Hydrogenation of aqueous nitrate and nitrite with ruthenium catalysts

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Abstract - Historically, development of catalysts for treatment of nitrate-contaminated water has focused on supported Pd-based catalysts, but high costs of the Pd present a barrier to commercialization. As part of an effort to develop lower cost hydrogenation catalysts for water treatment applications, we investigated catalysts incorporating Ru with lower cost. Pseudo-first-order rate constants and turnover frequencies were determined for carbon- and alumina-supported Ru and demonstrated Ru's high activity for hydrogenation of nitrate at ambient temperature and H₂ pressure. *Ex situ* gas pretreatment of the catalysts was found to enhance nitrate reduction activity by removing catalyst surface contaminants and exposing highly reducible surface Ru oxides. Ru reduces nitrate selectively to ammonium, and no aqueous nitrite intermediate is observed during reactions. In contrast, reactions initiated with nitrite yield a mixture of two endproducts, with selectivity shifting from ammonium towards N₂ at increasing initial aqueous nitrite concentrations. Experimental observation and Density Functional Theory calculations

24 together support a reaction mechanism wherein sequential hydrogenation of nitrate to nitrite and NO is
25 followed by parallel pathways involving the adsorbed NO: (1) sequential hydrogenation to ammonium,
26 and (2) N-N coupling with aqueous nitrite followed by hydrogenation to the detected N₂O intermediate
27 and N₂ endproduct. These findings open the door to development of alternative catalysts for purifying
28 and recovering nutrients from nitrate-contaminated water sources, and insights into the controlling
29 surface reaction mechanisms can guide rational design efforts aimed at increasing activity and tuning
30 endproduct selectivity.

31

32 **Keywords:** Ruthenium catalysts, nitrate reduction, catalyst pretreatment, isotope labeling, density
33 functional theory

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35 **1. Introduction**

36 Nitrate contamination of drinking water sources is among the greatest public health threats around the
37 world [1]. Nitrate concentrations exceeding health-based standards are routinely detected in drinking
38 water sources due to excess fertilizer applications and release of incompletely treated industrial and
39 domestic wastewater [2-4]. The growing contamination of drinking water sources raises health concerns
40 because nitrate can be transformed into hazardous chemicals, including nitrite, which causes
41 methemoglobinemia (i.e., blue baby syndrome), and potentially carcinogenic nitrosamines [5, 6]. As a
42 result, there is great interest in the development of efficient, robust and low-cost technologies for
43 treating nitrate-contaminated water.

44 Several technologies are available to separate nitrate from water, including ion exchange [7, 8], high
45 pressure membrane filtration [9], and electrodialysis [10], and have demonstrated their effectiveness in
46 full-scale practice [2, 11]. The principal drawback of these systems is the production of a nitrate
47 concentrate stream that requires further treatment before disposal [12, 13]. Biological denitrification is
48 widely used for the treatment of municipal and industrial wastewater, but concerns about pathogen
49 introduction, the need for costly organic carbon amendments and potential residuals, and biological
50 sludge production have limited application for drinking water treatment [14, 15]. More recently,
51 chemical reduction of nitrate has been increasingly explored. Zerovalent metals, including iron [16],
52 aluminum [17], and magnesium [18], stoichiometrically couple nitrate reduction with metal corrosion,

53 but reactions are hindered by the formation of oxide surface coatings, and the need to constantly
54 replenish the metals as reducing equivalents are consumed creates operational challenges.

55 As an alternative to stoichiometric metal reductants, our team and others have been investigating the
56 application of metal hydrogenation catalysts that couple nitrate reduction with H₂ oxidation [7, 19-23].
57 Nitrate can be transformed into two endproducts with different H₂ and acidity requirements:

58 Because the metals are acting as catalysts rather than stoichiometric reactants, they are not consumed in
59 the process or generate a secondary solid waste stream that requires disposal. H₂ is an inexpensive
60 electron donor that has lower life cycle environmental impacts than organic electron donors applied in
61 most biological denitrification processes [24]. To date, most work has focused on the development of
62 nitrate and nitrite treatment processes employing supported Pd-based catalysts [13, 25, 26]. Pd catalysts
63 are highly effective in converting nitrite, the first daughter product of nitrate reduction, to harmless N₂
64 gas at an incomparable rate [27-29], but monometallic Pd catalysts show little reactivity with nitrate [30,
65 31]. Deposition of a second “promoter” metal (e.g., Cu, In, Sn) together with Pd is typically required to
66 facilitate reduction of nitrate to nitrite [23, 31, 32]. A large body of literature has reported on aqueous
67 nitrate reduction with Pd-based bimetallic catalysts [20, 30, 31, 33-37], and our current understanding of
68 metal-catalyzed nitrate hydrogenation mechanisms has been limited to reactions occurring with these
69 materials. The prevailing reaction pathway follows a two-step process depicted in [Scheme 1](#): (1)

hydrogenation of nitrate to nitrite on bimetallic clusters followed by (2) further hydrogenation of nitrite on Pd sites to a mixture of N_2 and ammonium stable endproducts, the net processes being reflected by Eqs. (1-2) [22, 35, 38-40]. The proposed sequential reduction pathway is supported by the observation of nitrite as a transient reaction intermediate [23, 33], increasing with pH as the rate of Pd-catalyzed nitrite reduction decreases [39, 41], and isotope labeling experiments showing Pd-catalyzed reduction of NO to the same mixture of endproducts and selective conversion of N_2O to N_2 [22]. The distribution of endproducts, presumed to be controlled by the Pd-catalyzed reactions of nitrite or its daughter products (e.g., adsorbed NO), has been reported to vary with catalyst composition [31], metal nanoparticle size [42], support [43], and solution pH [44].

Although years of effort have been invested in improving the activity, endproduct selectivity, and long-term stability of Pd-based bimetallic catalysts [31, 45] (and to a lesser extent Pt-based catalysts [36, 46]), deployment of practical catalytic treatment systems remains limited, in large part, due to high costs of Pd [47]. Precious metal-free catalysts based on Ni have been explored [15, 48, 49], but instability in aqueous matrices [50], and serious concerns about the associated leaching of dissolved Ni^{2+} [51] and the pyrophoric nature of highly active Raney Ni [52] have limited further development efforts.

