

Cite this: *J. Mater. Chem. A*, 2026, **14**, 17237

# Hydroxylamine intermediate governs selectivity in nitrite hydrogenation on Pd-based catalysts for sustainable water treatment

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Catalytic hydrogenation of nitrate ( $\text{NO}_3^-$ ) and nitrite ( $\text{NO}_2^-$ ) is a promising route for drinking water purification and rebalancing the global nitrogen cycle. Recently, hydroxylamine ( $\text{NH}_2\text{OH}$ ) was detected as a persistent reaction intermediate although ammonium ( $\text{NH}_4^+$ ) and dinitrogen ( $\text{N}_2$ ) were assumed to be the only significant reaction products for several decades. In this work, we systematically investigate  $\text{NO}_2^-$  hydrogenation over  $\text{Pd}/\text{Al}_2\text{O}_3$  and  $\text{SnPd}/\text{Al}_2\text{O}_3$  while explicitly quantifying  $\text{NH}_2\text{OH}$  under various conditions, including changes in  $\text{H}_2$  partial pressure, the initial  $\text{NO}_2^-$  concentration, and reaction temperature, and through co-feeding of  $\text{NH}_2\text{OH}$ . We reveal that  $\text{NH}_4^+$  selectivity depends strongly on the  $\text{NO}_2^-$  conversion level, reflecting shifts in surface coverages as the reaction progresses. Suppression of both  $\text{NH}_2\text{OH}$  and  $\text{NH}_4^+$  formation is only achievable under  $\text{H}_2$ -deficient conditions, though this comes at the expense of lower overall hydrogenation activity. Elevated temperatures enhance  $\text{NH}_2\text{OH}$  decomposition and thereby promote  $\text{NH}_4^+$  formation, while leaving  $\text{N}_2$  selectivity largely unaffected. Co-feeding experiments further show that externally introduced  $\text{NH}_2\text{OH}$  does not influence the  $\text{NO}_2^-$  hydrogenation rate. We critically reviewed prior mechanistic studies on  $\text{NO}_2^-$  hydrogenation and propose a refined Langmuir–Hinshelwood scheme that explicitly incorporates  $\text{NH}_2\text{OH}$  as a desorbed intermediate. This work highlights the importance of  $\text{NH}_2\text{OH}$  in the reaction network and underscores the need to include it in the assessment of the reaction selectivity.

Received 5th January 2026  
Accepted 6th March 2026

DOI: 10.1039/d6ta00106h

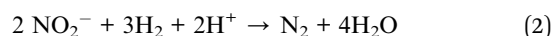
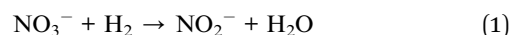
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## 1 Introduction

Nitrate ( $\text{NO}_3^-$ ) and nitrite ( $\text{NO}_2^-$ ) are water contaminants that pose a serious threat to both human health and aquatic ecosystems if not properly controlled. Although these species are natural components of the biogeochemical nitrogen cycle, the excessive use of nitrogen-based fertilizers has severely disrupted this balance in recent decades.<sup>1–4</sup> As a consequence, nitrogen nutrient levels have risen in inland, coastal, and marine waters, driving eutrophication.<sup>5</sup> Eutrophication negatively impacts entire ecosystems by reducing biodiversity of animals and plants. In addition, elevated nitrate and nitrite concentrations can directly affect human health. When present in drinking water, these species may cause methemoglobinemia—commonly known as “blue baby syndrome”<sup>6</sup> and have, therefore, strict limits (50 and 5 mg L<sup>-1</sup>, respectively).<sup>7</sup>

Catalytic nitrate and nitrite reduction has emerged as a promising technology to convert these species into harmless

dinitrogen ( $\text{N}_2$ ).<sup>8</sup> In contrast to alternative remediation methods such as reverse osmosis, ion exchange, or electrodialysis, catalytic reduction degrades the contaminants rather than concentrating them into waste brines.<sup>8</sup> Nitrate is first reduced to nitrite, which is then further hydrogenated to  $\text{N}_2$ . In this reaction network, the hydrogenation of nitrate to nitrite is the rate determining step (RDS) and requires a bimetallic catalyst (*e.g.* Sn–Pd, Cu–Pd, or In–Pd), while the subsequent nitrite hydrogenation can be catalyzed by Pd alone.<sup>9–12</sup>



The main challenge for application remains the formation of ammonium ( $\text{NH}_4^+$ ), which follows even stricter regulations (0.5 mg L<sup>-1</sup>).<sup>13</sup>



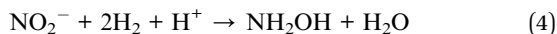
While the formation of  $\text{NH}_2\text{OH}$  in electro- and photocatalytic  $\text{NO}_3^-$  and  $\text{NO}_2^-$  reduction has been reported in the past,<sup>14–16</sup> its presence in thermo-catalytic conversion was only reported very recently. The results showed that hydroxylamine ( $\text{NH}_2\text{OH}$ ) is an

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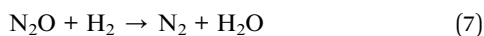
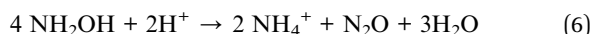
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omnipresent and long-lasting reaction intermediate under various reaction conditions on several different catalysts (eqn (4)).<sup>17</sup> Until then, a pervasive assumption in the field was that N<sub>2</sub> and ammonium (NH<sub>4</sub><sup>+</sup>) were the only relevant reaction products of thermocatalytic NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> hydrogenation under relevant reaction conditions for drinking water purification.<sup>8–12,18–22</sup>



Hydroxylamine is highly toxic and harmful for water bodies<sup>23</sup> and therefore represents a major challenge for the application of NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> as water purification technology. Upon extension of the reaction time, NH<sub>2</sub>OH can be hydrogenated to NH<sub>4</sub><sup>+</sup> (eqn (5)) or disproportionate into NH<sub>4</sub><sup>+</sup> and nitrous oxide (N<sub>2</sub>O, eqn (6)). The latter is quickly further hydrogenated into N<sub>2</sub> (eqn (7)).<sup>24</sup>



Thus, NH<sub>2</sub>OH is at least 50% decomposed into undesired NH<sub>4</sub><sup>+</sup>. In previous research it was shown that NH<sub>2</sub>OH decomposition proceeds exclusively *via* the hydrogenation pathway in the absence of NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> and in the presence of H<sub>2</sub> over a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. In contrast, in the presence of residual NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> or their remaining surface species adsorbed on the catalyst, the hydrogenation and the disproportionation pathway contribute to the NH<sub>2</sub>OH decomposition.<sup>17</sup>

In this study, NH<sub>2</sub>OH is used as a reaction marker to unravel the interplay between the reaction rate of NO<sub>2</sub><sup>-</sup> hydrogenation and the selectivity to NH<sub>2</sub>OH, NH<sub>4</sub><sup>+</sup> and N<sub>2</sub>. To do this we investigated detailed reaction kinetics for the NO<sub>2</sub><sup>-</sup> hydrogenation on Pd/Al<sub>2</sub>O<sub>3</sub> and SnPd/Al<sub>2</sub>O<sub>3</sub> catalysts at different H<sub>2</sub> partial pressures, initial NO<sub>2</sub><sup>-</sup> concentrations, and temperatures while monitoring the NH<sub>2</sub>OH and NH<sub>4</sub><sup>+</sup> concentrations to deliver a complete picture of the selectivity patterns and reaction order dependencies. The results drastically change the prevailing view that ammonia and nitrogen are the only two reaction products while showcasing the complex interdependence between hydrogen, nitrite, and hydroxylamine ratios in the observed kinetics and product distribution.

## 2 Materials and methods

### 2.1 Materials

Pd/Al<sub>2</sub>O<sub>3</sub> and Tin(II) chloride (SnCl<sub>2</sub>) were purchased from Fisher Scientific and potassium nitrate (KNO<sub>3</sub>), potassium nitrite (KNO<sub>2</sub>), benzaldehyde (≥99.5%), benzaldehyde oxime (≥96.5%) and hydroxylamine (50 wt% in H<sub>2</sub>O) were purchased from Sigma Aldrich.

### 2.2 Catalyst preparation

Pd/Al<sub>2</sub>O<sub>3</sub> was dried before use and sieved to a support particle size <25 μm. SnPd/Al<sub>2</sub>O<sub>3</sub> was prepared from the same Pd/Al<sub>2</sub>O<sub>3</sub>

(<25 μm) *via* controlled surface deposition.<sup>25,26</sup> Therefore, Pd/Al<sub>2</sub>O<sub>3</sub> was suspended in water and exposed to a continuous gas flow of 80 : 10 : 10 mL min<sup>-1</sup> H<sub>2</sub> : He : CO<sub>2</sub> to reduce the catalyst for 30 min at RT. SnCl<sub>2</sub> was dissolved in degassed Milli-Q water and a volume containing Sn in amounts corresponding to 40% of the monolayer capacity of Pd based on CO-chemisorption was added to the catalyst suspension. The suspension is stirred for another 30 min and subsequently filtered to recover the catalyst powder. The filter cake was dried in a vacuum at 70 °C followed by calcination (500 °C in 50 mL min<sup>-1</sup> air, 5 °C min<sup>-1</sup>, 5 h) and reduction (500 °C in 30 mL min<sup>-1</sup> H<sub>2</sub> and N<sub>2</sub> each, 5 °C min<sup>-1</sup>, 5 h) in a tube oven. The catalyst is stored in air at ambient temperature.

