Competitive Adsorption of Nitrite and Hydrogen on Palladium during Nitrite Hydrogenation

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Nitrite hydrogenation is studied in steady-state as well as transient operation using a Pd catalyst in a tubular membrane contactor reactor. A negative reaction order in hydrogen in steady state operation proofs that hydrogen and nitrite adsorb competitively. In transient operation, feeding nitrite to the Pd surface fully covered with hydrogen results initially in very low conversion of nitrite, speeding up once hydrogen is removed from part of the Pd surface. Additional proof for competitive adsorption between hydrogen and nitrite is provided by the observation that exposure of a nitrite-covered catalyst to hydrogen induces desorption of nitrite. Formation of ammonia in these experiments proceeds via two pathways, first via a fast reaction followed by extremely slow hydrogenation of adsorbed N atoms, which is kinetically not relevant. This information is relevant for designing effective and selective catalysts when operating at very low nitrite concentration.

Introduction

The concentration of nitrate in surface and ground water reservoirs has been steadily increasing over the last decades caused by increasing human population and intensified agriculture. Exposure to nitrate has been correlated with various adverse health effects, such as blue baby syndrome and intestinal cancer. Furthermore, it can lead to eutrophication in water reservoirs. For these reasons the European Union has limited the concentration of nitrate (NO$_3$\(^-\)) in drinking water to 50 mg/l and legislation in the United States is even more strict with 10 mg/l. Common methods to remove nitrate (NO$_3$\(^-\)) and nitrate include reverse osmosis, electro-dialysis, ion exchange and biological degradation. Biological degradation is generally not possible for drinking water because of the absence of nutrients for sustaining bacterial growth. The other methods have the drawbacks that nitrate rich waste streams are produced which cannot be simply disposed and the need to convert nitrate and nitrite remains. Therefore, catalytic hydrogenation of nitrates to nitrogen is a promising technique. This method uses noble-metal catalysts such as palladium or platinum in combination with a promoter, most commonly copper, to reduce nitrate to nitrogen. High selectivity is required because of the formation of ammonia as a non-desired by product. Despite significant research, the issue of preventing formation of ammonia is not yet resolved, especially when using practical continuous operated reactors. Both reaction rate and selectivity depend greatly on the hydrogen concentration at the catalyst surface. A high hydrogen concentration leads at one hand to fast conversion, but at the other hand also to low selectivity to N$_2$. Nitrate hydrogenation proceeds via two consecutive reactions. First nitrate (NO$_3$\(^-\)) is converted to nitrite (NO$_2$\(^-\)), requiring a bi-metallic catalyst (e.g. Pd–Cu). The second reaction step is catalyzed by a mono-metallic noble catalyst, generally palladium. In this step nitrite is hydrogenated to either nitrogen or ammonia in a very fast reaction. The key in this second step is to maintain a high reaction rate to attain complete conversion, without inducing high selectivity to ammonia.

Catalytic membrane reactors have been studied for nitrate and nitrite hydrogenation as such intensified reactors allow not only smaller reactor sizes and lower energy consumption, but also can improve the control on local concentrations at the active site. Brunet-Espinosa et al. demonstrated that a small tubular membrane contactor reactor (internal radius 0.9 mm) allows combining high conversion with high selectivity to N$_2$ by dosing a small amount of hydrogen all along the reactor length (Figure 1). The tube wall consisted of macro-porous α-alumina, in which carbon nanofibers are grown, acting as support for the palladium particles. The outside surface of the tube is covered with a PDMS layer to

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make it impermeable to water, while allowing gas (H₂) transport via diffusion.

It was demonstrated that this reactor design indeed results in high selectivity to N₂ at high conversion. It was also reported that, depending on the distribution of CNFs and Pd through the α-alumina wall, the reaction rate can be suppressed by increasing the hydrogen pressure. This result suggests a negative reaction order in H₂ indicative for competitive adsorption of NO₂⁻ and H₂, which is clearly not in agreement with kinetic data on nitrite and nitrate hydrogenation reported so far. Experiments in conventional slurry and fixed bed reactors resulted in reaction orders in nitrite varying between 1 and 0.7, whereas the reaction order in hydrogen is in the window between 0 and 0.3. It was argued that the apparent negative reaction order may be caused by the extreme broad window of the ratios of the NO₂⁻ and H₂ concentrations encountered at different positions in the membrane contactor reactor. The reader is referred to [28] for further details.