As a result of the low nitrate and nitrite reduction activity reported in early catalyst screening studies [27, 28], Ru hydrogenation catalysts have been largely overlooked for such applications. However, a renewed examination of the application of Ru-based catalysts is warranted because of the historically much lower price of Ru in comparison to Pd and Pt [47] as well as the metal's documented catalytic

89 activity for a diverse range of reactions, including hydrogenation, hydrodeoxygenation and
90 hydrodechlorination reactions [53, 54]. In addition, work on electrochemical reduction of nitrate (in
91 acidic media) has shown that Ru electrodes exhibit higher activity than Pt, Pd and Ir electrodes [55].
92 After recently screening a range of metal catalysts as alternatives to Pd for reduction of oxyanion
93 pollutants [56], this contribution focuses on a renewed evaluation of the kinetics and mechanisms of
94 nitrate and nitrite reduction by supported Ru catalysts. Reaction kinetics, product distribution analysis,
95 and catalyst characterization studies are combined with Density Functional Theory (DFT) calculations to
96 improve our understanding of interaction between nitrate (and nitrite) and Ru metal surfaces and
97 elucidate the origin of endproduct selectivity.

98

99 **2. Materials and methods**

100 **2.1. Catalysts**

101 A full listing of chemical reagents is provided in Supporting Information (SI; Section S1). Ru and Pd
102 catalysts immobilized on carbon and alumina supports (nominal 5 wt% metal) were purchased from
103 Sigma-Aldrich. Unless otherwise noted, the as-received Ru and Pd catalysts were pretreated *ex situ* in
104 flowing H₂ at 350°C for 2 h prior to use in aqueous oxyanion reduction experiments. The only exception
105 to this was for experiments specifically examining the effects of different *ex situ* pretreatments (see
106 section 3.2), wherein the as-received catalysts (no pretreatment), catalysts pretreated *ex situ* in flowing
107 N₂ at 350°C for 2 h, and catalysts pretreated *ex situ* in flowing H₂ as mentioned above were compared.

108 No precautions were taken following pretreatment to avoid surface passivation upon exposure to air.
109 Bimetallic Pd-Cu/C, Ru-Cu/C, and Ru-In/C catalysts were prepared by incipient wetness impregnation
110 [57] of 1 wt% of Cu (as $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) or In (as $\text{In}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$) on as-received commercial Pd/C and
111 Ru/C, respectively, followed by air drying at 110°C for 12 h and H_2 at 350 °C for 2 h.

112 Catalysts were extensively characterized, including metal content (inductively coupled
113 plasma-optical emission spectrometry, ICP-OES), specific surface area and average pore diameter of the
114 support materials (N_2 physisorption), metal dispersion (the percentage of Ru or Pd atoms present on the
115 clean surface of the immobilized metal nanoparticles, CO chemisorption), active surface (the percentage
116 of Ru or Pd atoms accessible to reactants under simulated *in situ* conditions, CO chemisorption),
117 morphology and size of the metal nanoparticles (transmission electron microscopy and high-angle
118 annular dark-field-scanning transmission electron microscopy, TEM and HAADF-STEM), Ru
119 reducibility (H_2 temperature-programmed reduction, H_2 TPR), and long-range structural order (X-ray
120 diffraction, XRD). Details of each methodology are provided in SI Section S2.

121 **2.2. Nitrate and nitrite reduction kinetics**

122 Aqueous nitrate and nitrite reduction kinetics were measured in an open semi-batch system under
123 continuous H_2 sparging (1 atm, 40 $\text{mL} \cdot \text{min}^{-1}$) at constant temperature (25 ± 0.5 °C). A 250 mL
124 three-neck reactor was filled with 150 mL deionized water and predetermined mass of catalyst. The
125 suspension was sonicated for 5 min and sparged with H_2 gas for 30 min before introducing a small
126 volume of NaNO_3 or NaNO_2 stock solution to initiate the reaction. Reaction progress was monitored by

periodic collection of suspension aliquots (1.5 mL) that were immediately filtered (0.22 μm cellulose acetate) to remove catalyst particles and quench reactions prior to analysis by ion chromatography (NO_3^- and NO_2^-) and colorimetric assay (NH_4^+). The suspension was mixed by a Teflon-coated magnetic stir bar at 700 rpm. Solution pH was maintained by HCl addition from an automatic pH-stat (Radiometer TitraLab 854). Catalyst activity was assessed by quantifying initial mass-normalized pseudo-first-order rate constants (k_0 , $\text{L}\cdot\text{g}_{\text{Ru/Pd}}^{-1}\cdot\text{min}^{-1}$) and turnover frequencies (TOF_0 , min^{-1}), defined as the number of nitrate or nitrite ions reduced per active surface site per minute. The active surface was estimated from CO chemisorption measurement using an assumed 1:1 CO:Metal adsorption stoichiometry [58, 59]. Additional details of the procedures for kinetics parameter calculations and aqueous analytical measurements are provided in SI Sections S3 and S4, respectively. A catalyst re-use experiment was carried out to evaluate the stability of Ru/C. After a semi-batch reaction was complete, the catalyst solid was collected on a filter (glass fiber filter; EMD Millipore), washed with deionized water several times, and vacuum dried at 65 $^\circ\text{C}$ overnight before re-suspending in water for the subsequent semi-batch reaction. The catalyst was also re-characterized after completion of the re-use experiment.

2.3. Isotope labeling experiments

Nitrogen mass balances and endproduct distributions were quantified using closed-bottle batch experiments with the aid of ^{15}N -labeled nitrate and nitrite salts to avoid the interference from atmospheric $^{14}\text{N}_2$ during mass spectrometry measurement of the N_2 endproduct [22]. A 160 mL serum bottle with 75 mL of an organic buffer, 4-morpholineethanesulfonic acid (MES) (pH 5.5, 40 mM), a

146 predetermined mass of catalyst, and a Teflon-coated magnetic stir bar was sealed by a 1.0 cm-thick
147 rubber stopper held in place by an Al crimp cap. Experiments were conducted at ambient temperature
148 ($21 \pm 1^\circ\text{C}$) and suspensions were mixed in the same manner as the semi-batch experiments. The reactor
149 was sparged with H_2 for 30 min to saturate the headspace and solution before introducing the target
150 oxyanion pollutant. A H_2 -sparged stock solution of $\text{Na}^{15}\text{NO}_3$ or $\text{Na}^{15}\text{NO}_2$ was then added to the reactor
151 to initiate the reaction, and 1.5 mL aqueous aliquots were withdrawn by syringe through the gas-tight
152 septa to monitor disappearance of the parent reactant and the evolution of aqueous intermediates and
153 products. Headspace samples (0.1 mL) were collected separately and immediately analyzed for labeled
154 gaseous intermediates and products (^{15}NO , $^{15}\text{N}_2\text{O}$, and $^{15}\text{N}_2$) by gas chromatography-mass spectrometry
155 (GC-MS, details in SI). Headspace gases were assumed to be maintained in equilibrium with the
156 aqueous phase at all times [60], which was supported by good nitrogen mass balance closure. Analyte
157 values in these experiments are reported in moles of nitrogen because products include both liquid and
158 gas species as well as both mono- and diatomic nitrogen species. The total mass of H_2 initially added to
159 the sealed batch reactor (~ 3.4 mmol) was in significant excess of the stoichiometric requirement for the
160 complete reduction of the added NO_3^- to NH_4^+ (~ 0.5 mmol).

