Detection of Hydroxylamine Intermediate Opens a New Perspective on Ammonia Selectivity in Metal-Catalyzed Nitrate Reduction

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Significance and Relevance

In the catalytic reduction of nitrates in drinking water, undesired NH_4^+ formation is the main drawback yet hindering this technology from industrial application. Despite that most studies claim nitrites (NO_2^-), ammonium cations (NH_4^+), and nitrogen (N_2) as the exclusive reaction products, we found hydroxylamine (NH_2OH) as additional product under typical NO_3^- reduction conditions (~pH 6). We observed the degradation of NH_2OH into NH_4^+ over time suggesting that NH_2OH may be formed in typical NO_3^- reduction systems, but might be overseen if not specifically searched for. This observation questions not only NH_4^+ selectivity in existing studies, but also gives a new perspective on the underlaying reaction mechanism of the catalytic NO_3^- reduction.

Introduction and Motivations

In the European Union around 14 % of the groundwater stations exceeded the NO_3^- limit of 50 mg/L, and about one third of the land waters and more than 80 % of the ocean waters in the EU are considered eutrophic, showing the demand for improved NO_3^- management.[1] Catalytic NO_3^- reduction is a potential technology to remove NO_3^- from water bodies by actually degrading it into harmless N_2, which makes it in this aspect superior to alternative techniques such as reverse osmosis, ion exchange or electrodialysis as no concentrated waste brines are generated.[2] Bimetallic Pd-Cu, Pd-Sn and Pd-In catalysts actively reduce NO_3^- in the presence of H_2 at RT and atmospheric pressure while the major challenge is the undesired NH_4^+ production as e.g. the limits in drinking water are even stricter than for NO_3^- (0.5 mg/L vs. 50 mg/L).[2]

The standard procedure in scientific literature is to determine NH_4^+, NO_2^- and NO_3^- concentrations by IC or HPLC, assuming that the remainder is N_2. Closing the N mass balance entirely is extremely challenging as gas and liquid phase samples exhibit a delay but must be matched. Additionally, contamination with atmospheric N_2 is difficult to suppress. Only few studies achieve a closed mass balance over parts of the reaction time,[4] or during the entire reaction only by using isotope labeled N.[3] In this study, we show an easy method to detect NH_2OH in NO_3^- reduction as it is easily overseen if not carefully checked for.

Materials and Methods

A Pd/Al_2O_3 catalyst (2.5 wt% Pd, 181 m^2/g, < 45 µm) was prepared via Strong Electrostatic Adsorption method ($[Pd(NH_4)_4](NO_3)_2$ and $NH_{3,aq}$). From this, a bimetallic $SnPd/Al_2O_3$ (Pd : Sn ratio 1.4 : 1) catalyst was prepared via sequential impregnation ($SnCl_2$ in ethanol). The catalysts were characterized by XRF, CO-chemisorption, N_2-physisorption, XRD and TEM. NO_3^- and NO_2^- (1 mM) were converted in a 1 L semi-batch reactor under continuous gas flow (H_2, CO_2, He) in the absence of mass transport limitations. Liquid samples were taken over time and benzaldehyde or acetone were added to derivatize NH_2OH into the corresponding oxime. NO_3^-, NO_2^- and NH_4^+ were quantified by ion chromatography and the oxime by HPLC or GC after derivatization.

Results and Discussion

In a conventional NO_3^- reduction experiment over a $SnPd/Al_2O_3$ catalyst, NO_2^- is only observed in traces (≤0.01 mM) and the NH_4^+ concentration increases with increasing NO_3^- conversion but plateaus after full NO_3^- depletion. However, we observed increasing NH_4^+ concentrations even after full NO_3^-

conversion. Therein, the NH_4^+ concentration increase was larger than the accessible moles of metal surface and could thus not be explained by desorption of surface N-species suggesting an additional reaction intermediate, which could be defined as NH_2OH by it trapping into an oxime with benzaldehyde or acetone (Figure 1 **B**).

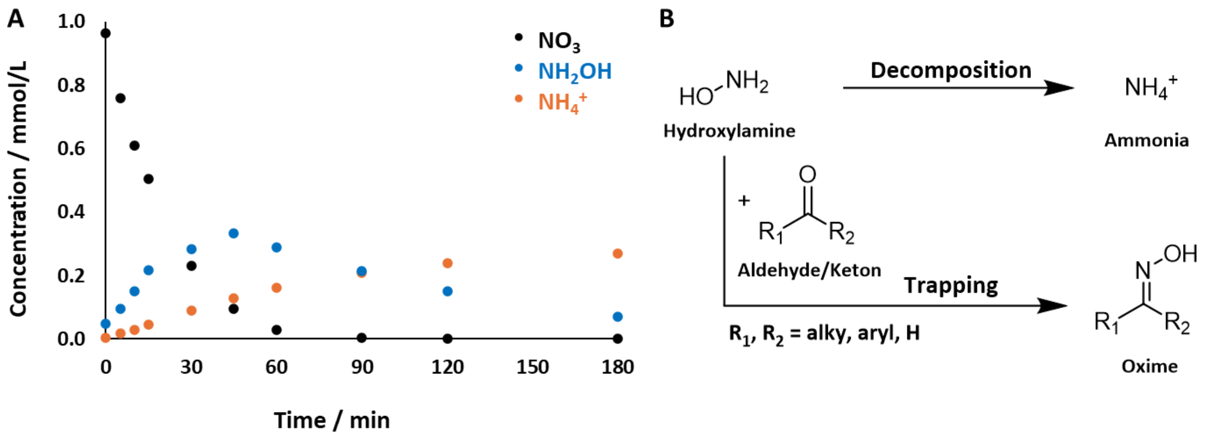

Figure 1: **A** Concentration profile of NO_3^- reduction reaction. Reaction conditions: 1 mM KNO_3, 50 mg $SnPd/Al_2O_3$, 80:10:10 mL/min H_2:CO_2:He, RT, 300 mL milli-Q water, 600 rpm. **B** Schematic reaction pathway of NH_2OH trapping into an oxime or decomposition into NH_4^+.

The typical concentration profile in Figure 1 **A** shows an initially strong NH_2OH formation resulting in a maximum NH_2OH selectivity of 47 %. Over time, NH_2OH decomposes mainly into NH_4^+, but as the sum of NH_2OH and NH_4^+ concentration decreases, also partly into N_2. The NH_2OH decomposition occurs also after catalyst removal and is thus non-catalytic. Experiments to elucidate whether the decomposition follows a hydrogenation or disproportionation are ongoing.

The addition of hydroxylamine scavenger in the reactor does not entirely suppress the NH_4^+ formation indicating that probably not all NH_4^+ is formed via the NH_2OH pathway or, less likely, the difference in oxime formation rate and NH_2OH decomposition rate is insufficiently large to trap all NH_2OH. These research questions are currently under investigation in our group also for the NO_2^- reduction on $SnPd/Al_2O_3$ and Pd/Al_2O_3 catalysts.

This study suggests that NH_2OH is possibly a key reaction intermediate in the NO_3^- reduction reaction over a $SnPd/Al_2O_3$ catalyst. Trapping this NH_2OH using acetone or benzaldehyde into an oxime offers a simple and transferrable quantification strategy, which can substantially improve our understanding of this reaction. The detection of NH_2OH as reaction intermediate should encourage to critically question reported NH_4^+ selectivity and more broadly the reaction mechanism behind NH_4^+ and N_2 formation.

References

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