The goal of this paper is to test the hypothesis of competitive adsorption of H₂ and NO₂⁻ on Pd by varying the nitrite concentration in steady-state experiments as well as by using transient experiments in with the membrane contactor reactor.

Results

Steady State Operation

The results shown in Figure 2a are adapted from [28], showing the effect of changing the hydrogen partial pressure outside the membrane on nitrite conversion. Figure 2b and 2c show similar results measured at higher NO₂⁻ concentration. The results show that the selectivity is shifting towards ammonia, as expected, with increasing H₂ concentration in the gas mixture. In addition, increasing hydrogen concentration causes the conversion to decrease at all three nitrite concentrations. The effect is partly suppressed though by increasing the NO₂⁻ concentration.

Transient Operation

Figure 3 shows the transient response on feeding a nitrite solution to the reactor to a fully hydrogen saturated Pd catalyst. The start of the experiment (time is zero) is defined as the moment just before the nitrite and ammonia concentration start to increase. The actual switch was made 50 minutes earlier, the delay being caused by the residence time between the pump and the sample-port of the IC. Figure 3a shows an oscillation in the nitrite concentration at the beginning of the experiment, after which nitrite slowly increases up to the concentration in the feed. Figure 3b zooms in on the first 20 h of the experiment, providing more details of the oscillation in the nitrite concentration. Ammonia forms only initially, quickly dropping to zero. Figure 3c presents a further zoom in on the first 4 hours of the experiment, together with the result of two blank experiments showing the nitrite responses with an empty reactor and a catalyst without any adsorbed hydrogen. Figure 3d shows the profiles of nitrite conversion and selectivity to ammonia, calculated from Figure 3b.

Both blank experiments in Figure 3c give a similar result that is clearly different from the transient nitrite concentration profile in the experiment, allowing an estimation of the amount of NO₂⁻ that is converted based on the nitrite profiles in Figure 3a, b and c. Initially, the nitrite conversion is significant as the breakthrough of NO₂⁻ is significantly delayed (Figure 3c) and 9.2 · 10⁻² µmol nitrite is converted, until the moment the first local maximal concentration is reached after 2 hours. After that, the nitrite concentration first reaches a minimum,
converting an additional $2.7 \cdot 10^{-2}$ µmol, where after a second local maximum is observed (converting an additional 0.12 µmol). Finally, it takes typically 60 h before conversion of nitrite stops, indicating exhaustion of hydrogen in the system as will be discussed in more detail later. The total quantity of consumed nitrite in the 60 h experiment (Figure 3a) is 1.9 µmol and the total amount of formed ammonia is $9.3 \cdot 10^{-4}$ µmol, calculated from Figure 3b.

Figure 4 presents the transient response on feeding 1 bar of hydrogen at the shell side and flowing milli-q water through the inside, directly after the experiment in Figure 3, showing desorption of nitrite and ammonia. The concentration of the nitrite flushed reaches nearly twofold (76 µmol/L) the feed concentration used during nitrite adsorption (40 µmol/L), indicating that the presence of H₂ induces desorption of nitrite. It should be noted that the absolute value of the maximum is not well reproducible but the increase in concentration is; this is caused by the fact that the frequency of sampling of the IC is limited so that the actual value of the maximum renders inaccurate. The ammonia concentration reaches a maximum concentration of 130 µmol/L a little bit later. Figure 4b compares the nitrite concentration gradient, identical to Figure 4a, with two blank experiments; i.e. with an empty tube and with a catalyst that was initially hydrogen free (as in Figure 3c). The 50 min delay in the blank experiments in Figure 4b is caused by the residence time in the system between the pump and the sample point of the IC. Changing the gas-phase in the reactor shell is almost instantaneous in contrast to changing the liquid in the reactor tube. Most of the delay is caused by the volume of the pump and of a filter that is mounted between the reactor and the IC, protecting the IC against e.g. CNFs. The ammonia and nitrite responses are about 10 minutes faster than the nitrite breakthrough in the blank experiments (Figure 4a & 4b).

It appears that the H₂-free catalyst desorbed a small amount of nitrite, resulting in a small plateau in the nitrite profile compared to the empty reactor. Therefore, the amount of nitrite desorbed during the experiment (Figure 4a) is calculated based on the blank with the empty reactor, resulting $8.9 \cdot 10^{-2}$ µmol. In any case, the amount of nitrite desorbing is very much lower when the catalyst was not reduced before NO₂⁻ was adsorbed. The amount of ammonia released during the first two hours (Figure 4a) amounts to $1.6 \cdot 10^{-1}$ µmol. However, the formation of ammonia continues at a very low rate as can be seen in Figure 4c, as a low concentration of ammonia is observed during 65 h. The total amount of ammonia formed is 0.3 µmol of ammonia.