161 2.4. Computational methods

162 DFT calculations of N-containing species associated with Ru metal surfaces were performed with
163 the Gaussian 09 suite of programs [61]. A Ru_{18} metal cluster structure was used to model Ru catalysts
164 based on the work of Aguilera-Granja *et al.* [62] and Zhang *et al.* [63]. It was shown that Ru and Rh

165 clusters with fewer than 20 atoms adopt simple cubic or distorted cubic structure. Geometry
166 optimizations of Ru clusters were completed at the PBE0 [64] level of theory with the Lanl2DZ basis set
167 [65, 66]. The core electrons of Ru atoms were modeled using the SDD effective core pseudo-potential
168 [65, 67]. The PBE0 functional was shown to be a reliable method in predicting both the properties and
169 reactions involved with transition metals and metal clusters [68], including Ru, with accuracies
170 approaching or exceeding other functionals commonly utilized in solid state systems [69].

171 Small molecule (i.e., nitrate, nitrite, and other reacting species) adsorption to the metal clusters were
172 optimized at the PBE0/Lanl2DZ(Ru)/6-31+G(d,p)(H, N, O) level of theory. The geometry optimization
173 of small molecules was performed with the Ru cluster fixed. Thermodynamic barriers were calculated
174 from the bottom of the well energies, as thermodynamic corrections would be an unnecessary addition
175 of error due to the frozen bond constraints given to the metal atom centers. The integral equation
176 formalism polarizable continuum model (IEF-PCM) [70] was used to implicitly model the aqueous
177 environment and was present in all optimizations and single point energy calculations. To correct for
178 spin contamination for unpaired electron intermediates, single point energies utilizing a restricted open
179 shell (RO) wavefunction were calculated at the ROPBE0/Lanl2DZ(Ru)/6-31+G(d,p)(H, N, O) level of
180 theory. When multiple conformations of adsorbed N-containing species were possible, the complexes
181 with the lowest energy were chosen for the calculation of reaction energies.

3. Results and discussion

3.1. Catalytic nitrate reduction

[Fig. 1](#) shows the catalytic reduction of aqueous nitrate on Ru/C in comparison to monometallic Pd/C and bimetallic Pd-Cu/C. In contrast to an earlier report of limited nitrate reactivity with Ru catalysts [28], these experiments demonstrate that Ru is an effective catalyst, exhibiting much greater activity than monometallic Pd/C of the same mass loading and similar activity to Pd/C after immobilization of 1 wt% Cu as secondary promoter metal. For all three catalysts shown in [Fig. 1](#), nitrate reduction kinetics follow a pseudo-first-order rate law over at least the first reaction half-life, and model fits of the data shown yield Ru- and Pd-mass-normalized pseudo-first-order rate constants of $4.13 \pm 0.30 \text{ L} \cdot \text{g}_{\text{Ru}}^{-1} \cdot \text{min}^{-1}$, $0.46 \pm 0.08 \text{ L} \cdot \text{g}_{\text{Pd}}^{-1} \cdot \text{min}^{-1}$, and $4.18 \pm 0.01 \text{ L} \cdot \text{g}_{\text{Pd}}^{-1} \cdot \text{min}^{-1}$ for Ru/C, Pd/C, and Pd-Cu/C catalysts, respectively. The rate constants are calculated using the metal loading reported in [Table 1](#). Control experiments conducted under continuous N₂ sparging (catalyst suspensions sparged with H₂ for 30 min followed by N₂ for another 60 min to displace H₂ before introducing nitrate to the reactor) show negligible loss of nitrate, demonstrating minimal adsorption onto the catalyst supports. Since the catalysts were subjected to the same *in situ* H₂ pre-reduction step before switching to N₂ sparging, this observation also indicates negligible direct reduction of nitrate by the metallic Ru or Pd phases. Initial rates of nitrate reduction vary linearly with catalyst loading between 0 and 0.5 g·L⁻¹ Ru/C ([Fig. S2](#)), indicating that catalyst suspensions were well mixed and external mass transfer limitations for the reactants (nitrate and H₂) were insignificant under the studied conditions. The estimated Weisz-Prater parameter (C_{WP}) (SI Section

201 S5) is $\ll 1$, indicating that the internal mass transfer within the porous catalyst support particles is also
202 not rate limiting. Ru/C exhibited good stability in batch re-use experiments, with activity decreasing
203 $< 5\%$ after each run (Fig. S3). Dissolved Ru measured in the supernatant of catalyst suspensions was
204 below 1 ppb, demonstrating negligible leaching of the active metal. Electron microscopy of the catalyst
205 collected following repeated re-use shows no agglomeration or growth of Ru nanoparticles (Fig. 3a and
206 3b). The small drop in activity observed between runs is speculated to be caused by material loss during
207 the filtration recovery protocol used between runs. Immobilization of secondary promoter metals (1 wt%
208 Cu and In) that have been reported to enhance nitrate reduction activity for Pd catalysts did not enhance
209 Ru/C reactions with nitrate (data not shown).

210 Reductive transformation of nitrate, rather than adsorption or other transformation process, is also
211 confirmed by the good nitrogen mass balance closure (Fig. 2a) observed using closed-bottle batch
212 experiments with the aid of a ^{15}N -labeled nitrate salt that eliminated potential artifacts from atmospheric
213 contamination during analysis of N_2 . For Ru/C, nitrate is converted selectively to ammonium without
214 producing any detectable $^{15}\text{N}_2$ by GC-MS analysis, and none of the transient aqueous or gaseous
215 intermediates typically observed for Pd-based catalysts (nitrite and N_2O) [39, 71] are detected.