### 2.3 Catalyst characterization

The metal loadings were determined with X-ray fluorescence (XRF). For the measurements a Bruker S8 Tiger Series 1 4 kW X-ray spectrometer was used. The samples were measured as powder, in a sample cup with a Mylar film, in a helium environment. The concentrations of each element were calculated from the Kα or Lα lines of all elements, using the internal database. The metal dispersion and metal particle sizes were determined by CO-chemisorption. Therefore, the samples were reduced in H<sub>2</sub> for 1 h and purged with He for 20 min followed by CO-pulsing (all at RT, Micromeritics Chemisorb 2750). A Pd : CO 1 : 1 ratio and the geometry factor for a hemisphere (6) are assumed. The Brunauer–Emmet–Teller (BET) surface area was determined *via* N<sub>2</sub> physisorption at -196 °C after outgassing for 24 h at 300 °C (Micromeritics Tristar 3000). The characterization results are summarized in Table 1.

### 2.4 Catalytic testing

In a typical experiment, Pd/Al<sub>2</sub>O<sub>3</sub> or SnPd/Al<sub>2</sub>O<sub>3</sub> was suspended in 297 mL of deionized water in a 1 L baffled glass reactor equipped with a four-blade magnetic stirrer. The catalyst was reduced *in situ* under continuous gas flow (80 : 10 : 10 mL min<sup>-1</sup> H<sub>2</sub> : CO<sub>2</sub> : He) for 1 h at 600 rpm. After the activation period, 3 mL of a KNO<sub>2</sub> stock solution was injected to reach the desired initial concentration and to initiate the reaction. Liquid samples were withdrawn periodically, passed through a 0.2 μm syringe filters to remove catalyst particles to terminate the reaction in the sample, and subsequently analyzed. NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> concentrations were analyzed *via* ion chromatography (IC, a Dionex ICS-3000 with electronic suppression, Thermo Fisher AS19 and CS12 columns with 20 mmol L<sup>-1</sup> potassium hydroxide (KOH) and 20 mmol L<sup>-1</sup> methane sulfonic acid (MSA) as eluents and an Automate 2000 autosampler). For NH<sub>2</sub>OH determination, 0.5 μL benzaldehyde was added right after sampling to derivatize NH<sub>2</sub>OH to benzaldehyde oxime.<sup>17</sup> Benzaldehyde oxime was quantified *via* HPLC (Shimadzu HPLC10AVP with an autosampler, a C18 hypersil gold column, a MeOH : H<sub>2</sub>O (30 : 70 V% eluent, and a UV-vis detector at 248 nm). IC and HPLC analysis were conducted from the same sample vial and RT refers to 22 °C. In some experiments the analysis of the gas phase was attempted but ambient N<sub>2</sub> could not sufficiently be suppressed to ensure satisfactory sensitivity.



Table 1 Catalyst material properties based on N<sub>2</sub> physisorption, XRF and CO-chemisorption

Catalyst	BET surface area	Pd loading	Sn loading	Average Pd particle size
Pd/Al <sub>2</sub> O <sub>3</sub>	110 m <sup>2</sup> g <sup>-1</sup>	8.1 wt%	—	10.3 nm
SnPd/Al <sub>2</sub> O <sub>3</sub>	—	8.4 wt%	0.7 wt%	—

In these approaches NO, NO<sub>2</sub> or N<sub>2</sub>O could be detected. The selectivity was calculated as  $S_{\text{NH}_4^+} = \frac{[\text{NH}_4^+]_t}{([\text{NO}_2^-]_0 - [\text{NO}_2^-]_t)}$  or  $S_{\text{NH}_2\text{OH}} = \frac{[\text{NH}_2\text{OH}]_t}{([\text{NO}_2^-]_0 - [\text{NO}_2^-]_t)}$  and the remaining fraction to 1 considered as N<sub>2</sub>.

### 3 Results and discussion

#### 3.1 NO<sub>2</sub><sup>-</sup> hydrogenation on Pd/Al<sub>2</sub>O<sub>3</sub> at RT

The NO<sub>2</sub><sup>-</sup> hydrogenation was conducted in a concentration window of 0.26–6.5 mmol L<sup>-1</sup> at 0.8 bar H<sub>2</sub> and at H<sub>2</sub> partial pressures between 0.05 and 0.8 bar for 0.8 mmol L<sup>-1</sup> NO<sub>2</sub><sup>-</sup> in the absence of internal (SI, Fig. 1) and external mass transport limitations.<sup>27,28</sup> Initial rate constants were obtained from concentration–time profiles (SI, Fig. 2) and plotted in log–log form (Fig. 1) to determine the reaction orders. At RT, a reaction order close to zero with respect to NO<sub>2</sub><sup>-</sup> and ~0.2 with respect to H<sub>2</sub> was observed, confirming previous results from our group.<sup>27,28</sup>

Thus, the NO<sub>2</sub><sup>-</sup> hydrogenation activity at room temperature is independent of the NO<sub>2</sub><sup>-</sup> concentration, while slightly accelerated by increasing H<sub>2</sub> partial pressure. The low sensitivity towards both NO<sub>2</sub><sup>-</sup> and H<sub>2</sub> concentrations suggests that the catalyst surface is predominantly covered by intermediates prior to the rate-determining step, leaving few sites available for additional NO<sub>2</sub><sup>-</sup> or H<sub>2</sub> adsorption. This interpretation is consistent with previous Attenuated Total Reflection Infrared Spectroscopy (ATR-IR) studies as discussed later.<sup>29–31</sup>

To evaluate the selectivity of the reaction, NH<sub>4</sub><sup>+</sup> and NH<sub>2</sub>OH concentrations were measured delivering a typical reaction profile as shown in Fig. 2A. Initially both NH<sub>4</sub><sup>+</sup> and NH<sub>2</sub>OH concentrations increase with decreasing NO<sub>2</sub><sup>-</sup> concentration. While the NH<sub>4</sub><sup>+</sup> concentration consistently increases, the

NH<sub>2</sub>OH concentration passes through a maximum and subsequently decreases illustrating its intermediary nature. The remaining part of the converted NO<sub>2</sub><sup>-</sup> is assumed to be N<sub>2</sub>. The NH<sub>4</sub><sup>+</sup> selectivity ranges from <1% to 10%, depending on the H<sub>2</sub> partial pressure and the NO<sub>2</sub><sup>-</sup> conversion level. The NH<sub>4</sub><sup>+</sup> concentration increases at a faster rate when NO<sub>2</sub><sup>-</sup> is near full conversion, reflecting shifts in surface coverages during the reaction. When plotted as a function of NO<sub>2</sub><sup>-</sup> conversion, the NH<sub>4</sub><sup>+</sup> selectivity follows a U-shaped dependence (Fig. 2B). Before NO<sub>2</sub><sup>-</sup> injection (*i.e.*, at the start of the reaction), the catalyst is activated in H<sub>2</sub>-saturated water, giving high surface H-coverage and a high H : N ratio, which promotes NH<sub>4</sub><sup>+</sup> formation. As the reaction proceeds, H-coverage decreases while N-coverage increases, favoring N–N coupling and thereby enhancing N<sub>2</sub> selectivity. At high NO<sub>2</sub><sup>-</sup> conversion, N-species are depleted, the H : N ratio shifts back toward higher H-coverage, and NH<sub>4</sub><sup>+</sup> selectivity increases again. Thus, the time required to achieve a pseudo steady state is an intrinsic disadvantage of batch experiments due to their transient nature. The competitive adsorption of NO<sub>2</sub><sup>-</sup> and H<sub>2</sub> was demonstrated by Postma *et al.*<sup>32</sup> and Huang *et al.*<sup>28</sup> but is often not considered in batch experiments. This highlights the importance of monitoring NH<sub>4</sub><sup>+</sup> selectivity over the entire conversion range, since relying on initial selectivity is likely biased by the initial high H-coverage. While NH<sub>4</sub><sup>+</sup> formation generally decreases with decreasing H<sub>2</sub> partial pressure, substantial NH<sub>4</sub><sup>+</sup> suppression occurs only under strongly H<sub>2</sub>-deficient conditions (0.05 bar, Fig. 2B), which also reduces the NO<sub>2</sub><sup>-</sup> hydrogenation rate. This dependence reflects the higher H<sub>2</sub> demand for NH<sub>4</sub><sup>+</sup> formation relative to NO<sub>2</sub><sup>-</sup> hydrogenation (3 vs. 1.5 H<sub>2</sub> per NO<sub>2</sub><sup>-</sup>, see eqn (2) and (3)).

Despite the intermediary character of NH<sub>2</sub>OH, monitoring NH<sub>2</sub>OH is crucial as its maximum concentration at RT is typically observed around full NO<sub>2</sub><sup>-</sup> conversion (Fig. 1C), thus representing a point where the reaction could otherwise be

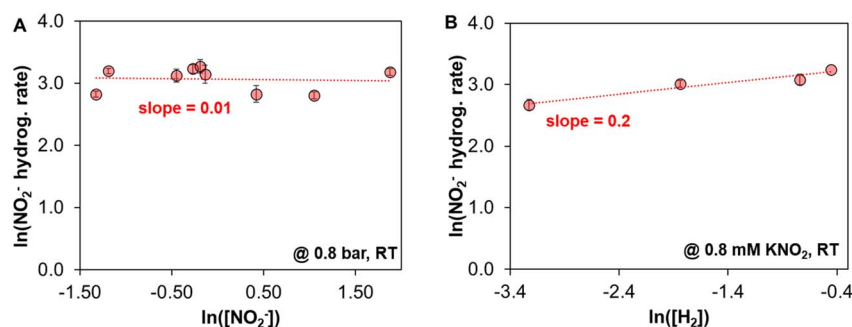


Fig. 1 Effect of NO<sub>2</sub><sup>-</sup> (A) and H<sub>2</sub> concentration (B) on the NO<sub>2</sub><sup>-</sup> hydrogenation rate on Pd/Al<sub>2</sub>O<sub>3</sub>. Reaction conditions: 300 mL H<sub>2</sub>O, 0.3–6.5 mmol L<sup>-1</sup> KNO<sub>2</sub>, 10 mg Pd/Al<sub>2</sub>O<sub>3</sub>, 10 mL min<sup>-1</sup> CO<sub>2</sub>, 5–80 mL min<sup>-1</sup> H<sub>2</sub> and He to balance to 100 mL min<sup>-1</sup> total flow, RT, 600 rpm.