Figure 3. Transient response on feeding a nitrite solution to the hydrogen saturated membrane reactor. Experiments were performed at room temperature with 40 µmol/L nitrite solution and liquid flow rate of 0.05 ml/min. a) The nitrite concentration curve during the full experiment; b) The nitrite and ammonia concentration curve at the beginning of the experiment; c) presents the nitrite response for two blank experiments together with the nitrite response in figure b, i.e. first, the reactor is replaced with an empty tube with identical dimensions and second, the reactor is not treated with hydrogen; d) conversion and selectivity curve based on graph c.
Transient Operation

The total quantity of nitrite consumed (1.9 µmol) and ammonia formed (9.3·10⁻² µmol) during exposure to nitrite in Figure 3a and 3b, can be related to the amount of hydrogen available in and on the catalyst. Overnight treatment in 1 bar H₂ results in the formation of palladium hydride (PdH₀.₇)[32,33] Based on the amount of Pd in the reactor it can be calculated that 3.48 µmol H is available. Furthermore, we assume the presence of a monolayer of hydrogen at the surface of the Pd-hydride; it can be estimated that this equals to 0.60 µmol H, based on an average Pd particle size of 9 nm. It should be noted that this assumption is necessary to explain the amounts of NH₄⁺ produced and NO₂⁻ converted as observed. Thus, we assume that in total 4.1 µmol atomic hydrogen is available. Considering that conversion of one NO₂⁻ ion to NH₄⁺ consumes 6 H atoms, whereas conversion to N₂ consumes only 3 H atoms, it can be estimated that 1.3 µmol NO₂⁻ can be converted to products. The remaining 0.6 µmol NO₂⁻ apparently adsorbs on the catalyst, forming about a monolayer of N-containing species on the catalyst surface. This implies that 1.3 µmol nitrite is indeed converted to N₂ because it is not reasonable to assume that a multilayer of N containing species can form. Interestingly, slowly feeding nitrite to a fully hydrogenated catalyst, causes significant nitrite consumption, but hardly any ammonia is formed. This is not in line with the general observations in steady state experiments where a high H/N ratio in the feed causes high selectivity to ammonia. It may be speculated that this is caused by the presence of Pd [ิ-hydride or absence of free dissolved H₂ in the transient experiment, in contrast to a steady-state experiment.

The break-through curve in Figure 3c allows calculation of the amount of nitrite consumed during the first two hours: i.e. 0.09 µmol. Again, the amount of ammonia formed is two orders of magnitude smaller. Therefore, in this time window nitrite either adsorbs causing a surface coverage of 15%, or is converted to N₂, consuming 0.27 µmol H, or a combination of these two options. Surprisingly, after 2 hours (Figure 3) nitrite consumption stops almost completely, followed by a rapid acceleration in consumption during the third hour. These effects are assigned to competition between H and nitrite at the Pd surface. H_ads first prevents further adsorption or reaction of nitrite, causing the conversion of nitrite to decrease to almost zero after 2 hours. Nevertheless, the slow consumption of adsorbed H is making additional surface sites available for adsorption and conversion of nitrite to N₂, liberating even more adsorption sites and accelerating the reaction rate, as seen in the third hour. In other words, these observations support the hypothesis that adsorption of hydrogen and nitrite compete. On the other hand, it also follows that a relatively small fraction of the H atoms, or a small fraction of surface sites are available to respectively adsorb or convert 0.09 µmol NO₂⁻ during the first two hours, as discussed above.

The reason for the second, much weaker local maximum in the nitrite concentration (Figure 3) after about 8 hours remains unclear. It may be speculated that this is caused by consump-