216 The effect of solution pH on nitrate reactions with Ru/C was evaluated in the open semi-batch
217 systems using HCl/NaOH to maintain pH (Fig. S4). Ru-mass-normalized pseudo-first-order rate
218 constants are relatively constant between pH 5-8, but decrease significantly at lower and higher pH
219 conditions. Since gaseous nitrogen species cannot be measured in the open semi-batch reactors sparged

continuously with H₂, a stringent mass balance analysis of endproducts was not feasible. However, ammonium product yields reached $\geq 90\%$ of the initial nitrate concentrations for all pH conditions, consistent with the high selectivity measured in the closed reactor experiment conducted at pH 5.5 using ¹⁵N-labeled species (Fig. 2a).

Comparison between metal dispersion and active surface in Table 1 suggests that 30 min of H₂ treatment at 25 °C is sufficient to re-reduce a large fraction of any surface oxides that might form upon air passivation of *ex situ* H₂ pretreated catalysts. Despite the heterogeneity in particle morphology (Fig. 3 and Fig. S5) and an assumed 1:1 CO:Metal adsorption stoichiometry for all catalysts irrespective of metal particle size and support, metal dispersion values derived from CO chemisorption analysis [73] are reasonably consistent with particle sizes observed by electron microscopy (Table 1). The rate constants for monometallic catalysts correspond to initial turnover frequencies (TOF₀) of $2.1 \pm 0.2 \text{ min}^{-1}$ for Ru/C and $0.42 \pm 0.07 \text{ min}^{-1}$ for Pd/C based on active metal surface. TOF₀ of nitrate reduction on Ru/C is five times greater than that of Pd/C. The higher reactivity of monometallic Ru/C than Pd/C is especially noteworthy because the Pd/C reactivity observed in Fig. 1 is actually much greater than that reported in earlier studies that found either no reaction with nitrate or a very low extent of reaction [30, 31, 56, 74-76]. Trawczyński *et al.* [71] calculated TOF₀ of nitrate reduction on an in-house prepared Pd/C catalyst to be $\sim 0.03 \text{ min}^{-1}$, which is one order-of-magnitude lower than the TOF₀ calculated from data for Pd/C in Fig. 1. Considering that deionized water ($\geq 18 \text{ M}\Omega\cdot\text{cm}^{-1}$) was used for all experiments and known promoter metals for Pd catalyst including Cu, In, and Sn were not detected by Energy

239 Dispersive X-ray spectroscopy analysis of Pd/C, we believe that the higher activity of Pd/C observed
240 here is not due to promoter metal contamination from solution or surface residues present following
241 synthesis of catalyst support.

242 The nature of active sites in Pd-Cu bimetallic catalysts is not well understood or characterized.
243 Although it is technically possible to estimate surface atoms by H₂ chemisorption [23, 77], we believe
244 the measurement does not represent bimetallic sites and chose not to calculate the TOF₀ for nitrate
245 reduction on Pd-Cu/C or compare the intrinsic activity between Ru and Pd-Cu bimetallic surface.
246 However, it can be seen from [Table S1](#) that the Pd-Cu/C catalyst prepared for comparison in this study
247 exhibits activity on a Pd mass-normalized basis that is comparable with other studies that focused in
248 greater depth on the activity and mechanism of such bimetallic catalysts.

249 **3.2. Effect of pretreatment on nitrate reduction activity**

250 The high activity of Ru/C with nitrate observed here in comparison with earlier reports warrants
251 further examination. Several studies have documented that the reactivity of supported metal
252 nanoparticles is influenced by nanoparticle size and shape, chemical state, support properties and
253 metal-support interaction, which are subject to the starting materials (support material and metal
254 precursor), synthesis methods and activation steps [36, 78]. The present study used commercially
255 produced catalysts to take advantage of materials with optimized industrial production and adapted for
256 large scale applications. However, the high reactivity with aqueous nitrate of Ru catalysts was
257 demonstrated with the catalyst pretreated *ex situ* in flowing H₂ at 350 °C for 2 h prior to use, and the

258 as-received Ru/C and Ru/Al₂O₃ show low or no activity. To further characterize the effects of *ex situ*
259 pretreatment on catalyst activity, we had commercial Ru/C, Ru/Al₂O₃, Pd/C and Pd/Al₂O₃ subjected to
260 *ex situ* heat treatment (350 °C, 2 h) in both inert gas (N₂) and reducing gas (H₂) and tested of their nitrate
261 reduction activity. The metal mass-normalized pseudo-first-order rate constants for nitrate reduction
262 with these materials are calculated and presented in Fig. 4. *Ex situ* pretreatment of Ru/C, either with
263 flowing H₂ or N₂, leads to more than a threefold increase in catalyst activity compared to the as-received
264 catalyst. The effect of pretreatment is most pronounced for Ru/Al₂O₃, in that the catalyst is only active
265 after pretreatment in flowing H₂. In comparison, pretreatment has no effect on the activity of Pd/C.
266 Pd/Al₂O₃ exhibited no activity for nitrate reduction irrespective of catalyst pretreatment.

267 A battery of characterization analyses was conducted to rationalize the dramatic influence of *ex situ*
268 pretreatment on Ru catalysts. XRD scan of Ru/C (Fig. 5a) shows mainly peaks associated with
269 crystalline carbon phases, but no significant peaks for Ru metal (ca. 44° and 38°, JCPDS card No.
270 06-0663) or RuO₂ (ca. 28°, 35° and 54°, JCPDS card No. 43-1027), indicating small crystal size below
271 XRD detection limit. The XRD pattern for Ru/Al₂O₃ (Fig. 5b) shows crystalline RuO₂ in both the
272 as-received and *ex situ* N₂ pretreated materials, but these features disappear and new features
273 characteristic of crystalline Ru metal appear in the H₂ pretreated Ru/Al₂O₃. For both Ru/C and Ru/Al₂O₃
274 catalysts, the catalyst activity (Fig. 4) roughly correlates with the active Ru surface of catalysts (Table
275 S2), suggesting that catalyst pretreatment increased the Ru surface area active for catalytic reaction.