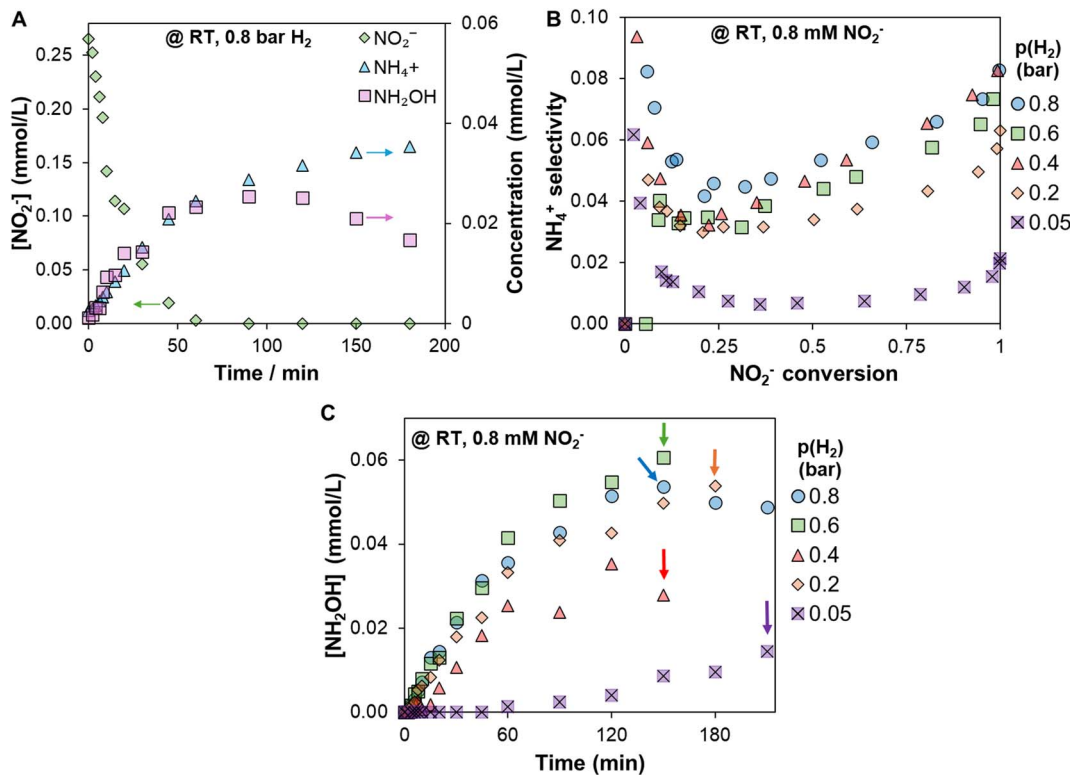


Fig. 2 Typical concentration profile of  $\text{NO}_2^-$  hydrogenation (A),  $\text{NH}_4^+$  selectivity as a function of  $\text{NO}_2^-$  conversion (B) and  $\text{NH}_2\text{OH}$  concentration as a function of time in which arrows indicate full  $\text{NO}_2^-$  conversion (C). Reaction conditions: 300 mL  $\text{H}_2\text{O}$ , 10 mg  $\text{Pd}/\text{Al}_2\text{O}_3$ , 0.8 mmol  $\text{L}^{-1}$   $\text{KNO}_2$ , 10 mL  $\text{min}^{-1}$   $\text{CO}_2$ , 5–80 mL  $\text{min}^{-1}$   $\text{H}_2$  and He to balance to 100 mL  $\text{min}^{-1}$  total flow, RT, 600 rpm.

mistakenly considered complete. While the  $\text{NH}_2\text{OH}$  selectivity ranges from 3–8% at  $\text{H}_2$  partial pressures ranging from 0.2 to 0.8 bar (SI, Fig. 3), the  $\text{NH}_2\text{OH}$  production is minimized when using very low  $\text{H}_2$  partial pressure (0.05 bar, Fig. 2C). This drastic change in selectivity, however, comes at the expense of reduced  $\text{NO}_2^-$  hydrogenation. This behavior is consistent with the higher  $\text{H}_2$  demand for  $\text{NH}_2\text{OH}$  formation compared to  $\text{N}_2$  formation (2 vs. 1.5  $\text{H}_2$  per  $\text{NO}_2^-$ , see eqn (2) and (4)).

Varying the initial  $\text{NO}_2^-$  concentration had little influence on  $\text{NH}_4^+$  and  $\text{NH}_2\text{OH}$  formation (Fig. 3A and B, respectively) which is consistent with an apparent reaction order of zero in

$\text{NO}_2^-$ , implying that the surface coverages are only mildly influenced by variation of the  $\text{NO}_2^-$  concentration. At the highest initial  $\text{NO}_2^-$  concentration, the formation of  $\text{NH}_4^+$  and  $\text{NH}_2\text{OH}$  appears to be slightly reduced. This can be rationalized by increased N-coverage on the catalyst surface resulting in a higher N–N coupling probability which is in line with findings of Xu *et al.*<sup>27</sup>

### 3.2 $\text{NO}_2^-$ hydrogenation on $\text{Pd}/\text{Al}_2\text{O}_3$ at 40 °C

The same set of experiments was performed at 40 °C to investigate the effect of reaction temperature. The  $\text{H}_2$  reaction order

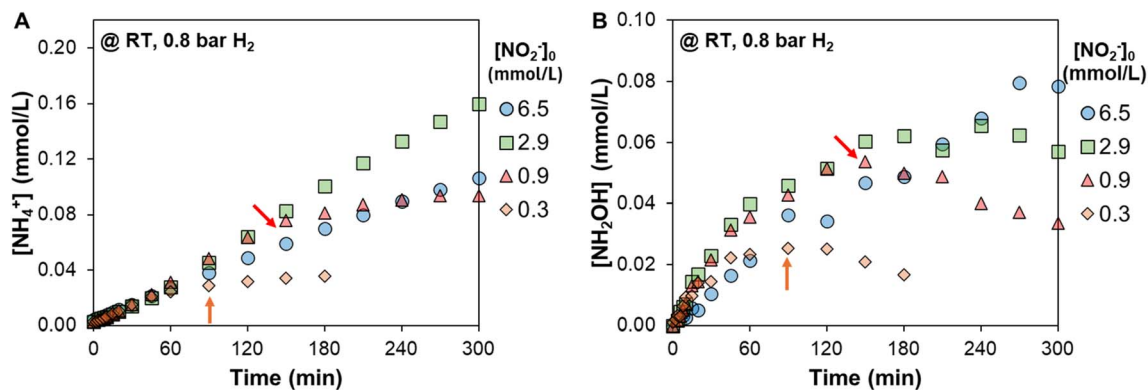


Fig. 3  $\text{NH}_4^+$  concentration (A) and  $\text{NH}_2\text{OH}$  concentration (B) at RT as a function of time at different initial  $\text{NO}_2^-$  concentrations. Arrows indicate the time of full  $\text{NO}_2^-$  conversion, if reached. Reaction conditions: 300 mL  $\text{H}_2\text{O}$ , 10 mg  $\text{Pd}/\text{Al}_2\text{O}_3$ , 80 : 10 : 10 mL  $\text{min}^{-1}$   $\text{H}_2$  :  $\text{CO}_2$  : He, RT, 600 rpm.



remained  $\sim 0.2$  while the  $\text{NO}_2^-$  hydrogenation activity is more sensitive to changes in the initial  $\text{NO}_2^-$  concentration at  $40^\circ\text{C}$  illustrated by a positive reaction order of 0.24 below  $0.8\text{ mmol L}^{-1}$   $\text{NO}_2^-$  and a negative reaction order of  $-0.47$  above  $0.8\text{ mmol L}^{-1}$  (SI, Fig. 4).

A typical concentration profile at  $40^\circ\text{C}$  is shown in the SI, Fig. 5. At  $40^\circ\text{C}$ , the  $\text{NH}_4^+$  selectivity increases from 3–8% (RT, Fig. 2B) to 10–15% or even to 25% ( $0.6\text{ bar}$ , Fig. 4A) and the U-shape is less pronounced, or at  $0.6\text{ bar}$  even disappeared entirely. In contrast, the maximum  $\text{NH}_2\text{OH}$  concentration at  $40^\circ\text{C}$  decreased by  $\sim 50\%$  compared to RT and the maximum  $\text{NH}_2\text{OH}$  concentration is no longer observed near full  $\text{NO}_2^-$  conversion (Fig. 4B). Instead, the  $\text{NH}_2\text{OH}$  concentrations declined already before completion of  $\text{NO}_2^-$  hydrogenation. This indicates that elevated temperatures favor  $\text{NH}_2\text{OH}$  decomposition, lowering the measurable bulk  $\text{NH}_2\text{OH}$  concentration.

