Pseudo-first-order rates are normalized by active metal weight ($n > 8$). ^b Pseudo-first-order rates are normalized by metal surface area ($n > 8$). ^c Calculated half-lives for 10 mg L⁻¹ active metal.

normalized by Fe content for comparison with monometallic Fe. Normalized pseudo-first-order rates and the corresponding half-lives are summarized in Table 3.

Additionally, pseudo-first-order rates were normalized by the available metal surface area to provide the relative effectiveness of each metal surface for catalyzing NDMA reduction in water. Using the metal loadings and specific surface areas given in Table 1, normalized pseudo-first-order rates were calculated for each catalyst, as summarized in Table 3. The main analysis of this paper focuses on metal weight normalized kinetics since this is standard convention, while surface area normalized kinetics are interesting as an alternative comparative metric of catalyst surface activity.

Metal Weight Normalized Kinetics. There are two main merits to metal weight normalization: (1) it has been the convention in reductive catalysis literature and yields comparative data, and (2) it facilitates sizing catalytic reactors by engineers since they purchase catalyst by weight.

Fe and Fe-Ni were tested for comparison with previous studies (33); the resulting pseudo-first-order rates were 0.13 and 0.65 L g_{me}⁻¹ h⁻¹, respectively. As noted earlier, hydrogen headspace was not used in the Fe, Fe-Ni, or Mn batches because these metals generate atomic hydrogen from water, as evidenced by slightly increasing pH during the reduction. Improvement in Fe catalyst performance by addition of Ni was observed, as expected. However, absolute rates are difficult to compare between this and the previous studies because (1) this study used a powdered catalyst in a mixed batch reactor, while the previous study used Fe and Fe-Ni filings packed into a column reactor; and (2) the previous study used 0.25% by weight Ni on Fe, while this study used 42% by weight Ni on Fe (i.e., the surface coverage of Fe and Ni are expected to be quite different between the two studies). Gui et al. reported pseudo-first-order rates of 0.057 h⁻¹ and 21 h⁻¹ for Fe and Fe-Ni, respectively (33). While the present study did not observe a 340-fold increase in pseudo-first-order rate, the normalized pseudo-first-order rate showed a 5-fold increase.

Mn was also tested in this study because it is an inexpensive electron-donating metal similar to iron in reductive capacity and has been used previously in this research group for TCE dehalogenation. The observed normalized pseudo-first-order reduction rate of 0.07 L g_{me}⁻¹ h⁻¹ for Mn was not significantly different than that observed for Fe, although it is likely that Mn was consumed during the reaction while Fe was proposed as a conservative catalyst during NDMA reduction (34). Since Fe, Fe-Ni, and Mn must obtain atomic hydrogen from water, their respective NDMA reduction rates could be slowed by the introduction of this potentially rate-determining step.

Ni catalyst was tested with dihydrogen as the electron donor because of the improved performance observed with

addition of Ni to Fe in this and previous studies (33). Catalytic NDMA reduction using Ni had a normalized pseudo-first-order rate of 8.3 L g_{me}⁻¹ h⁻¹, comparable to the observed reduction rate using Pd. These results indicate that Ni may be an economically attractive alternative to Pd catalyst, although longevity and regeneration efficacy must be explored before making an accurate comparison of the two metal catalysts.

Pd catalysts showed great efficacy for NDMA reduction in this study. For Pd and Pd-Cu, normalized pseudo-first-order rates of 11.5 and 66.5 L g_{me}⁻¹ h⁻¹ were observed, respectively. It was not expected that NDMA would partition to the γ -alumina support used for Pd and Pd-Cu catalysts in this study; experiments validated this expectation. No NDMA loss was observed in repeated trials using only the γ -alumina support under identical reaction conditions.

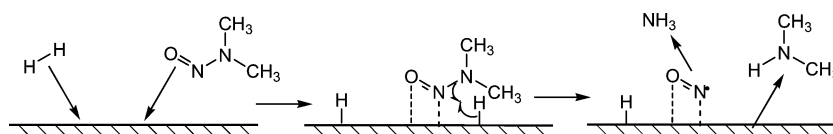
The significant improvement of Pd catalyst performance with the addition of a small amount of Cu was explored by running separate experiments with monometallic Cu catalyst; no NDMA loss was observed in these experiments. Because monometallic Cu did not catalyze NDMA reduction, the increase in the observed reduction rate by Cu addition to Pd catalyst was attributed to the combined effect of Cu and Pd. Literature reveals that Pd can rapidly activate dihydrogen to atomic hydrogen (37) which then diffuses throughout the bulk Pd (40); the results of this study show that Pd can also activate NDMA for reduction as it was converted to DMA in Pd experiments. However, since no NDMA removal was observed using monometallic Cu and there was significant improvement with Cu enhancement of Pd, it is hypothesized that Cu can activate NDMA but not hydrogen. Therefore, in the Pd-Cu studies, Cu is proposed to rapidly activate NDMA which is then reduced by atomic hydrogen at the Pd surface.