276 Increasing surface area often results from decreased particle size, which is not the case for Ru/C in
 277 this study. The size distribution of Ru particles in the as-received Ru/C (1.9 ± 0.6 nm, Fig. 3c) is not
 278 statistically different from that measured following the *ex situ* H₂ pretreatment process (2.2 ± 0.8 nm,
 279 Fig. 3a). Another possibility is that the Ru catalyst surface in the as-received Ru/C is blocked by
 280 residues from synthesis, which may be partially or fully removed by the high temperature pretreatment
 281 processes. H₂ TPR analysis provides evidence to support this hypothesis. The TPR profiles (Fig. 6) of *ex*
 282 *situ* H₂- and N₂-pretreated Ru/C are similar, with a first reduction peak located between 50 and 55 °C and
 283 a second broad reduction peak above 400 °C. The reduction peak temperature of supported Ru oxides
 284 formed during catalyst calcination has been reported to vary between 65 °C and 185 °C [79, 80]. Though
 285 the temperature of the first reduction peak observed here falls below this range, the H₂ consumption
 286 quantified from the peak area (Table S2) is consistent with the theoretical stoichiometry for H₂
 287 consumption during RuO₂ reduction [79]:

288 The Ru oxides formed upon re-oxidation of pretreated Ru upon exposure to ambient air are redox-labile,
 289 enabling re-reduction by H₂ at 25 °C. The second reduction peak is assigned to the direct reduction of
 290 aldehyde, quinone and phenol groups on the carbon support [81]. The TPR profile for as-received Ru/C
 291 is markedly different from those of *ex situ* pretreated Ru/C. A much larger H₂ consumption and a dip in
 292 the TCD signal match the features of surface species decomposition and desorption, supporting the
 293 hypothesis that the as-received catalyst surface is blocked by residues that desorb upon heat pretreatment.

294 Temperature-programmed desorption study of as-received Ru/C and *ex situ* H₂ pretreated Ru/C in Ar
295 provides further confirmation of surface species desorption at 47 °C for as-received Ru/C (Fig. S6).
296 Therefore, as-received Ru/C consists of highly reducible Ru oxides that are covered by surface
297 contaminants. The *ex situ* pretreatment of Ru/C increased catalyst activity mainly by removing these
298 surface contaminants while causing minimal effect on Ru oxides particles.

299 The as-received Ru/Al₂O₃ and *ex situ* N₂ pretreated Ru/Al₂O₃ exhibit a TPR pattern consistent with
300 RuO₂ reduction reported in the literature, which is also in agreement with the crystalline RuO₂ identified
301 by XRD analysis. Although the stoichiometry for H₂ consumption of RuO₂ in these two Ru/Al₂O₃
302 catalysts is similar to that of RuO₂ in *ex situ* H₂- and N₂-pretreated Ru/C (Table S2), the Ru oxides on
303 the two supports show significant differences in reducibility as evidenced by the much lower reduction
304 peak temperature of Ru/C catalysts. Besides, the surface of RuO₂ in *ex situ* H₂- and N₂-pretreated Ru/C
305 is easily reduced by H₂ at 25 °C, while the surface of RuO₂ in as-received Ru/Al₂O₃ and *ex situ* N₂
306 pretreated Ru/Al₂O₃ is not reducible with H₂ at 25 °C (Table S2). In contrast, *ex situ* H₂ pretreated
307 Ru/Al₂O₃ shows a small H₂ consumption peak at 45 °C, similar to the highly reducible RuO₂ in *ex situ*
308 H₂- and N₂-pretreated Ru/C and consistent with crystalline metallic Ru in *ex situ* H₂ pretreated Ru/Al₂O₃
309 identified by XRD analysis. Based on these observations, it can be concluded that *ex situ* H₂
310 pretreatment activates Ru/Al₂O₃ by reducing the crystalline RuO₂ to a metallic Ru phase, whose surface
311 is re-oxidized upon exposure to ambient temperature air to a more redox-labile form of RuO₂ (e.g., less
312 crystalline) that can be re-reduced by H₂ at 25 °C. A complete re-oxidation of pretreated Ru/C compared

313 with partial re-oxidation of H₂ pretreated Ru/Al₂O₃ is attributed to a much smaller size of Ru
314 nanoparticles in Ru/C than in Ru/Al₂O₃. The *ex situ* N₂ pretreatment fails to activate Ru/Al₂O₃ due to the
315 inability of N₂ to transform crystalline RuO₂ to redox-labile species. Therefore, it is further confirmed
316 that redox-labile surface Ru oxides are essential to achieve good performance in catalytic nitrate
317 reduction applications.

318 3.3. Catalytic nitrite reduction

319 Based on the prevailing mechanism for nitrate reduction with Pd-based catalysts, the first reduction
320 intermediate is anticipated to be nitrite [32, 82, 83], and the fact that no nitrite intermediate is observed
321 when monitoring nitrate reactions (Fig. 2a) would suggest nitrite reduction is much faster than nitrate
322 reduction at comparable conditions (similar to observations reported for Pd catalysts under most
323 conditions [31, 74, 84]). Compared to nitrate, reduction of nitrite is less well described by a
324 pseudo-first-order rate law, with the reaction appearing to accelerate as nitrite concentration continues to
325 drop after the first two half-lives (Fig. 7a). Nevertheless, the pseudo-first-order rate constants for nitrite
326 reduction over the first two half-lives was calculated to provide a rough measure of catalyst activity to
327 compare with that measured for nitrate reduction under similar conditions. Surprisingly, the observed
328 reaction kinetics for nitrite are markedly slower than for nitrate under the same conditions. The
329 mass-normalized pseudo-first-order rate constant for nitrite reduction derived from the model fit of data
330 in Fig. 7a is $1.44 \pm 0.15 \text{ L} \cdot \text{g}_{\text{Ru}}^{-1} \cdot \text{min}^{-1}$, corresponding to an TOF₀ of $0.73 \pm 0.06 \text{ min}^{-1}$. This value is
331 about one third of the TOF₀ for nitrate measured under the same conditions ($2.1 \pm 0.2 \text{ min}^{-1}$). The lower

activity of nitrite in comparison to nitrate contrasts with typical results reported for Pd-based bimetallic catalysts, where nitrite is much more reactive than the parent nitrate ion [39, 74]. Nitrite reaction with Pd/C at the same conditions shown in Fig. 7a yields a TOF_0 of $57.7 \pm 9.2 \text{ min}^{-1}$.

