



Nitrate reduction with bimetallic catalysts. A stability-addressed overview

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ABSTRACT

Nitrate (NO_3^-) pollution of water bodies is a serious environmental problem worldwide. One of the major concerns about NO_3^- contamination is the lack of cost-effective solutions for its removal from potential drinking water resources. Current technologies, such as ion exchange, reverse osmosis and electro dialysis, produce a reject with high NO_3^- concentration. Catalytic reduction is an emerging technology, capable of transforming NO_3^- into harmless N_2 . A critical issue is to achieve almost complete selectivity to this last species so that the final concentrations of NO_2^- and NH_4^+ can fit the stringent allowed limits. Numerous studies have been carried out evaluating the activity and N_2 selectivity of bimetallic catalysts. Catalyst deactivation by surface fouling, irreversible oxidation of the metal promoter, metal leaching and aggregation of metallic particles remain a major challenge for full-scale implementation of catalytic nitrate reduction. Therefore, it is necessary to develop highly stable catalyst and/or effective solutions for catalyst regeneration. The existing literature on this respect is reviewed hereby.

1. Introduction

One of the main problems associated with the use of natural sources of water is the presence of nutrients, mainly nitrate (NO_3^-) and phosphate (PO_4^{3-}), which mainly contaminate groundwater, exceeding in many cases the limit values recommended by the World Health Organization (WHO) and other national and supranational regulations. The presence of NO_3^- in water bodies is caused by the discharge of poorly treated industrial and urban wastewater, the deposition of livestock manure and the use of nitrogen fertilizers in the intensive agriculture because of it is considered that 50 % of them drains from fields to pollute surface and groundwater [1–4].

Nitrate discharges in water are associated to eutrophication, which causes undesired effects as macroalgal biomass blooms, oxygen deficits, and the decrease in the abundance of fish and decapods as well as the number of their species [5–7]. On the other hand, the ingestion of NO_3^- can produce several human health problems [8–10]. This leads to the need of establishing concentration limits in drinking waters. The European Union [11] establishes maximum concentrations of 50, 0.1 and 0.5 mg/L for NO_3^- , NO_2^- and NH_4^+ , respectively. The WHO recommends lower NO_3^- concentration of 10 mg/LN- NO_3^- (44 mg/LN O_3^-). Nitrite can undergo nitrosation reactions in the gastrointestinal tract and bladder with amines and amides giving rise to N-nitroso compounds, which are some of the most potent known carcinogens [10,12,13]. NH_4^+ can

influence metabolism by shifting the acid-base equilibrium, disturbing the glucose tolerance, and reducing the tissue sensitivity to insulin [14]. Several methods are currently available to remove NO_3^- from water. There are two different groups of techniques on the fate of the NO_3^- , which can be classified as non-destructive and destructive treatments, whose main features are summarized in Table 1. The first group includes ion exchange, reverse osmosis and electro dialysis, which produce a reject with a high concentration of NO_3^- . On the other hand, the destructive treatments (biological denitrification and catalytic reduction) are addressed to convert NO_3^- into harmless nitrogen gas (N_2). As can be seen in Table 1, the advantages of catalytic denitrification over other conventional environmental technologies are the absence of sludge production and pre-treatment, low energy consumption and low space requirements. However, the production of NO_2^- and NH_4^+ above the allowed limits and the common catalyst deactivation have so far hindered full-scale implementation of catalytic nitrate reduction.

Catalytic reduction of NO_3^- (CRN), first studied by Vorlop and Tacke [16], emerged as a destructive treatment based on the transformation of NO_3^- and NO_2^- to N_2 . It operates at mild conditions (ambient temperature and pressure) using, mainly, hydrogen in low amount as reactant, its efficiency depending on the activity and selectivity of the catalysts [1,3,4,15]. In general, bimetallic catalysts are more effective for nitrate reduction than monometallic ones [17–19]. The formation of undesirable NH_4^+ is the main drawback hindering thus far the application of

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catalytic NO_3^- reduction [3,4,16], together with catalyst deactivation when used in real waters [20–24]. Therefore, the efforts of the scientific community are focused on the development of new catalysts exhibiting high N_2 selectivity and proven stability.

Several review papers about catalytic reduction of nitrate have been published in the last decade [3,4,25]. Barrabés and Sá [25] offering an overview on monometallic and bimetallic catalysts used to date. Martínez et al. [3] included a detailed analysis of the reduction mechanism, together with the influence of pH, the use of continuous reactors, membrane-assisted systems and electrocatalytic reduction. Tokazhanov et al. [4] offered an exhaustive review of monometallic and bimetallic catalysts supported on active and passive materials, where the effect of important factors such as noble and promoter metal loading, pH and buffer systems, catalyst loading, nitrate concentration, and H_2 flow rate were evaluated.

