Catalytic reduction of aqueous nitrates by metal supported catalysts on Al particles

Weirong Zhao [a,b,*], Xi Zhu [a], Yan Wang [a], Zhuyu Ai [a], Dongye Zhao [b,*]

[a] Department of Environmental Engineering, Zhejiang University, Hangzhou 310058, China
[b] Environmental Engineering Program, Department of Civil Engineering, Auburn University, Auburn, AL 36849, USA

HIGHLIGHTS

- Metal catalysts loaded on elemental Al effectively reduce nitrate.
- 0.4%Pd–4%Cu/Al presents the best nitrogen selectivity of 34.1% at pH 4.0 and 4 h.
- Nitrate converts to nitrite on Al and Cu surface, and to nitrogen on Pd surface.
- Intermediate nitrite and adsorbed H on Pd surface are crucial for nitrogen formation.

GRAPHICAL ABSTRACT
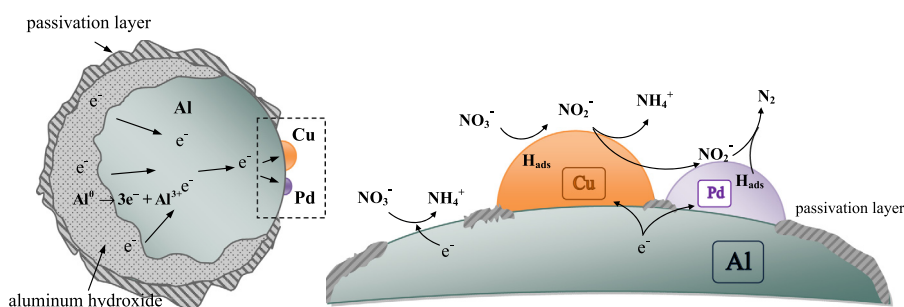
ARTICLE INFO

ABSTRACT

To facilitate the reduction of nitrate to nitrogen in water, a class of mono- or dual-catalyst particles was prepared by loading mono-metals (Cu, Ni) or bimetals (Pd–Cu, Pt–Cu, Au–Cu, and Ru–Cu) on Al particles. The prepared catalyst-loaded Al samples were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy, and transmission electron microscopy analysis. Batch kinetic experiments indicate that 0.4%Pd–4%Cu/Al at pH 4.0 resulted in the highest selectivity for nitrogen (N_2). Kinetic studies reveal that nitrate can be first reduced to nitrite on the Al and Cu surface at a relatively slow rate and subsequently was rapidly reduced to nitrogen on the noble metal surface and to ammonia on the Al and Cu surface. The selectivity for nitrogen formation can be influenced by the type of metals deposited and the concentration of intermediate nitrite and atomic hydrogen adsorbed on the Pd surface.

1. Introduction

Nitrate is widely present in groundwater and surface waters, and nitrate contamination of drinking water has attracted considerable attention due to its adverse health effects [1,2]. Zero valent iron (ZVI) has been demonstrated to be able to reduce nitrate efficiently [3–7]. In this system, ZVI is the electron donor, and nitrate is more preferably removed at lower pH (⩽4.0) [8–10]. Recently, nanoscale ZVI (NZVI) [11–15] has attracted considerable attention for its much greater surface area and reactivity than conventional granular ZVI. Liou et al. observed that the NZVI offered 340 times greater nitrate reduction rate than ZVI [12].

However, the rapid oxidation of ZVI and NZVI in water often limits the reactive lifetime of the catalysts [16], and the nitrate reduction rate by ZVI still needs to be improved. Therefore, catalyst-loaded iron, aluminum, or magnesium particles, such as Pd/Fe [17], Ni/Fe [18], Cu/Al [19], Ni/Sn [20], and Cu/Mg [21], have been prepared and tested accordingly. The application of Al, Sn,

* Corresponding authors. Address: Department of Environmental Engineering, Zhejiang University, Hangzhou 310058, China. Tel./fax: +86 571 8898 2032 (W. Zhao). Tel.: +1 334 844 6277; fax: +1 334 844 6290 (D. Zhao).
  E-mail addresses: weirong@mail.hz.zj.cn (W. Zhao), zhaodon@auburn.edu (D. Zhao).

and Mg as electron donors and the introduction of a second metal, such as Cu and Ni, as a catalyst can enhance the nitrate reduction rate remarkably [4,18,22].