The isotope labeling mass balance closure experiment conducted with nitrite as a starting reactant (Fig. 2b) further reveals a distinct behavior of Ru-catalyzed nitrite reduction. In contrast to the experiment initiated with nitrate, nitrite reduction yields a mixture of N_2 and ammonium endproducts, and N_2O is observed as a reaction intermediate. Whereas the sole product of nitrate reduction detected is ammonium irrespective of initial nitrate concentration (Fig. 8a), the distribution of N_2 :ammonium observed in nitrite reduction experiments shifts increasingly towards N_2 with increasing initial nitrite concentration (Fig. 8b).

3.4. Site-limited reduction kinetics

As mentioned earlier, measured nitrite concentrations drop below pseudo-first-order kinetic model predictions as the reaction progresses and nitrite concentration decreases (Fig. 7a). To examine this further, TOF_0 of nitrate and nitrite reduction were determined at varying initial concentration of each oxyanion. Results of these measurements (Fig. 7b) reveal contrasting behavior for nitrate and nitrite. For nitrate, the observed trend is consistent with the classical Langmuir-Hinshelwood model for heterogeneous reactions, where TOF_0 increases with increasing initial nitrate concentration until it approaches a maximum value due to saturation of available surface reaction sites [86]. Similar behavior has been documented for many heterogeneous catalytic reactions, including nitrate, nitrite, and bromate

351 reactions with Pd-based catalyst [33, 87, 88]. The small drop in TOF_0 observed at the highest initial
352 nitrate concentration tested may result from competitive adsorption between nitrate and H_2 on the same
353 reaction sites [89]. A contrasting and atypical behavior is observed for nitrite, where TOF_0 values are
354 greatest at the lowest initial nitrite concentration and decrease to minimum value with increasing nitrite
355 concentration. To rationalize this trend within the framework of a Langmuir-Hinshelwood model
356 requires an assumption that nitrite competes directly with H_2 for the same reaction sites and the former
357 has a much higher affinity for the sites than the latter, thereby inhibiting uptake and dissociation of the
358 required H_2 reductant at higher nitrite concentrations. An important implication of this finding is that the
359 relative reactivities observed for nitrate versus nitrite (e.g., [Fig. 7a](#)) are heavily dependent upon the
360 initial oxyanion concentrations used in the reactions. The heightened reactivity of nitrite at low nitrite
361 concentrations can also potentially explain why the species is not observed as a reaction intermediate
362 during Ru catalyst reactions initiated with nitrate; when nitrite is formed at low concentrations on the
363 catalyst surface, its rapid turnover under these conditions prevents detection in the overlying aqueous
364 solution. The competition between nitrite and H_2 adsorption may also contribute to the observed shift in
365 endproduct selectivity towards ammonium at lower initial nitrite concentration ([Fig. 8b](#)); conversion of
366 nitrite to ammonium has a relatively higher stoichiometric requirement for H_2 than reduction to N_2 , so
367 an increase in H_2 :nitrite ratio could favor the pathway for ammonium production by increasing surface
368 coverage of hydrogen and decreasing surface coverage of nitrogen species. The decreasing nitrite

369 concentration is also expected to reduce the rate of N-N pairing reactions necessary to N_2O and N_2 .
370 Detailed pathways will be discussed in the following section.

371 Since separate reactions conducted with nitrate and nitrite suggest that the oxyanions both compete
372 with H_2 for chemisorption at Ru active sites, competitive reactions between the two oxyanions were
373 further examined by reaction initiated with mixtures of nitrate and nitrite. Fig. 7c shows the reaction of
374 an equimolar mixture of nitrate and nitrite at the same conditions as the individual oxyanion reactions
375 shown in Fig. 7a. Interestingly, despite the fact that nitrite reacts slower than nitrate when the two
376 oxyanions are reacted with Ru/C separately, the presence of nitrite severely inhibits nitrate reduction.
377 Nitrate reduction kinetics proceeds in two phases. A severely inhibited reduction phase is observed
378 while nitrite is present, but the reaction accelerates once the nitrite is fully depleted. Variation of the
379 ratio of initial nitrate and nitrite confirmed competition between the two oxyanions for available
380 catalysts reaction sites, since the initial rate of nitrate reduction in the first phase increases with
381 increasing nitrate/nitrite ratio, which is the same case for nitrite reduction measured in the presence of
382 nitrate (Table S3).

383 3.5. Proposed reaction pathway

384 Ru catalysts behave differently from Pd-based catalysts in nitrate reduction product selectivity. For
385 example, Ru catalysts favor complete selectivity for ammonium (Fig. 2a), in contrast with a mixture of
386 ammonium and N_2 endproducts reported for Pd-based bimetallic catalysts [23, 31]. Consistently high
387 (and possibly complete) selectivity for ammonium was observed for Ru catalysts under various solution

388 pH, whereas the ratio between ammonium and N_2 varies with shifting pH conditions for Pd-based
389 bimetallic catalysts [31, 41, 72]. On the other hand, Ru catalysts and Pd-based catalysts share similarity
390 in nitrite reduction product selectivity. For Ru/C, the distribution of N_2 :ammonium shifts increasingly
391 towards N_2 with increasing initial nitrite concentration (Fig. 8b), similar to trends reported for Pd-based
392 catalysts [85]. Scheme 1 depicts the generally accepted mechanism of nitrate reduction on Pd-based
393 catalysts. The experimental observations of nitrite reduction with Ru catalysts appear to be consistent
394 with the reaction pathways proposed for Pd-based catalysts. Reactions initiated with nitrite yield
395 transient intermediates and endproducts consistent with the two parallel pathways for NO reduction (Fig.
396 2b). It may not be straightforward to apply the scheme to nitrate reduction with Ru catalysts considering
397 the differences mentioned above and that reactions initiated with nitrate show no detectable nitrite
398 intermediate (Fig. 2a). However, the lack of observed nitrite intermediate is consistent with the elevated
399 turnover rate of this species observed at low initial concentrations (Fig. 7b) and selective reactivity of
400 nitrite in the presence of nitrate (Fig. 7c). Along this line, the complete selectivity for ammonium is
401 possibly a result of high selectivity to ammonium at low nitrite concentration (Fig. 8b).