As  $\text{NH}_2\text{OH}$  primarily decomposes to  $\text{NH}_4^+$ , faster  $\text{NH}_2\text{OH}$  decomposition explains the higher  $\text{NH}_4^+$  selectivity at  $40^\circ\text{C}$ . Notably, the  $\text{N}_2$  selectivity, calculated as the remainder of  $\text{NH}_4^+$  and  $\text{NH}_2\text{OH}$  selectivity, is largely unchanged across most  $\text{H}_2$  partial pressures at both RT and  $40^\circ\text{C}$  (Fig. 4C). Thus, the additional  $\text{NH}_4^+$  at  $40^\circ\text{C}$  can be attributed to accelerated  $\text{NH}_2\text{OH}$  decomposition. Only at  $0.6\text{ bar}$  of hydrogen the

nitrogen selectivity is substantially lower while  $\text{NH}_4^+$  selectivity reaches a higher value, suggesting increased  $\text{NH}_4^+$  formation from  $\text{NO}_2^-$ .

This kinetic study indicates that the formation of  $\text{NH}_4^+$  can be suppressed under  $\text{H}_2$ -deficient conditions, albeit at the expense of lower overall  $\text{NO}_2^-$  hydrogenation rates. The selectivity toward  $\text{NH}_2\text{OH}$  depends on both hydrogen partial pressure and temperature. At low  $\text{H}_2$  partial pressures, the selectivity to hydroxylamine is low due to hydrogen starvation on the catalyst surface, which limits its formation rate. With increasing temperature,  $\text{NH}_2\text{OH}$  selectivity also declines because of its accelerated decomposition to ammonia. This intricate interplay between surface coverage and activation barriers for hydroxylamine formation and decomposition highlights the inherent difficulty in controlling the selectivity toward hydroxylamine and ammonia in this reaction.

### 3.3 $\text{NO}_2^-$ hydrogenation on $\text{Pd}/\text{Al}_2\text{O}_3$ with $\text{NH}_2\text{OH}$ co-feeding

To evaluate the effect of  $\text{NH}_2\text{OH}$  on the selectivity and the  $\text{NO}_2^-$  hydrogenation activity,  $\text{NH}_2\text{OH}$  was co-fed in concentrations ranging from  $0.1$ – $0.85\text{ mmol L}^{-1}$  under  $\text{H}_2$  deficient ( $0.05\text{ bar}$ ) and  $\text{H}_2$  rich ( $0.8\text{ bar}$ ) conditions at both RT and  $40^\circ\text{C}$ . As expected, higher  $\text{NO}_2^-$  hydrogenation rates were observed at

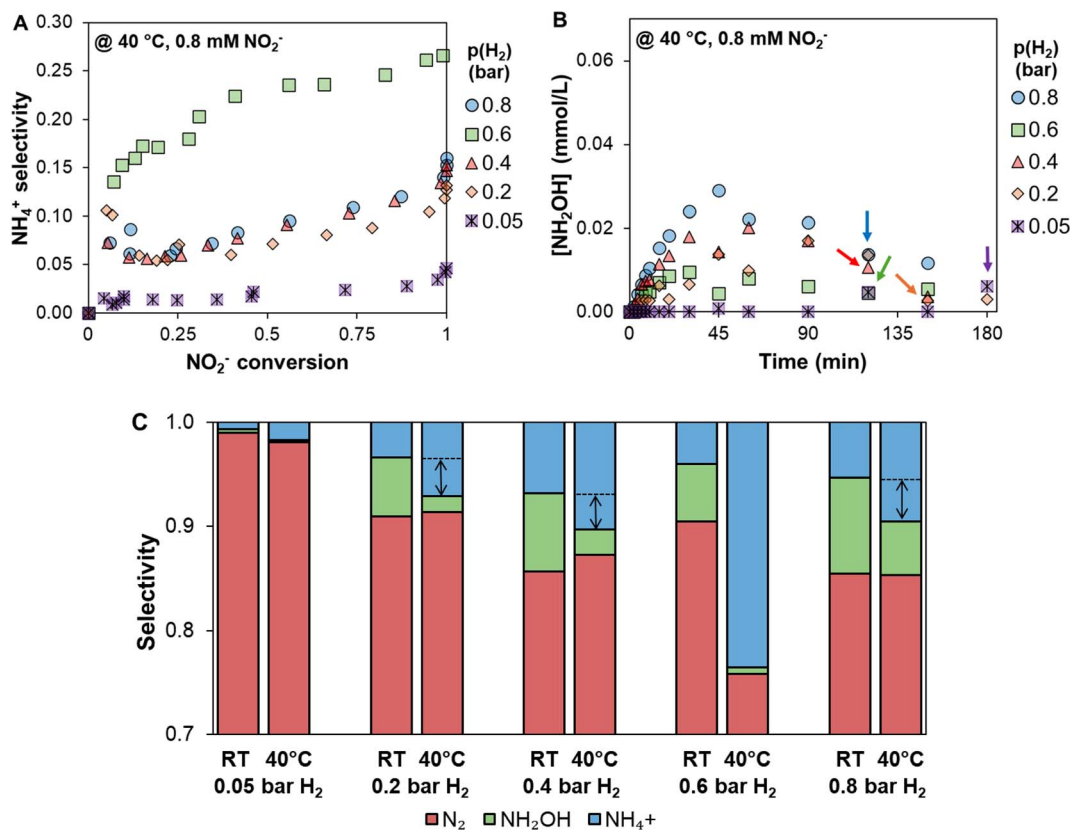


Fig. 4  $\text{NH}_4^+$  selectivity as a function of  $\text{NO}_2^-$  conversion (A), the  $\text{NH}_2\text{OH}$  concentration profile (B) both at  $40^\circ\text{C}$  and selectivity distribution at  $\sim 50\%$   $\text{NO}_2^-$  conversion at RT and  $40^\circ\text{C}$  and at different  $\text{H}_2$  partial pressures (C). Arrows indicate full  $\text{NO}_2^-$  conversion (B) or the difference in  $\text{NH}_4^+$  selectivity. Reaction conditions:  $300\text{ mL H}_2\text{O}$ ,  $10\text{ mg Pd}/\text{Al}_2\text{O}_3$ ,  $0.8\text{ mmol L}^{-1}\text{ KNO}_2$ ,  $10\text{ mL min}^{-1}\text{ CO}_2$ ,  $5$ – $80\text{ mL min}^{-1}\text{ H}_2$  and He to balance to  $100\text{ mL min}^{-1}$  total flow, RT or  $40^\circ\text{C}$ ,  $600\text{ rpm}$ .



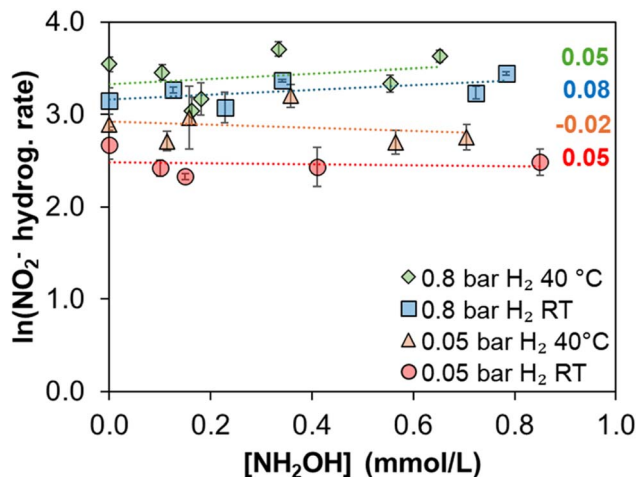


Fig. 5 Effect of  $\text{NH}_2\text{OH}$  on the  $\text{NO}_2^-$  hydrogenation rate on  $\text{Pd}/\text{Al}_2\text{O}_3$  at different  $\text{H}_2$  partial pressures and different temperatures. Reaction conditions:  $0.8 \text{ mmol L}^{-1} \text{KNO}_2$ ,  $300 \text{ mL H}_2\text{O}$ ,  $10 \text{ mg Pd}/\text{Al}_2\text{O}_3$ ,  $10 \text{ mL min}^{-1} \text{CO}_2$ ,  $5$  or  $80 \text{ mL min}^{-1} \text{H}_2$  and  $\text{He}$  to balance to  $100 \text{ mL min}^{-1}$  total flow, RT or  $40 \text{ }^\circ\text{C}$ ,  $600 \text{ rpm}$ .

elevated temperature and higher  $\text{H}_2$  partial pressure. Surprisingly, the presence of co-fed  $\text{NH}_2\text{OH}$  did not affect the  $\text{NO}_2^-$  hydrogenation activity regardless of temperature or  $\text{H}_2$  partial pressure as illustrated by apparent reaction orders close to zero (Fig. 5).

Reporting the  $\text{NH}_4^+$  and  $\text{NH}_2\text{OH}$  selectivity in  $\text{NH}_2\text{OH}$  co-feeding experiments is complex as co-fed  $\text{NH}_2\text{OH}$  represents

an additional N-source resulting in an ill-defined denominator for the selectivity calculation. For instance, the  $\text{NH}_2\text{OH}$  selectivity could formally reach negative values and might therefore be misleading. To avoid this complexity, we report the  $\text{NH}_4^+$  and  $\text{NH}_2\text{OH}$  concentrations as a function of time. Figures with the same data as a function of  $\text{NO}_2^-$  conversion deliver the same trends and are shown in the SI, Fig. 6.