It is currently unknown whether the mechanisms of nitrosamine activation on Pd and Cu are similar or whether varying the Cu loading will significantly impact reaction kinetics. In analogy to reduction of nitrate using Pd-Cu catalyst, one can speculate that the reaction is initiated by the interaction of the oxygen atom with the Cu surface. The mechanism will depend on many factors including whether or not atomic hydrogen can diffuse from Pd through Cu to adsorbed NDMA. More work is needed to clarify the reaction mechanism on monometallic Pd and bimetallic Pd-Cu surfaces.

Surface Area Normalized Kinetics. While the metal weight normalization discussed above is very useful for practical implementation of reductive catalytic technology to remediate contaminated waters, it does not account for the actual surface availability of each metal for reaction. For example, the supported Pd catalysts had a much higher surface area than the Fe and Ni powders. To address this issue, pseudo-first-order rates were separately normalized by the metal surface area in each trial using the catalyst physical properties in Table 1. For Pd and Pd-Cu, the metal surface area is the BET surface area multiplied by the metal dispersion, taken from ref 32; all other catalysts had solid metal surfaces so the BET surface areas were used. Mn was not analyzed using this metric because the BET surface area was extremely low.

As seen in Table 3, normalizing the pseudo-first-order rates by surface area instead of metal weight gives a different view of which catalysts are more effective for NDMA reduction. Ni appears to be the key catalyst for NDMA reduction as monometallic Ni and Fe-Ni show kinetic rates of 5.53 and 2.17 L m_{me}⁻² h⁻¹, respectively—much greater than the other catalysts. These results indicate that a high surface area Ni catalyst would be ideal for NDMA reduction. However, high surface area Ni (e.g., Raney-Ni) is pyrophoric because the finely divided Ni oxidizes rapidly and exothermically, making the catalyst unsafe for field implementation where air contact is virtually unavoidable. Additionally, little is

SCHEME 1



known about Ni deactivation and regeneration in various water matrices. Pd and Pd–Cu have been well-studied in this respect, and Pd has been shown robust under sulfide poisoning and oxidative regeneration for periods of years (30, 41). So, despite the kinetic advantages revealed by a surface area normalization of kinetic rates, precious metal catalysts (Pd-based) seem to be the best choice for further exploration since they have a viable future in implementation.

NDMA Reduction Products. Product formation was studied for three metal catalysts due to kinetic and practical considerations: Pd, Pd–Cu, and Ni. The expected end products of catalytic NDMA reduction are DMA and ammonium, both of which are benign. Direct infusion of time point samples to the MS source plate detected only NDMA and DMA; no intermediate masses were observed in any of these sample screenings. Therefore, the hypothesized reduction mechanism shown in Scheme 1 appears to occur entirely at the metal surface; desorption does not occur until the amine group has been completely reduced due to lack of intermediate detection in any sample. A carbon mass balance was sufficient to show quantitative formation of DMA from NDMA. The formation of DMA is noteworthy because it is a precursor to NDMA and may lead to the formation of NDMA if the product water were subsequently chloraminated but at very low yield. The NDMA yield in synthetic batch experiments emulating wastewater treatment systems was 370 ng L⁻¹ from 4 h contact of 5.1 mg L⁻¹ monochloramine with 4.5 mg L⁻¹ DMA (42). This relatively low yield is promising for application of reductive catalysis to NDMA destruction because anticipated reformation post-treatment is low (<1%). It is not yet determined whether the initial reaction with surface hydrogen atoms involves N=O or N–N bond cleavage. The ultimate fate of the nitrosyl nitrogen atom is still under investigation.

Expected products from earlier studies using Fe and Fe–Ni catalysts were DMA and ammonium; ammonium was not detected in any samples of this study for unknown reasons, and nitrogen gas, another possible product, was not measured. It is unlikely that ammonium was lost to head-space partitioning since the species prefers to remain in water (unlike ammonia which partitions significantly to the gas phase). One potential source deals with the ammonium detection method itself: the ammonium cyanurate reagent is designed to buffer the aqueous sample to pH > 10 to ensure that ammonia is the dominant species. Then, NH₃-N is detected using a photometric probe. If the pH is not sufficiently increased by the reagent, no ammonia would be formed for detection. This issue is currently under evaluation and will be verified by independently buffering samples to pH > 10 and verifying with a secondary method (e.g., UV/vis).