402 It should be pointed out that Scheme 1 only provides a macroscopic picture for the reaction. When
403 considering the reaction from the microscopic viewpoint, the mechanism involves much more diverse
404 intermediates that are adsorbed on the surface or in the aqueous phase. To obtain molecular insights into
405 the mechanism of the reaction over Ru, DFT calculations were conducted to evaluate the
406 thermodynamics of adsorption and transformation steps. Adsorption energies and conformations of

major reactants, hypothesized intermediates and products are provided in SI Table S4. The elementary steps underlying the reaction pathways in Scheme 1 are illustrated in Fig. 9, and the energetics of each step are listed in Table S5. The strong adsorption of NO_2^- (-1.3 eV) and NO (-2.0 eV) from water to the Ru cluster surface may be contributing to the fact that desorbed aqueous species of the latter two were never observed during reactions initiated with nitrate. The further sequential reduction of NO_{ads} to $\text{NH}_{3,ads}$ occurs through a series of exothermic reaction steps. Previous observations of the complete selectivity for ammonium in reactions initiated with nitrate (Fig. 8a) and the shift in endproduct selectivity towards N_2 for nitrite reactions conducted with higher initial aqueous concentrations (Fig. 8b) indicate that buildup of aqueous nitrite concentrations is a prerequisite for the reaction pathway leading to diatomic nitrogen species. We found that initiating N-N coupling by reaction of the NO_{ads} intermediate with aqueous nitrite is exothermic, and subsequent reduction of the resulting intermediate to form both the detectable N_2O intermediate and stable N_2 endproduct are also favorable. Some have proposed that NO_{ads} dissociates first to N_{ads} and O_{ads} on catalyst metal surfaces before reacting further to form the observed products [30, 85]. DFT calculations indicate that this route cannot be ruled out based on energetics, but coupling between N_{ads} and NO_{ads} is unfavorable. The findings from DFT calculations that both reaction pathways are thermodynamically favorable implies that the kinetic factors, rather than thermodynamic constraints, are likely responsible for controlling the reaction product selectivity. Calculations of kinetic properties will be needed to provide further insights into the reaction rates and endproduct selectivities observed in experiments.

3.6. Implications for technology development

Results of this study demonstrate that Ru catalysts effectively reduce nitrate at ambient temperature and H₂ pressure. Ru possesses many of the benefits of other Pt group metal catalysts (e.g., high stability) but is less expensive than Pd and Pt, showing potential to reduce barriers to catalyst technology adoption for treatment of recalcitrant water contaminants. The reductant (H₂) is low cost, can be generated on-site electrochemically, and has lower life-cycle environmental impacts than organic electron donors typically used in biological denitrification processes [24]. The catalysts used in the study are a commercially available material from a vendor capable to high volume production, making the process accessible to near-term commercial applications. The sole endproduct from nitrate reduction by the supported Ru catalysts investigated was ammonium, indicating that Ru catalysts are not suitable for treating drinking water with dilute nitrate in a single process. On the other hand, highly selective conversion of nitrate to ammonium, especially in concentrate matrices like waste ion exchange regenerant brines [90], if followed by separation unit processes (e.g., membrane electrolysis [91]), may be a promising strategy for sustainably recovering an economically valuable product (e.g., (NH₄)₂SO₄), which is in line with a growing interest in resource recovery from waste streams [92]. A number of technology development challenges remain to demonstrate viability, safety, and to de-risk the technology, but findings in this study suggest a path forward for development of an economical and sustainable technology for treatment and resource recovery from nitrate-contaminated water sources.

444 Rational design that emphasizes “design-for-purpose” is important to advance next-generation water
445 treatment technologies [93]. Pt group metals are known to activate H₂. In order to couple H₂ oxidation
446 with nitrate reduction, the activity of nitrate activation on Ru and the steps controlling selectivity need to
447 be understood and is the objective of this study. Examination of the reaction mechanism revealed that
448 selectivity for N₂ endproduct is limited during nitrate reduction with the Ru catalyst formulations
449 examined here because N-N coupling requires significant aqueous nitrite concentrations to buildup and
450 pairing between adsorbed N species is negligible. This suggests a target for future Ru catalyst design:
451 tailor active sites for selective adsorption with nitrate over nitrite and/or reducing barriers to mobility
452 and pairing of adsorbed N species. Surface alloying may be used to alter small molecule binding
453 strength and rates of surface species diffusion [94, 95]. Alternatively, bio-inspired catalyst structures that
454 attempt to mimic the multi-component features and activated metalloenzyme centers of biological
455 systems may offer a promising strategy for enhancing catalyst activity. For example, Liu and co-workers
456 recently demonstrated >100-fold improvement in catalytic reduction of the recalcitrant oxyanion
457 perchlorate by modifying the Re component within Pd-Re/C bimetallic catalysts by complexing with
458 oxazoline ligands that enhance the metal’s oxygen atom transfer (OAT) reactivity [96], mimicking the
459 design of Mo-centered OAT metal complexes in the perchlorate reductase enzyme. Inspired by the
460 heme-containing active sites of nitrate and (per)chlorate reductase, Ford and co-workers constructed a
461 non-heme iron complex for catalytic nitrate and perchlorate reduction, and the homogeneous catalyst is

regenerated by electrons and protons provided by 1,2-diphenylhydrazine [97]. Biomimetic catalysts incorporating Ru as the active metal center for nitrate or nitrite reduction have not been reported to date.

4. Conclusions

Supported Ru nanoparticles showed promising catalytic performance in reducing nitrate in water at ambient temperature and H₂ pressure. It is demonstrated that Ru has a high intrinsic activity in nitrate activation, which is five times higher than that of Pd under standard testing conditions. The key features for supported Ru catalysts that need to be controlled to achieve high activity are that reduced Ru surface can be obtained by H₂ reduction at reaction temperature and that the surface is not blocked by synthesis residues. Ru reduces nitrate selectively to ammonium, while nitrite is reduced to yield a mixture of N₂ and ammonium, with selectivity shifting towards N₂ at increasing nitrite:hydrogen ratio. The reaction mechanism is proposed that sequential hydrogenation of nitrate to nitrite and NO is followed by parallel pathways involving the adsorbed NO: (1) sequential hydrogenation to ammonium, and (2) N-N coupling with aqueous nitrite followed by hydrogenation to the detected N₂O intermediate and N₂ endproduct. Future work is needed to strategically design catalyst to control selectivity and develop integrated processes for nitrogen recovery.