At RT, the  $\text{NH}_2\text{OH}$  concentration remained essentially constant at its initial co-feed level regardless of the  $\text{H}_2$  partial pressure (Fig. 6A for  $0.8 \text{ bar}$  and SI, Fig. 6 for  $0.05 \text{ bar}$ ). Because  $\text{NH}_2\text{OH}$  formation and decomposition occur simultaneously, only the net concentration change can be tracked. Thus, from the concentration profile alone, it cannot be determined whether  $\text{NH}_2\text{OH}$  formation and decomposition are in balance or whether no  $\text{NH}_2\text{OH}$  is formed in the first place. The  $\text{NH}_4^+$  concentrations, however, increase with increasing  $\text{NH}_2\text{OH}$  co-feed at RT as illustrated by the first two clustered columns in Fig. 6D. This suggests that  $\text{NH}_2\text{OH}$  is not a passive spectator but  $\text{NH}_2\text{OH}$  formation and decomposition are in balance with the  $\text{NH}_2\text{OH}$  decomposition contributing to increased  $\text{NH}_4^+$  formation. Under  $\text{H}_2$ -deficient conditions ( $0.05 \text{ bar}$ ), the  $\text{NH}_4^+$  concentrations were consistently lower, as expected and discussed in Sections 3.1 and 3.2.

At  $40 \text{ }^\circ\text{C}$  and low  $\text{H}_2$  partial pressure the  $\text{NH}_2\text{OH}$  concentrations decrease over time resulting in slightly higher  $\text{NH}_4^+$  concentrations (Fig. 6B and D (third clustered columns), respectively). The decrease in the  $\text{NH}_2\text{OH}$  concentration supports the earlier observations that the  $\text{NH}_2\text{OH}$  decomposition is promoted at elevated temperatures. At  $40 \text{ }^\circ\text{C}$  and high  $\text{H}_2$

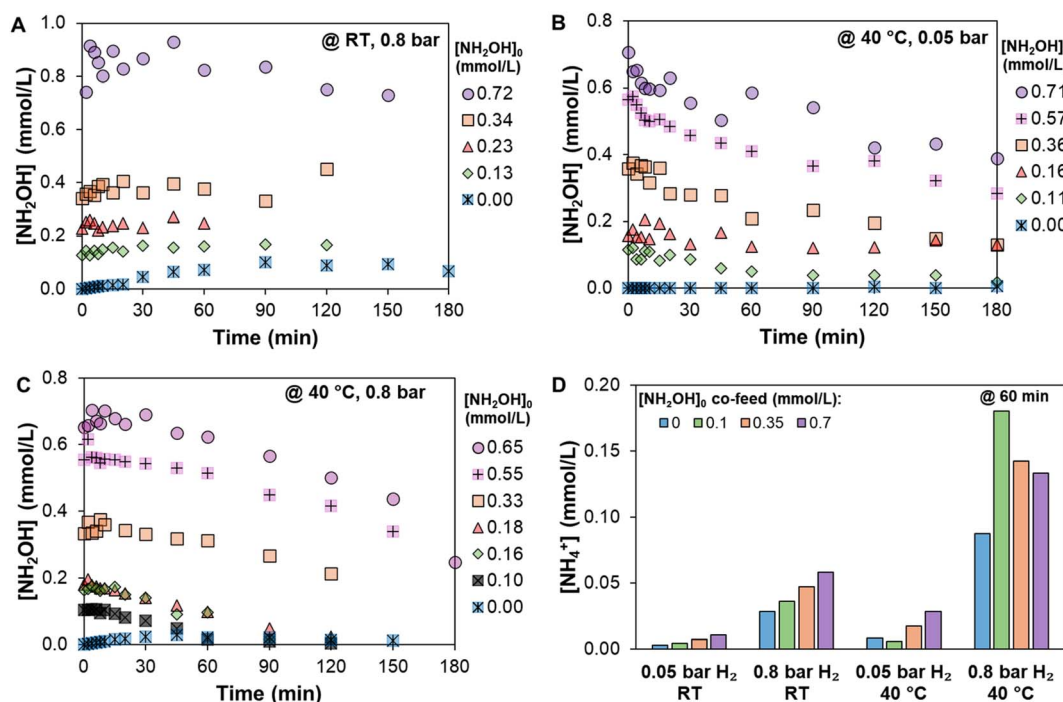


Fig. 6  $\text{NH}_2\text{OH}$  concentration as a function of time at different  $\text{NH}_2\text{OH}$  co-feed concentrations at RT or  $40 \text{ }^\circ\text{C}$  and at  $0.8$  or  $0.05 \text{ bar H}_2$  (as stated in the chart, A–C) and the  $\text{NH}_4^+$  concentration at different rounded  $\text{NH}_2\text{OH}$  co-feed concentrations after  $60 \text{ min}$  of reaction (D). Reaction conditions:  $300 \text{ mL H}_2\text{O}$ ,  $0.8 \text{ mmol L}^{-1} \text{KNO}_2$ ,  $10 \text{ mg Pd}/\text{Al}_2\text{O}_3$ ,  $80$  or  $5 \text{ mL min}^{-1} \text{H}_2$ ,  $10 \text{ mL min}^{-1} \text{CO}_2$  and  $\text{He}$  to make up to  $100 \text{ mL min}^{-1}$ , RT or  $40 \text{ }^\circ\text{C}$ ,  $600 \text{ rpm}$ .



**Table 2** Overview of the main trends of the  $\text{NH}_2\text{OH}$  co-feeding experiments with respect to  $\text{NO}_2^-$  hydrogenation activity,  $\text{NH}_2\text{OH}$  concentration and  $\text{NH}_4^+$  formation under different reaction conditions

Effect of $\text{NH}_2\text{OH}$ co-feeding	RT		40 °C	
	0.05 bar	0.8 bar	0.05 bar	0.8 bar
$\text{NO}_2^-$ hydrog. activity	Constant		Activity unchanged	
$[\text{NH}_2\text{OH}]$	Increasing with $[\text{NH}_2\text{OH}]_0$		Decreasing	
$\text{NH}_4^+$ formation	Increasing with $[\text{NH}_2\text{OH}]_0$		Increased at high $[\text{NH}_2\text{OH}]_0$	Increasing non-linearly

partial pressure, substantially higher  $\text{NH}_4^+$  concentrations are obtained than under all other conditions which underlines faster  $\text{NH}_2\text{OH}$  decomposition at elevated temperature and the need for sufficient  $\text{H}_2$ . Interestingly, the  $\text{NH}_4^+$  concentrations show a non-linear behavior with respect to the  $\text{NH}_2\text{OH}$  co-feed levels under these conditions. While all co-feed experiments deliver higher  $\text{NH}_4^+$  concentrations than the baseline experiment without any  $\text{NH}_2\text{OH}$  co-feed, the increase in the  $\text{NH}_4^+$  concentration was more pronounced at lower co-feed levels (Fig. 6D, last clustered columns). A possible explanation could be that at high  $\text{NH}_2\text{OH}$  concentrations the surface is increasingly covered with  $\text{NH}_2\text{OH}$  species. This may result in lower H-coverage at high  $\text{NH}_2\text{OH}$  co-feed than at low  $\text{NH}_2\text{OH}$  co-feed leading to higher N:H ratios and therefore more N-N coupling and less  $\text{NH}_4^+$  formation. More broadly, this underscores the complex interplay of the different surface species and its relevance for the reaction mechanism.

As summarized in Table 2, these findings indicate that the  $\text{NO}_2^-$  hydrogenation activity is unaffected by  $\text{NH}_2\text{OH}$  co-feeding. Instead, the hydroxylamine co-feeding led to higher  $\text{NH}_4^+$  formation rates, indicating that this intermediate regulates the product selectivity. This increased  $\text{NH}_4^+$  formation correlates with faster  $\text{NH}_2\text{OH}$  decomposition, which is more pronounced at elevated temperatures.

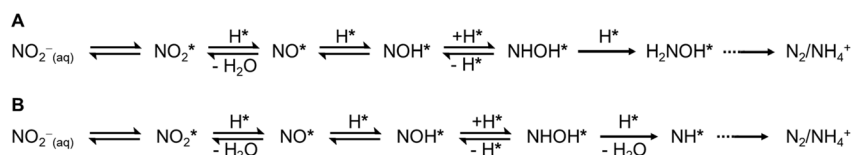
### 3.4 Reviewing the $\text{NO}_2^-$ hydrogenation reaction mechanism on $\text{Pd}/\text{Al}_2\text{O}_3$

Only very few studies propose a reaction mechanism considering elementary steps of the surface reaction and, to the best of our knowledge, none of them considers the desorption of  $\text{NH}_2\text{OH}$ .<sup>27,28,33</sup> Thus, earlier published mechanistically relevant findings based on ATR-IR spectroscopy,<sup>29–31</sup> DFT<sup>28,33–35</sup> and reaction kinetics<sup>27,28</sup> are critically discussed and a revised reaction mechanism under consideration of desorbed  $\text{NH}_2\text{OH}$  is provided. Mechanistic studies on  $\text{NO}_2^-$  over metals other than  $\text{Pd}$ <sup>36</sup> or  $\text{NO}_3^-$  hydrogenation<sup>37–41</sup> were not considered as the initial hydrogenation from  $\text{NO}_3^-$  to  $\text{NO}_2^-$  is the RDS of this

reaction and the surface coverages in  $\text{NO}_3^-$  and  $\text{NO}_2^-$  are thus not comparable.