Furthermore, it has been challenging that ZVI often resulted in a high selectivity of ammonium [4,23,24], which itself is of concern. It was found that certain noble metallic catalysts are able to facilitate conversion of nitrate to nitrogen. Catalysts, such as Pd–Cu/CeO$_2$ [25], Pd–Cu/TiO$_2$ [26,27], Pd–In/TiO$_2$ [28], Pd–Cu/γ-Al$_2$O$_3$ [29,30], and Rh (Pd, Pt, or Ir)–Cu/activated carbon [31], have been tested for nitrate reduction in hydrogen flow. The product distribution in the reduction depends on the identity and mass loading of the metallic catalysts employed. The Pd–Cu loaded on various supports has been developed as the most popular bimetallic catalyst for nitrate reduction with both a good nitrate reduction rate and N$_2$ selectivity [32]. The nitrogen selectivity in the reduction products in the hydrogen flow reached 70% with the catalyst Pd–Cu/activated carbon [31].

Although the selectivity of nitrogen by dual catalysts loaded on metal oxide in hydrogen flow is quite favorable, nitrate reduction without hydrogen flow is still required, especially when it is difficult to provide hydrogen, such as during groundwater remediation. Furthermore, the amount of noble metal used in those materials is often quite high (e.g., Pd–Cu/TiO$_2$ containing 2% of Pd [26] and Pd–Cu/ACo containing 1% of Pd [31]) to achieve the highest nitrogen selectivity. Nitrate reduction by dual catalysts loaded on metal powders is a promising way to handle this problem. Lo et al. [33] prepared Cu–Pd/Fe particles by depositing Cu and Pd successively and achieved an optimum nitrogen selectivity of 29.6%. Though this nitrogen selectivity was not as high as those by dual catalysts loaded on metal oxide in hydrogen flow, it offers a new way to reduce nitrate to nitrogen, which will be often more facilitated in some situation.

Aluminum has much lower reduction potential ($E^\circ = -1.676$ V) and much smaller density ($\rho = 2.70$ g/cm^3) than iron ($E^\circ = -0.43$ V, $\rho = 7.86$ g/cm^3). The passivation layer of aluminum oxide can protect aluminum from corrosion by water, and this layer can be thinned by mild acid treatment to facilitate electron transfer out of the aluminum to the target nitrate [12,34,35]. Therefore, loading metallic catalysts on Al is feasible to take advantage of the strong reducing power of aluminum and the outstanding N$_2$ selectivity of the metallic catalysts.

In this study, metallic catalyst-loaded aluminum particles were synthesized for nitrate selective reduction. The type and loading amount of the noble metal catalysts on the aluminum particles were manipulated to maximize N$_2$ selectivity. The influences of pH and the addition of hydrogen were also studied to investigate the role of atomic hydrogen adsorbed (H$_{ads}$(M)). Finally, a modified mechanism of nitrate reduction was proposed based on the evidence in the reaction to elucidate the formation of nitrogen and other products in the nitrate reduction process.