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Captions

Scheme 1. Nitrate hydrogenation pathway on Pd-based bimetallic catalysts

Fig. 1. Measured reaction timecourses for nitrate reduction and first-order model fits on 5 wt% Ru/C, 5 wt% Pd/C, and 5 wt% Pd-1 wt% Cu/C in the semi-batch reactor system ($0.2 \text{ g}\cdot\text{L}^{-1}$ catalyst, $[\text{NO}_3^-]_0 = 1.6 \text{ mM}$, 1 atm H_2 continuous sparging except in control experiments where 1 atm N_2 continuous sparging was used, pH 5.0 maintained by pH stat, $25 \pm 0.5^\circ\text{C}$). Error bars represent standard deviations of triplicate reactions.

Table 1. Properties of catalysts used for nitrate activity test

Fig. 2. Timecourses showing aqueous and gaseous intermediates and products during Ru/C-catalyzed reduction of ^{15}N -labeled (a) nitrate and (b) nitrite monitored in closed-bottle batch systems ($0.2 \text{ g}\cdot\text{L}^{-1}$ catalyst, $[\text{NO}_3^-]_0$ or $[\text{NO}_2^-]_0 = 1.6 \text{ mM}$, initially 1 atm H_2 , pH 5.5 buffered by 40 mM MES, $21 \pm 1^\circ\text{C}$). Error bars represent standard deviations of triplicate reactions (smaller than symbol if not visible).

Fig. 3. HAADF-STEM images of (a) *ex situ* H_2 pretreated Ru/C, (b) Ru/C after re-use experiment, (c) as-received Ru/C and (d) *ex situ* H_2 pretreated Ru/ Al_2O_3 . The insets show Ru particle size distributions.

Fig. 4. Influence of catalyst pretreatments (as-received catalyst or *ex situ* pretreated in flowing H_2 or N_2 at 350°C for 2 h) on reactivity with aqueous nitrate ($0.2 \text{ g}\cdot\text{L}^{-1}$ catalyst with nominal 5 wt% Ru or Pd, $[\text{NO}_3^-]_0 = 1.6 \text{ mM}$, 1 atm H_2 continuous sparging, pH 5.0 maintained by automatic pH stat, $25 \pm 0.5^\circ\text{C}$). Error bars represent standard deviations of triplicate reactions (smaller than symbol if not visible). NR = no reaction observed.

Fig. 5. XRD patterns of (a) Ru/C and (b) Ru/ Al_2O_3 collected after different *ex situ* pretreatments. Peaks assigned to Ru metal ($\circ$) and RuO_2 (*) are indicated.

Fig. 6. TPR profiles of (a) as-received Ru/C, (b) *ex situ* N_2 pretreated Ru/C, (c) *ex situ* H_2 pretreated Ru/C, (d) as-received Ru/ Al_2O_3 , (e) *ex situ* N_2 pretreated Ru/ Al_2O_3 , and (f) *ex situ* H_2 pretreated Ru/ Al_2O_3 . TCD signals are normalized with sample mass.

Fig. 7. (a) Comparison of Ru/C-catalyzed nitrite reaction kinetics with nitrate reaction at standard conditions ($0.2 \text{ g}\cdot\text{L}^{-1}$ Ru/C, $[\text{NO}_3^-]_0$ or $[\text{NO}_2^-]_0 = 1.6 \text{ mM}$). (b) TOF_0 of Ru/C-catalyzed nitrate and nitrite reduction as a function of initial concentration of the target oxyanion ($0.2 \text{ g}\cdot\text{L}^{-1}$ Ru/C). (c) Measured timecourses for the simultaneous reduction of nitrate and nitrite added to a suspension containing Ru/C ($0.2 \text{ g}\cdot\text{L}^{-1}$ catalyst, $[\text{NO}_3^-]_0 = [\text{NO}_2^-]_0 = 1.6 \text{ mM}$). Other conditions include 1 atm H_2 continuous sparging, pH 5.0 maintained by automatic pH stat, and $25 \pm 0.5^\circ\text{C}$. Error bars in panels a-b represent standard deviations of triplicate reactions.

663

664 **Fig. 8.** Effect of initial (a) nitrate and (b) nitrite concentration on NH_4^+/N_2 product selectivity (yellow:
665 NH_4^+ ; blue: N_2). Product selectivity is based on percent molar N concentration. Error bars represent
666 standard deviations of triplicate reactions (smaller than symbol if not visible).

667

668 **Fig. 9.** Energy profile of the most thermodynamically favorable reaction pathways for aqueous nitrate
669 and nitrite reduction on Ru_{18} clusters as calculated using PBE0 functional and LANL2DZ
670 (Ru)/6-31+G(d,p)(N, H, O) basis sets.

671
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 676 mM, 1 atm H_2 continuous sparging except in control experiments where 1 atm N_2 continuous sparging
 677 was used, pH 5.0 maintained by pH stat, $25 \pm 0.5^\circ\text{C}$). Error bars represent standard deviations of
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679 **Table 1.** Properties of catalysts used for nitrate activity test

Catalyst	BET surface area (m ² ·g ⁻¹)	Total pore volume ^a (cm ³ ·g ⁻¹)	Average pore diameter ^b (nm)	Metal loading (wt%)	Metal dispersion (%)	Active surface (%)	Chemisorption particle size (nm)	TEM particle size (nm)	TOF ₀ (min ⁻¹) ^c
Ru/C	859.7	0.74	3.46	5.38 ^d	38	32	3.5	2.2±0.8	2.1±0.2
Ru/Al ₂ O ₃	93.1	0.36	15.34	5 ^e	15	9	8.8	8.1±3.0	2.4±0.5
Pd/C	856.9	0.72	3.35	6.24 ^d	17	19	6.5	4.1±2.2	0.42±0.07
Pd/Al ₂ O ₃	98.4	0.24	9.69	5.85 ^d	16	15	6.9	4.2±1.1	NR ^f

680 ^aAdsorption total pore volume at P/P₀ = 0.97. ^bCalculated from total pore volume and BET surface area. ^cCalculated based on active surface. ^dMeasured by
681 ICP-OES analysis. ^eNominal value provided by supplier. ^fNo reaction observed.

Fig. 2. Timecourses showing aqueous and gaseous intermediates and products during Ru/C-catalyzed reduction of ¹⁵N-labeled (a) nitrate and (b) nitrite monitored in closed-bottle batch systems (0.2 g·L⁻¹ catalyst, [¹⁵NO₃⁻]₀ or [¹⁵NO₂⁻]₀ = 1.6 mM , initially 1 atm H₂, pH 5.5 buffered by 40 mM MES, 21 ± 1°C). Error bars represent standard deviations of triplicate reactions (smaller than symbol if not visible).

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