**3.4.1 Role of  $\text{NH}_2\text{OH}$ .** Ebbesen *et al.* conducted ATR-IR studies on the decomposition of  $\text{NH}_2\text{OH}$  on  $\text{Pd}/\text{Al}_2\text{O}_3$ . They showed that in the absence of  $\text{H}_2$  and  $\text{NO}_2^-$ ,  $\text{NH}_2\text{OH}$  decomposes into  $\text{NH}_4^+$  and another species that initially was assumed to be  $\text{NH}_2$ .<sup>31</sup> In following studies using isotope labelling, Rao *et al.* showed that this species contains oxygen and was therefore defined as  $\text{NO}_x\text{H}_y$  which represents  $\text{HNO}^*$ ,  $\text{NOH}^*$ ,  $\text{NHOH}^*$  and/or  $\text{NH}_2\text{OH}^*$  (unpublished work, SI, Fig. 7). The three species were indistinguishable from one another. Subsequent titration of the  $\text{NO}_x\text{H}_y^*$  species with  $\text{H}_2$  in the ATR-IR cell showed that  $\text{NO}_x\text{H}_y^*$  is converted into  $\text{NH}_4^+$ .<sup>31</sup> Notably,  $\text{NO}^*$  was not observed in these experiments suggesting at least one irreversible reaction step from  $\text{NO}^*$  towards  $\text{NO}_x\text{H}_y^*$  on the Pd catalyst. In our latest work we reported  $\text{NH}_4^+$  selectivity <100% in batch experiments converting  $\text{NH}_2\text{OH}$ . This indicates that  $\text{N}_2$  or  $\text{N}_2\text{O}$  can be formed from  $\text{NH}_2\text{OH}$  even in the absence of  $\text{NO}_2^-$  and  $\text{H}_2$  *via* catalytic disproportionation.<sup>17</sup> Generally, these results suggest that there is a direct pathway from  $\text{NH}_2\text{OH}$  towards  $\text{NH}_4^+$ , while  $\text{NH}_2\text{OH}$  can also merge into the mechanistic pathway that leads to  $\text{N}_2$ , but  $\text{NH}_2\text{OH}$  cannot form  $\text{NO}^*$ .

**3.4.2 Langmuir–Hinshelwood or Eley–Rideal mechanism for  $\text{N}_2$  formation.** Xu *et al.* formulated a  $\text{NO}_2^-$  hydrogenation mechanism based on extensive kinetic studies.<sup>27</sup> All possible Langmuir–Hinshelwood (LH) equations were derived and compared with the apparent reaction orders in a broad concentration regime. Four of these LH type reaction mechanisms match the observed reaction orders. Two of these mechanisms proceed *via* a  $\text{N}^*$  species (see SI, Fig. 8C and D) and were excluded as earlier work of Zhao *et al.* claimed  $\text{N}^*$  species to be kinetically irrelevant.<sup>29</sup> Zhao observed increasing  $\text{NH}_4^+$  concentrations although  $\text{NO}_2^-$  was entirely converted and suggested  $\text{N}^*$  as strongly adsorbed surface species that only very slowly converts into  $\text{NH}_4^+$ .<sup>29</sup> While this seemed a reasonable explanation as  $\text{N}^*$  species are IR inactive and could therefore not be observed in ATR-IR studies, it cannot be excluded that



**Fig. 7** Suggested  $\text{NO}_2^-$  hydrogenation mechanisms by Xu *et al.*<sup>27</sup>





Huang *et al.*<sup>28</sup> suggested a co-limitation of the hydrogenation of NO\* to HNO\* and the consecutive hydrogenation of HNO\* to HNOH\* as the RDS based on their kinetic model.<sup>28</sup> DFT calculations in their work delivered lower activation barriers for HNOH\* formation *via* HNO\* than *via* NOH\*. While NOH\* might still form and couple with NH\* to form N<sub>2</sub>, we focus on HNO\* for the subsequent pathway to HNOH\*. Huang *et al.*<sup>28</sup> suggested that the degree of rate control shifts based on the reaction conditions but is under typical reaction conditions (RT, 0.8 bar H<sub>2</sub> partial pressure) at about 90% for the NO\* hydrogenation to HNO\*.

While the observed reaction kinetics in this work are similar and therefore confirm the previous model not considering NH<sub>2</sub>OH, the model cannot explain the RDS in the presence of NH<sub>2</sub>OH sufficiently. If NO\* hydrogenation was also the dominant RDS under NH<sub>2</sub>OH rich conditions, all following steps were quasi-equilibrated and thus NH<sub>2</sub>OH<sub>(aq)</sub> was equilibrated with NH\* according to the 0<sup>th</sup> law of thermodynamics. NH\* can be coupled with NO\* to form N<sub>2</sub> and NO\* is easily formed from NO<sub>2</sub><sup>-</sup> and surface abundant; thus an acceleration of the NO<sub>2</sub><sup>-</sup> hydrogenation with increasing NH<sub>2</sub>OH co-feed (NH<sub>2</sub>OH reaction order > 0) would be expected. In other words, the NO\* → NOH\* RDS could be bypassed owing to the abundance of NH\*. However, the observation is 0<sup>th</sup> order in NH<sub>2</sub>OH; thus, there must be another RDS under NH<sub>2</sub>OH rich conditions.

The H-assisted dissociation of the N–O bond in HNOH\* to NH\* can be a RDS based on the expected apparent reaction orders derived from the LH equations by Xu *et al.*<sup>27</sup> without considering NH<sub>2</sub>OH. A similar derivation under NH<sub>2</sub>OH rich conditions was derived (see the SI) and resulted in a reaction order range of [−1, 0] for NO<sub>2</sub><sup>-</sup> and [−1, 1] for NH<sub>2</sub>OH which covers the observed orders. Notably, in ATR-IR titration experiments of the surface abundant NO\* and NO<sub>x</sub>H<sub>y</sub>\* species it was observed that NO\* is more quickly converted than NO<sub>x</sub>H<sub>y</sub>\*<sup>29,30</sup> supporting that HNOH\* → NH\* is a realistic RDS.<sup>24</sup> Controversially, if HNOH\* → NH\* is the RDS under NH<sub>2</sub>OH rich conditions, one might expect the reaction to be accelerated with increasing NH<sub>2</sub>OH concentration due to increased HNOH\* coverage. However, if the surface is saturated with NH<sub>2</sub>OH (and its equilibrated species including HNOH\*), changes in NH<sub>2</sub>OH in the solution would not affect the reaction rate. This surface saturation of NH<sub>2</sub>OH species under NH<sub>2</sub>OH rich conditions agrees with ATR-IR experiments that showed that NH<sub>x</sub>O<sub>y</sub> is a surface abundant species when feeding NH<sub>2</sub>OH.<sup>30,31</sup>

Thus, we suggest that the RDS varies even more on the surface coverages than reported by Huang *et al.*<sup>28</sup> In the absence of NH<sub>2</sub>OH the RDS lies dominantly on the NO\* → NOH\* hydrogenation while it shifts to HNOH\* → NH\* under NH<sub>2</sub>OH abundant conditions. In between these two extreme cases the degree of rate control shifts non-linearly and therefore accounts for intriguing trends such as decreasing NH<sub>4</sub><sup>+</sup> formation with increasing NH<sub>2</sub>OH co-feed (Fig. 6D) or higher NH<sub>4</sub><sup>+</sup> formation at 0.6 bar H<sub>2</sub> and elevated temperature (Fig. 4C). NH\* remains the last common reaction intermediate in the pathways towards N<sub>2</sub> and NH<sub>4</sub><sup>+</sup>. Thus, the surface coverage of H\* and various N\* species determines the probability whether NH\* proceeds *via* the N<sub>2</sub> or NH<sub>4</sub><sup>+</sup> pathway. Clearly, higher H-coverage increases

the probability for NH<sub>4</sub><sup>+</sup> formation, which is consistent with increased NH<sub>4</sub><sup>+</sup> selectivity at the beginning of a reaction and approaching full NO<sub>2</sub><sup>-</sup> conversion and lower NH<sub>4</sub><sup>+</sup> formation under H<sub>2</sub> deficient conditions as discussed in Section 3.1.

In conclusion, the recent discovery of NH<sub>2</sub>OH as a desorbed reaction intermediate clearly highlights the need for the incorporation of NH<sub>2</sub>OH into the NO<sub>2</sub><sup>-</sup> hydrogenation mechanism. In our revised mechanistic scheme we (1) account for the adsorption equilibrium of NH<sub>2</sub>OH, (2) include the hydrogenation equilibrium of HNOH\* and NH<sub>2</sub>OH\* representing the possibility for NH<sub>2</sub>OH to merge into the N<sub>2</sub> formation pathway, and (3) suggest a changing degree of rate control depending on the surface coverages with NO hydrogenation as the dominant RDS in the absence of NH<sub>2</sub>OH and the H-assisted N–O dissociation of HNOH\* to NH\* as the RDS under NH<sub>2</sub>OH rich conditions. This mechanism emphasizes that the selectivity is determined by NH\* conversion, either reacting with H\* to form NH<sub>4</sub><sup>+</sup> or by coupling with an N-species to form N<sub>2</sub>, depending on the surface coverage of H and HNO\*/NOH\* or NO\*. Our proposed mechanism provides a coherent picture of the reaction mechanism consistent with the experimental data and previous results obtained from our group. Nonetheless, the dominant surface mechanism will inevitably depend on catalyst characteristics and operating conditions, and other mechanistic interpretations may also be reasonable.