For all three catalysts, pseudo-first-order decay was observed at elevated initial NDMA concentrations with rates comparable to those of the kinetic studies. DMA was formed quantitatively with NDMA removal; the carbon mass balance was in excess of 97% for each catalyst analyzed. Figure 3 shows the removal of NDMA and formation of DMA using Pd catalyst; similar results were recorded for all catalysts tested (data not shown).

As expected, no significant pH change was observed in the product studies since the metal catalysts tested were hypothesized to activate dihydrogen to form atomic hydrogen as the reducing agent. This mechanism is different than that

reported for Fe and Fe–Ni, where the metal surfaces obtained atomic hydrogen from water and a pH change is noted for significantly contaminated sites (33); similar mechanism differences are well-known for TCE reduction with Pd and Fe catalysts.

Hypothesized Reaction Mechanism. A hypothesized diagram of the NDMA reduction mechanism on mono-metallic surfaces (Pd and Ni) is shown in Scheme 1 based on prior studies using zerovalent iron for NDMA reduction (33) and Pd for TCE dechlorination (30, 43). In the first step, NDMA and dihydrogen move through solution to active metal sites; mass transfer calculations were performed and are provided as Supporting Information to this manuscript. At the metal surface, NDMA and dihydrogen are adsorbed and activated; atomic hydrogen is very reactive and mobile at the metal surface. The N–N bond is cleaved, the amine group is reduced to DMA, and the nitrosyl radical remains to be further reduced. Previous studies found ammonium as the product of the nitrosyl nitrogen (as shown) suggesting the nitrosyl radical is reduced to ammonium. The lack of ammonium detection is possibly due to detection method issues discussed earlier; further studies to isolate ammonium will be necessary along with surface adsorption studies in order to validate this mechanism.

For bimetallic Pd–Cu, the mechanism of Scheme 1 could be modified based on the limited insights gained in this study. Since Pd is well-known for its ability to activate dihydrogen to atomic hydrogen (37, 40), it is hypothesized that Pd supplied atomic hydrogen to NDMA that was activated at Cu sites. This preliminary insight warrants significant further research to substantiate such a hypothesis.

Technology Application. This study has shown that mono- and bimetallic catalysts—specifically Pd, Pd–Cu, and Ni—are effective for NDMA reduction in controlled aqueous environments. Safety concerns may limit the practicability of high surface area Ni catalysts, but Pd catalysts have been tested successfully at TCE-contaminated groundwater sites such as Lawrence Livermore National Laboratory (41). Extrapolation from powdered catalyst batches to columns packed with spherical beaded catalyst allowed prediction of contact times necessary for site remediation at the site. While the kinetic rates for NDMA reduction using Pd and Pd–Cu catalyst are slower than those reported for many halogenated

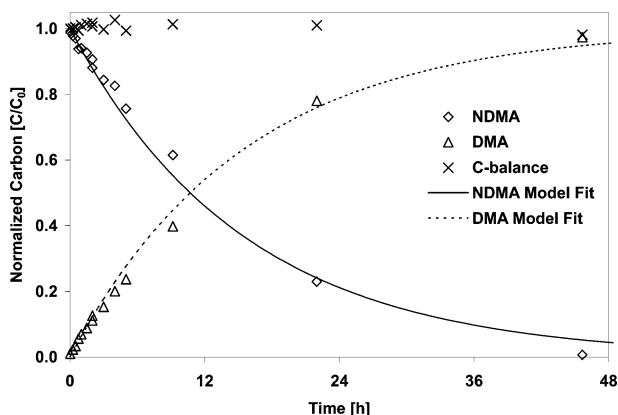


FIGURE 3. NDMA reduction product study using 1% Pd on γ -Al₂O₃ powder showing pseudo-first-order NDMA reduction and correlated DMA formation.

hydrocarbons, they are significantly faster and potentially much more cost-effective than existing NDMA remediation technologies. Further research into catalyst poisoning and regeneration methods will help determine the practical application of this technology to treating drinking and highly treated wastewater streams.

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Supporting Information Available

Mass transfer limitations were evaluated in depth and have negligible impact on the results of this study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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