2. Materials and methods

2.1. Preparation of catalyst-loaded Al

First, 0.3 g of the Al powder and 5 mL of Ar-purged deionized water were mixed in 43-mL serum bottles. For mono-catalyst deposited Al (i.e., 4%Cu/Al, 4%Ni/Al, and 4%Pd/Al), 9 mL of metal salt (CuSO$_4$, NiSO$_4$, and Na$_2$PdCl$_4$·3H$_2$O) with certain concentrations was added to the Al-containing serum bottles to a weight ratio of metal to Al of 4%. For dual-catalyst loaded Al particles, taking 0.4%Pd–4%Cu/Al as an example, certain concentrations of 8 mL of CuSO$_4$ and 1 mL of noble metal ions (Na$_2$PdCl$_4$·3H$_2$O, H$_2$PtCl$_6$·6H$_2$O, AuCl$_3$·HCl·4H$_2$O, or RuCl$_3$·nH$_2$O) were added to insure the weight ratios of noble metal:Cu:Al at about 0.4%:4%:1%. Next,

4 mL of dilute sulfuric acid (0.3 mM) was added to thin the passivation layer on the surface of Al particles and to facilitate reductive deposition of the metal catalysts by Al. The bottles were placed on a rotating reactor to mix the solutions thoroughly for 4 h at room temperature (25 °C) to deposit the metals on the Al surface completely. All steps mentioned above were carried out in a glove box filled up with pure nitrogen to avoid metal oxidation during the preparation of catalyst-loaded Al.

2.2. Materials characterization

All mono- or dual-catalyst loaded Al particles were washed with deionized water, collected through vacuum filtration, and were dried under a stream of N$_2$ (50 mL/min) at 90 °C for 3 h before characterization.

Powder X-ray diffraction (XRD-6000, Rigaku, Japan) patterns were measured to analyze the crystal phases of the samples with Cu Kα radiation (model D/max RA). The accelerating voltage was 25 kV, while the applied current was 40 mA. The X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Thermo, USA) measurements were performed using an Al Kα X-ray source (1486.6 eV). The C1s level at 284.8 eV was used as an internal standard to correct the shift of the binding energy. The morphology of the prepared catalysts (0.4%Pd–4%Cu/Al) was examined with scanning electron microscopy (SEM, SIRON, FEI, Netherlands) and elemental information from the chosen region was obtained with energy-dispersive X-ray spectroscopy (EDX) in conjunction with SEM. The nanostructure of the samples was examined by a transmission electron microscope (TEM) and a high resolution TEM (HRTEM, JEM-2010, Jeol, Japan) at an accelerating voltage of 200 kV.

2.3. Nitrate reduction tests

After the preparation of catalyst-loaded Al in Section 2.1, the 43-mL serum bottles without any treatment was filled with 25 mL of pH-adjusted deionized water or saturated H$_2$ (0.813 mmol/L) water and capped with Teflon septa (leaving no head space) in the glove box filled with pure nitrogen. The pH of the reactant solutions was adjusted by changing the amount of sulfuric acid and sodium bicarbonate dissolved in the 25 mL of water mentioned above. Nitrate reduction was initiated by spiking 100 μL of a nitrate stock solution (0.9829 mol/L) by syringe into the particle suspensions, which resulted in an initial nitrate concentration of 2.29 mmol/L and a Al/nitrate mass ratio of 1.54. The bottles were then mixed on a rotary shaker (40 rpm) operated at room temperature (25 °C) and atmospheric pressure. At selected intervals, the aqueous samples were taken and filtered by syringe filters with pore size of 0.22 μm and then analyzed for nitrate, nitrite, and ammonium concentrations, respectively.

To test the reactive lifetime of the materials, the nitrate reduction process was carried out in four consecutive cycles. In the first cycle, the experiment was performed in the same way mentioned above. At the end of the first three cycles, the concentration of nitrate in the solution was measured. Next, the initial nitrate concentration of the next cycle was brought back to its original value of 2.29 mmol/L by spiking a certain amount of the nitrate stock solution (0.9829 mol/L) into the reaction serum bottles based on the current nitrate concentration. Control experiments without the addition of the particles were performed in parallel. All of the experimental points were duplicated.

2.4. Chemical analysis

The concentrations of nitrate, nitrite, and ammonium were analyzed by spectrophotometry following the standard method [36] with a UV spectrophotometer (TU-1901, Pgeneral, China).