### 3.5 NO<sub>2</sub><sup>-</sup> hydrogenation on SnPd/Al<sub>2</sub>O<sub>3</sub> – activity, selectivity and NH<sub>2</sub>OH co-feeding

The same set of experiments, varying the NO<sub>2</sub><sup>-</sup> concentration from 0.3–8 mmol L<sup>-1</sup> and the H<sub>2</sub> partial pressure from 0.05–0.8 bar, was conducted on a SnPd/Al<sub>2</sub>O<sub>3</sub> catalyst. This catalyst was prepared from the previously tested Pd/Al<sub>2</sub>O<sub>3</sub> by Controlled Surface Deposition (CSD), introducing Sn corresponding to 0.4 monolayers relative to the accessible Pd surface atoms. Remarkably, the overall NO<sub>2</sub><sup>-</sup> hydrogenation activity remained largely unaffected by Sn doping. Since the activity was unchanged, we assume, as for Pd/Al<sub>2</sub>O<sub>3</sub>, that mass transport limitations are absent (SI, Fig. 1). The derived reaction orders are likewise similar to those observed for Pd/Al<sub>2</sub>O<sub>3</sub>: the order in NO<sub>2</sub><sup>-</sup> remains close to zero (Fig. 9A), while the order in H<sub>2</sub> increases from 0.2 (Pd/Al<sub>2</sub>O<sub>3</sub>) to 0.5 (SnPd/Al<sub>2</sub>O<sub>3</sub>, Fig. 9B), indicating a higher sensitivity to changes in H<sub>2</sub> partial pressure. This can be rationalized by the partial blockage of Pd sites by Sn, which cannot dissociate H<sub>2</sub>, thereby reducing the effective H availability. In NH<sub>2</sub>OH co-feeding experiments, the NO<sub>2</sub><sup>-</sup> hydrogenation activity also remained unchanged, resulting in an apparent reaction order in NH<sub>2</sub>OH close to zero at both 0.8 and 0.05 bar H<sub>2</sub> (Fig. 9C).

The selectivity trends on SnPd/Al<sub>2</sub>O<sub>3</sub> mirror those on Pd/Al<sub>2</sub>O<sub>3</sub>: NH<sub>2</sub>OH concentrations increase over the course of the reaction, peaking near full NO<sub>2</sub><sup>-</sup> conversion (Fig. 10B), while NH<sub>4</sub><sup>+</sup> selectivity exhibits a U-shaped dependence on conversion (Fig. 10A) as discussed in Section 3.1. As for Pd/Al<sub>2</sub>O<sub>3</sub>, variations in the initial NO<sub>2</sub><sup>-</sup> concentration have only minor effects on product distribution (SI, Fig. 9), and both NH<sub>4</sub><sup>+</sup> and NH<sub>2</sub>OH



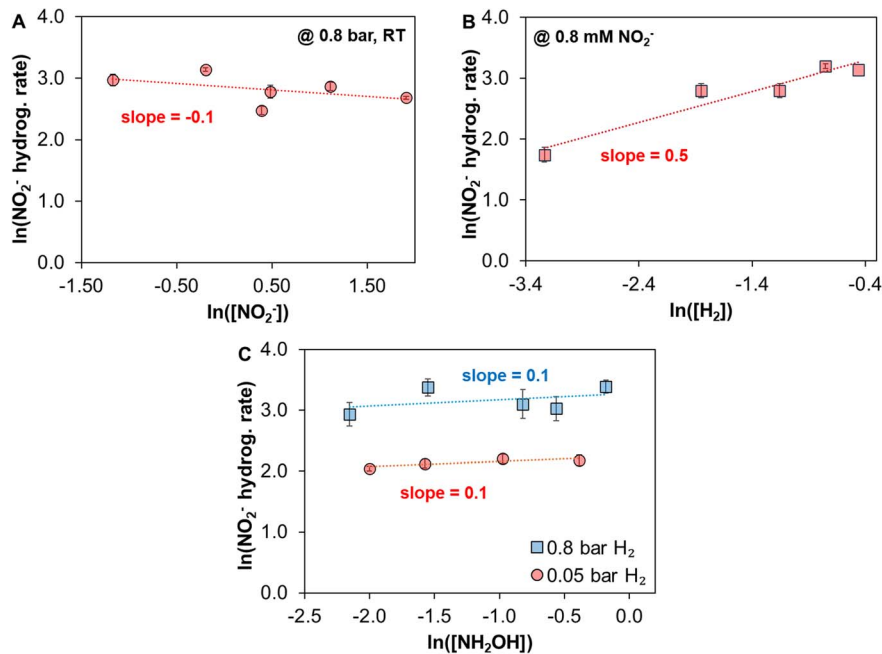


Fig. 9 Effect of  $\text{NO}_2^-$  (A),  $\text{H}_2$  (B) and  $\text{NH}_2\text{OH}$  concentration (C) on the  $\text{NO}_2^-$  hydrogenation rate on  $\text{SnPd}/\text{Al}_2\text{O}_3$ . Reaction conditions: 300 mL  $\text{H}_2\text{O}$ , 10 mg  $\text{SnPd}/\text{Al}_2\text{O}_3$ ,  $10 \text{ mL min}^{-1} \text{CO}_2$ ,  $5\text{--}80 \text{ mL min}^{-1} \text{H}_2$  and He to balance to  $100 \text{ mL min}^{-1}$  total flow, RT, 600 rpm.

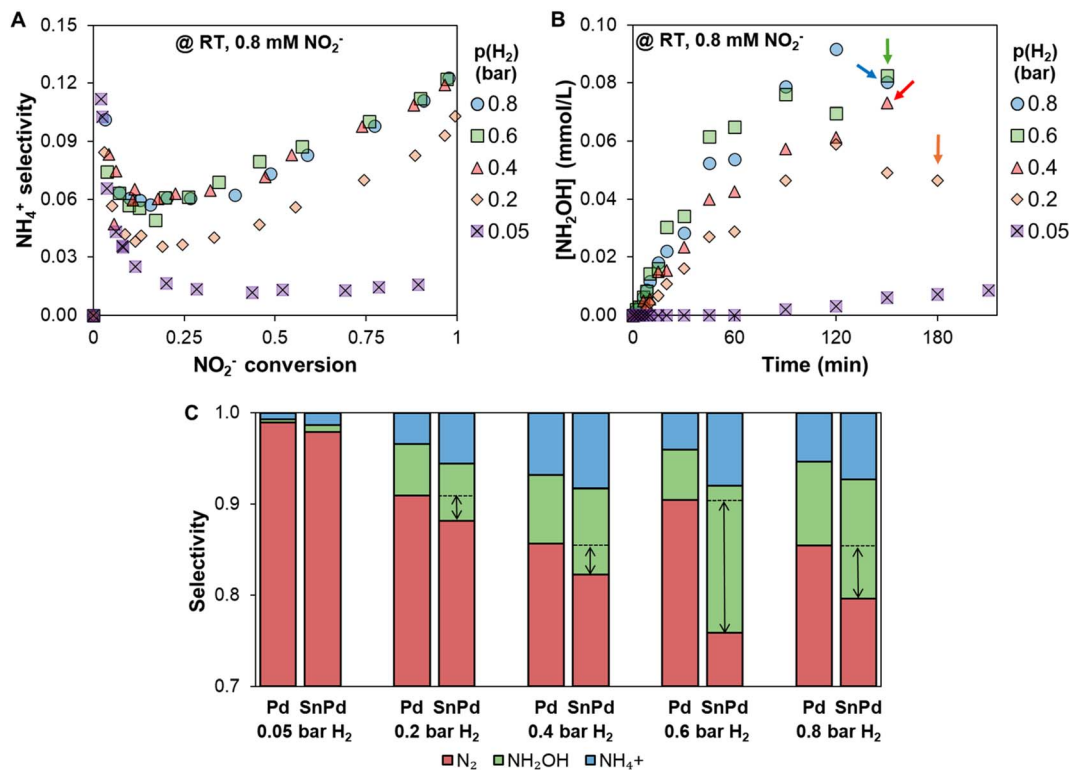


Fig. 10  $\text{NH}_4^+$  (A) and  $\text{NH}_2\text{OH}$  (B) concentrations as a function of  $\text{NO}_2^-$  conversion and time, respectively, and selectivity distribution at  $\sim 50\%$   $\text{NO}_2^-$  conversion on Pd and SnPd at different  $\text{H}_2$  partial pressures (C). Pd data are the same as in Fig. 4 and replotted for intuitive comparison. The arrows in (C) indicate the difference in  $\text{N}_2$  selectivity. Reaction conditions: 300 mL  $\text{H}_2\text{O}$ , 10 mg  $\text{SnPd}/\text{Al}_2\text{O}_3$ ,  $10 \text{ mL min}^{-1} \text{CO}_2$ ,  $5\text{--}80 \text{ mL min}^{-1} \text{H}_2$  and He to balance to  $100 \text{ mL min}^{-1}$  total flow, RT or  $40^\circ\text{C}$ , 600 rpm.