Discussion

Steady State Operation

The trends in conversion with hydrogen partial pressure in Figure 2 confirms that the reaction can be suppressed by hydrogen, resulting in an apparent negative reaction order in H₂. As discussed in [22], this suggests competitive adsorption between nitrite and hydrogen assuming a Langmuir-Hinshelwood mechanism. The observation in Figures 2b and 2c demonstrate that this effect becomes weaker at higher NO₂⁻ concentrations, consistent with the assumption of competitive adsorption of H₂ and nitrite.
tion of roughly a mono-layer of H atoms at that moment in the experiment, but it may also be caused by partial disappearance of Pd-hydride in combination with a broad Pd particle size distribution. Additional work would be needed to confirm this. Ebbesen et al. performed similar transient experiments using ATR-IR spectroscopy, reporting very similar results. First, the formation of ammonia is confirmed when nitrite is introduced to a catalyst saturated with hydrogen and second, formation of adsorbed species is observed, assigned to NO and NH₄⁺. This agrees well with the overall balance over the experiment during 80 hours. The amount of H present can account for conversion of 1.3 μmol nitrite to N₂; thus, the remaining 0.6 μmol is responsible for formation of NO and NH₄⁺. Apparently, the total surface coverage at the end of the experiment is about 1 monolayer (ML). Unfortunately this cannot be confirmed quantitatively with ATR-IR experiments although the intensities reported do indicate significant surface coverage. It should be noted that the typical time constant of the experimental results in this work is about 2 orders of magnitude larger compared to the ATR-IR experiments, which is simply caused by a similar difference in the ratio of the amount of nitrite fed per time unit and the amount of Pd surface present in both experiments.

In the second part of the experiment (Figure 4), the adsorbed species are exposed to H₂. The most important observation is that presence of H₂ causes desorption of nitrite, providing direct evidence for competitive adsorption of these species. It can be estimated that about 0.032 (±0.02) μmol NO₃⁻ desorbed in the window between 40 and 80 minutes, based on the difference with the blank experiment. This equals about 5% of a ML. Remarkably, the desorption is observed earlier than the nitrite flushing out in Figure 4b, which is caused by the fact that changing the gas-phase in the reactor shell is almost instantaneous compared to the response time of the liquid in the tube. In other words, hydrogen is already present while nitrite is not yet flushed out, obtaining strong evidence for competitive adsorption of H₂ and NO₃⁻. Next, a plateau is observed until about 140 minutes, desorbing 0.016 μmol nitrite, at the same concentration that is observed for a short time with a reactor that was not pre-treated with H₂. Note that the delay of 40 minutes in Figure 4 is caused by the residence time in tubing and filters between the reactor and IC sample point.

Two domains can be distinguished regarding the formation of ammonia. Fast initial formation of ammonia is probably caused by presence of NH₄⁺ species on the catalyst surface. During about 15 minutes before appearance of the NH₄⁺ peak, the catalyst is already exposed to hydrogen; it is likely that during this period adsorbed NO species are converted to N₂, based on the IR study by Ebbesen et al. The additional delay of 30 minutes before this is caused by the residence time in the equipment between the reactor and the IC sample-valve. After this fast formation of ammonia, ammonia is being formed slowly but continuously during more than 60 hours, as can been seen in Figure 4c. This observation agrees well with result by Zhao et al. showing strong evidence for the presence of atomic nitrogen (Nads) on the surface as the adsorbed species is not visible with IR spectroscopy. This species is converted to ammonia at a very low pace and therefore it is probably not kinetically relevant. The amount of ammonia formed is about 0.14 μmol, equivalent to 0.25 ML. The small variation in ammonia concentration between 200 and 700 minutes in Figure 4c, involving a tiny amount of ammonia, is not yet understood.

In summary the following reaction scheme is proposed. Starting from Pd fully saturated with hydrogen, nitrite first cannot adsorb resulting in very low conversion, except for rapid formation of a very small amount of ammonia. Partial removal of hydrogen accelerates nitrite hydrogenation, forming nitrogen exclusively. When hydrogen on the Pd is starting to deplete, nitrous species are trapped on the Pd surface in various forms, NH₃ads, NOxads, and N₂ads. Exposure of the catalyst to hydrogen and nitrite-free water induces desorption of NO₂⁻, but also hydrogenation of the surface species. Based on previous work we propose that NO₂ads reacts relatively fast to N₂, whereas NH₃ads converts to NH₄⁺. Finally, very slow hydrogenation of N to NH₄⁺ is confirmed in this work.

The notice of competitive adsorption of nitrite and H₂ is important for designing catalytic processes for removing nitrate and nitrite from drinking water, as concentrations of such contaminants is usually rather low and, more importantly, need to be removed to increasingly stricter and lower levels. Therefore, the hydrogen concentration is preferably low in the part of the reactor with low nitrate/nitrite concentration, in order to prevent hydrogen poisoning.