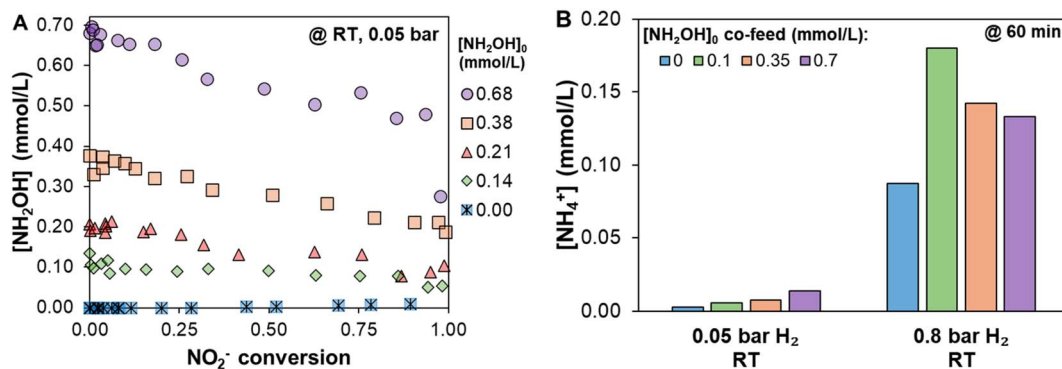


Fig. 11  $\text{NH}_2\text{OH}$  concentration as a function of  $\text{NO}_2^-$  conversion at different  $\text{NH}_2\text{OH}$  co-feed concentrations at 0.05 bar  $\text{H}_2$  (A) and the  $\text{NH}_4^+$  concentration at different rounded  $\text{NH}_2\text{OH}$  co-feed concentrations after 60 min of reaction (B). Reaction conditions: 300 mL  $\text{H}_2\text{O}$ , 0.8 mmol  $\text{L}^{-1}$   $\text{KNO}_3$ , 10 mg  $\text{SnPd}/\text{Al}_2\text{O}_3$ , 80 or 5 mL  $\text{min}^{-1}$   $\text{H}_2$ , 10 mL  $\text{min}^{-1}$   $\text{CO}_2$  and He to make up to 100 mL  $\text{min}^{-1}$ , RT, 600 rpm.

concentrations are lower under  $\text{H}_2$ -deficient conditions (Fig. 10).

Notably, the  $\text{NH}_2\text{OH}$  and  $\text{NH}_4^+$  selectivity are mildly increased on  $\text{SnPd}/\text{Al}_2\text{O}_3$  for all  $\text{H}_2$  pressures  $\geq 0.2$  bar resulting in 4–16% lower  $\text{N}_2$  selectivity upon Sn doping (Fig. 10C). While this appears contradictory to the notion of reduced H coverage caused by Sn blocking of Pd sites, this suggests that Sn also shifts the balance of surface reactions away from N–N coupling and towards  $\text{NH}_4^+$  formation. Formation of  $\text{N}_2$  requires N–N bond formation *via* coupling between a reduced N adsorbate (e.g.,  $\text{NH}^*$ ) and a more oxidized N adsorbate (e.g.,  $\text{NO}^*/\text{NOH}^*/\text{HNOH}^*$ ), which therefore requires co-adsorption of these intermediates in close proximity on Pd ensembles. Introducing Sn partially dilutes Pd, reducing the probability for such coupling configurations and thus slightly suppressing the  $\text{N}_2$  pathway.<sup>42</sup> In contrast, sequential hydrogenation steps toward  $\text{NH}_4^+$  rely primarily on  $\text{H}^*$  availability and are less sensitive to the availability of larger Pd ensembles.<sup>42</sup> This is consistent with the much higher mobility (lower diffusion barrier) of  $\text{H}^*$  on Pd compared with N-species,<sup>34</sup> which favors hydrogenation when coupling upon Pd dilution. The same argumentation applies to  $\text{NH}_2\text{OH}$  formation, since it does not require N–N coupling but follows from stepwise hydrogenation. However, we cannot rule out that the presence of Sn modifies the electronic structure of neighboring Pd surface atoms, increasing the rate of hydrogenation to  $\text{NH}_4^+$ .

The  $\text{NH}_2\text{OH}$  co-feeding experiments at high  $\text{H}_2$  partial pressure (0.8 bar) on  $\text{SnPd}/\text{Al}_2\text{O}_3$  reproduce the trends observed on  $\text{Pd}/\text{Al}_2\text{O}_3$ : the  $\text{NH}_2\text{OH}$  concentration remains essentially constant, while more  $\text{NH}_4^+$  is formed when  $\text{NH}_2\text{OH}$  is co-fed (SI, Fig. 10 and 11B). Interestingly, the same non-linearity is observed in decreasing  $\text{NH}_4^+$  formation with increasing  $\text{NH}_2\text{OH}$  co-feed concentration, as on Pd at elevated temperature. Under  $\text{H}_2$ -deficient conditions,  $\text{NH}_2\text{OH}$  depletion is more pronounced on  $\text{SnPd}$  than on Pd (Fig. 11A and SI, Fig. 6F) and the  $\text{NH}_4^+$  concentration increases with increasing  $\text{NH}_2\text{OH}$  co-feed concentration (Fig. 11B). The  $\text{NH}_2\text{OH}$  co-feeding results can be rationalized by the ability to disproportionate into  $\text{NH}_4^+$  and  $\text{N}_2$  without net consumption of  $\text{H}_2$ . Under  $\text{H}_2$ -deficient conditions this disproportionation pathway gains relative

importance, because pathways that rely on  $\text{H}_2$  uptake are suppressed. On  $\text{SnPd}/\text{Al}_2\text{O}_3$  this is more pronounced; thus the presence of Sn facilitates the  $\text{NH}_2\text{OH}$  decomposition. This is in line with the enhanced N–O bond activation ability of Sn also allowing to break the first N–O bond in  $\text{NO}_3^-$ . As a result,  $\text{NH}_2\text{OH}$  is more readily consumed on  $\text{SnPd}/\text{Al}_2\text{O}_3$  than on  $\text{Pd}/\text{Al}_2\text{O}_3$ , consistent with the stronger decrease in the  $\text{NH}_2\text{OH}$  concentration observed at low  $\text{H}_2$  partial pressure.

In conclusion,  $\text{SnPd}/\text{Al}_2\text{O}_3$  exhibits  $\text{NO}_2^-$  hydrogenation activity and selectivity trends very similar to  $\text{Pd}/\text{Al}_2\text{O}_3$ . The main differences are a higher sensitivity to  $\text{H}_2$  in both activity and selectivity, likely due to lower H affinity on  $\text{SnPd}$ . Also, the  $\text{NH}_2\text{OH}$  and  $\text{NH}_4^+$  selectivities are increased resulting in a lower  $\text{N}_2$  selectivity on  $\text{SnPd}$ .

In the bigger picture, these results show the demanding challenges for  $\text{NO}_3^-$  hydrogenation aiming for high  $\text{N}_2$  selectivity. The  $\text{NO}_3^-$  hydrogenation requires a bimetallic catalyst such as  $\text{SnPd}/\text{Al}_2\text{O}_3$  for the initial  $\text{NO}_3^-$  hydrogenation to  $\text{NO}_2^-$  which represents the RDS of this reaction. As a result,  $\text{NO}_2^-$  is commonly detected in traces or not detected in the liquid bulk at all. Thus, the surface coverage of N-species in the  $\text{NO}_3^-$  hydrogenation on the Pd sites is lower and shifts the coverage towards higher H : N ratios favoring  $\text{NH}_4^+$  and  $\text{NH}_2\text{OH}$  formation. This in combination with the higher  $\text{NH}_4^+$  production affinity of  $\text{SnPd}$  itself highlights the fundamental challenges of selective  $\text{NO}_3^-$  hydrogenation for drinking water purification.

## 4 Conclusion

In this study, we have demonstrated that  $\text{NH}_2\text{OH}$  is a key intermediate in the catalytic hydrogenation of  $\text{NO}_2^-$ . The selectivity towards  $\text{NH}_4^+$  is strongly conversion-dependent, with both  $\text{NH}_2\text{OH}$  and  $\text{NH}_4^+$  formation substantially suppressed only under  $\text{H}_2$ -deficient conditions, albeit at the expense of lower overall  $\text{NO}_2^-$  hydrogenation activity. Elevated temperature accelerates  $\text{NH}_2\text{OH}$  decomposition, thereby lowering the  $\text{NH}_2\text{OH}$  concentration. However, rather than enhancing  $\text{N}_2$  formation, this shift promotes  $\text{NH}_4^+$  selectivity leaving  $\text{N}_2$  selectivity largely unaffected. Co-feeding experiments confirmed that the presence of  $\text{NH}_2\text{OH}$  does not influence the



intrinsic NO<sub>2</sub><sup>-</sup> hydrogenation rate and that NH<sub>2</sub>OH formation and decomposition are balanced. The latter suggests that a continuous process could in principle be designed in a way that NH<sub>2</sub>OH would not excessively accumulate due to its intermediary nature. The activity and selectivity patterns for Pd/Al<sub>2</sub>O<sub>3</sub> and SnPd/Al<sub>2</sub>O<sub>3</sub> were very similar with higher NH<sub>2</sub>OH and NH<sub>4</sub><sup>+</sup> formation on SnPd/Al<sub>2</sub>O<sub>3</sub> being the main differences.

We critically reviewed the NO<sub>2</sub><sup>-</sup> hydrogenation mechanism and provided a revised LH-based scheme including NH<sub>2</sub>OH as desorbed species. The revised mechanism highlights that NH<sub>2</sub>OH can merge into the N<sub>2</sub> formation pathway and suggests the RDS to be strongly dependent on the surface coverages.

## Author contributions

J. Betting: methodology, investigation, writing – original draft; Y. Preedawichitkun: investigation; T. Sooknoi: funding acquisition, writing – review & editing; J. Faria Albanese: funding acquisition, supervision, writing – review & editing; L. Lefferts: supervision, writing – review & editing.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d6ta00106h>.

## Acknowledgements

We gratefully acknowledge the financial support of the LNG-Zero project (grant number 20002675). We also thank the Royal Golden Jubilee PhD Program (RGJ-PhD Program Grant Number N41A640277) and the National Research Council of Thailand (NRCT Grant Number N42A680527).

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