Conclusions

This paper provides evidence for competitive adsorption between nitrite and hydrogen during catalytic reduction of nitrite on Pd. Under steady state operation the system behaves according to the Langmuir-Hinshelwood model, showing negative reaction orders in hydrogen in case of low concentrations of nitrite. Transient operation of the membrane reactor confirmed this competitive adsorption via two observations; first, H₂ induces desorption of NO₂⁻ and second, the consumption of NO₂⁻ via adsorption and conversion on a catalyst saturated with hydrogen is enhanced when the coverage of the catalyst with hydrogen decreases during the experiment. Ammonia production via hydrogenation of the N-containing species on the catalyst surface proceeds via a fast and a slow pathway, both producing about equal amounts of ammonia. The slow path is attributed to unreactive atomic N species adsorbed on the Pd surface, which are kinetically irrelevant under steady state conditions.

Experimental Section

Materials Used

Macro porous alumina (α-Al₂O₃) tubes, length 200 mm, inner and outer diameter 0.9 and 1.9 mm respectively, were purchased from Hyflux CEPARATION Technologies, Europe. They are cut to pieces of approximately 55 mm in length to serve as support for the carbon
nanofibers. Nickel nitrate hexahydrate (Merck), urea (Merck) and nitric acid (65%, Merck) were used to deposit nickel on the alumina tubes. Ethylene (99.95% PRAXAIR), hydrogen and nitrogen (99.999% INDUGAS) were used to grow CNFs without any further purification. Palladium acetylacetonate (Alfa Aesar) and toluene (> 99.9%, Merck) were used to deposit palladium. Toluene (> 99.9%, Merck) and a two component PDMS RTV 615 kit (permacol B.V.) consisting of a vinyl terminated pre-polymer (RTV-A) and a Pt-catalyzed cross-linker (RTV-B) were used for the preparation of the PDMS solution. Sodium nitrite (> 99%, Merck) was used as nitrite source for the catalytic tests.

Reactor Preparation

The synthesis of the used membrane reactor is described in detail in [28]. In summary, deposition-precipitation technique was used to load nickel on the alumina tubes. Nickel was reduced and sintered at 850 °C in a hydrogen/nitrogen mixture (50/50) for 2 h. The temperature was decreased to 600 °C under inert atmosphere (nitrogen), followed by CNF growth in a quartz tube reactor of 10 mm diameter at 600 °C using a gas mixture containing 20% ethylene, 7% H2, and 73% N2. Next, the temperature was cooled to room temperature under 80 ml/min of nitrogen gas.

Sonication in milliQ water was used to remove any loose carbon nanofiber strands. After drying the sample, palladium was deposited using palladium acetylacetonate as precursor and calcined and reduced at 250 °C. The outer wall of the alumina tube was coated with a home-made PDMS membrane.

Catalytic Test

Two sets of experiments were performed, i.e. steady state experiments and experiments in transient operation. The experiments and results of steady state operation have already in part been reported earlier in [28] and are repeated here for clarity reasons.

In steady state experiments, a nitrite solution (44 μmol/L NO2- ) saturated with argon was flowed inside the tube at a flowrate of 0.05 ml/min, while the shell of the membrane reactor was exposed to a gas mixture containing between 0.02 and 1.0 bar of hydrogen, balanced with argon. The gas flowrate (typically 50 ml/min) was sufficient to prevent any change in the H2 concentration in the shell caused by H2 consumption. Hydrogen diffuses through the PDMS membrane and meets the nitrite at the palladium catalyst. In this case, competitive adsorption of hydrogen and ammonia can be taken into account.

Characterization

The characterization of the membrane reactor is described in detail in [28], and is summarized in Table 1. All experiments were performed with a reactor with a homogeneous distribution of CNFs and Pd through the α-alumina tube.

Characterization of the membrane reactor.

| Table 1. Characterization of the membrane reactor. |
|--------------------------------------------------|
| CNF growth time [min] | 45 |
| Carbon percentage [wt. %] | 8.5 |
| Total CNF pore filling [vol. %] (Hg porosimetry) | 29 |
| CNF pore filling in carbon region [vol. %] | 29 |
| Surface area [m²/g] reactor | 22.0 |
| Pd loading [gPd/100 g reactor] | 0.077 |
| Pd particle size [nm] (HR-SEM) | 8-9 |

Conflict of Interest

The authors declare no conflict of interest.

Keywords: nitrite · hydrogenation · competitive adsorption · membrane reactor · carbon nanofiber

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