The main objective of this review is the analysis of the scientific literature focused on the study of the performance of bimetallic catalysts in terms of reaction rate, nitrate conversion and NH_4^+ formation, updating the state of the art. Besides, a reaction mechanism based on the different routes proposed by other authors is presented. In addition, unlike other previously published reviews, the current one collects the existing information on catalyst deactivation by analysing the studies on the stability of catalysts both in batch reaction cycles and in continuous systems. Finally, this overview reports on catalyst regeneration procedures presented in the literature, which can increase the catalyst useful life, a crucial issue regarding potential application.

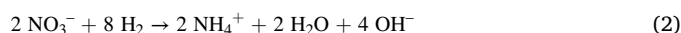
2. Mechanism of nitrate catalytic reduction

The reaction mechanism for NO_3^- removal using bimetallic catalysts has been widely studied [16,26–32]. H_2 has been most commonly used as reducing agent, although some researchers have evaluated the use of HCOOH [33,34]. The most widely used bimetallic catalysts consist of a noble (Pd or Pt) and a promoter (Cu, Sn or In) metal. Bimetallic sites, consisting of noble metal active sites adjacent to the promoters, coexist in the catalyst along with monometallic sites, both noble metal and promoter sites. However, monometallic sites isolated from the promoter metal do not show activity for the catalytic reduction of nitrate. In a first step, NO_3^- adsorbs on the promoter metal surface of bimetallic sites, where it is reduced to NO_2^- [28]. This reduction causes oxidation of the promoter metal, which returns to its initial state due to hydrogen activation by the noble metal [27]. Nitrite can be desorbed into solution and re-adsorbed on a monometallic active site of the noble metal where it can be reduced to NO and subsequently to end products (N_2 or NH_4^+) directly or producing N_2O as reaction intermediate. Nitrite can be also reduced *in situ* at the metal noble bimetallic sites [29,30,35]. The main nitrogenated compounds involved in catalytic reduction of NO_3^- are: NO_2^- , NO, N_2O , N_2 , NH_2OH , $\text{NH}_3/\text{NH}_4^+$ [27–29,31,32,36–46]. Hydroxylamine (NH_2OH) has been detected as intermediate with Pd/ TiO_2 ,

Pd/ Al_2O_3 , Pd/ SiO_2 , Pd/ CeO_2 catalysts at concentration below 0.25 mmol/L [44]. Fig. 1 shows an overall reaction pathway elaborated from the results obtained in several works, using a Pd bimetallic catalyst, the most used noble metal in catalytic reduction of nitrate.

The NO reduction step controls the selectivity towards the reaction products, being NO_3^- reduction to NO_2^- the rate-controlling reaction of the process. The hydrogenation of NO_2^- leads to a double reaction pathway. This species can be reduced to NH_4^+ through the production of NH_2OH , while the most accepted reaction pathway describes that NO_2^- is reduced to NO and then to final products. Some works suggest that this last starts from NO adsorption on the catalyst surface [26,38,39,47]. Mikami et al. [48] proposed a reaction scheme where N_2 is produced by recombination of N atoms or by the reaction between N and NO on Pd sites, whereas NH_4^+ is formed by the reaction between N and chemisorbed H [49].

As an overall process, the catalytic reduction of nitrate by bimetallic catalysts can be summarized in eqs. (1) and (2). In both, hydroxide ions (OH^-) are formed in stoichiometric amounts:



These OH^- can be adsorbed on the active sites of the bimetallic catalyst, competing with NO_3^- and NO_2^- , restricting the nitrate reduction and favoring the accumulation of nitrites in the aqueous phase at high pH values [3,48,50]. Moreover, the hydroxide species adsorbed on the catalyst surface can act as blocking barriers disabling the pairing of N-species diffusing on the surface [3,27]. This results in a lower availability of noble metal active sites where only NH_4^+ can be formed. Carbon dioxide [19,23,24,51–56], formic [33,34,57] or hydrochloric [58–62] acids have been the most used agents to maintain acidic pH. Among them, CO_2 allows better control of the pH inside the catalyst pores because its efficient distribution in the reaction system [3].

3. Bimetallic catalysts

Table S1 provides information on the catalysts used, including metal phase, metal loading and supports, reaction conditions, reactor used, initial NO_3^- concentration, catalyst loading, and initial pH. In addition, it includes values of the kinetic constant (k) or reaction rate ($-r_A$) reported or calculated from results shown in the papers, nitrate conversion ($X\text{-NO}_3^-$) and ammonium ($S\text{-NH}_4^+$) and nitrogen ($S\text{-N}_2$) selectivities. The most used noble metal is Pd, which appears in about 80 % of the catalysts reported in those studies, followed by Pt and with a lesser presence Rh, Ru and Ir. Respect to the promoter metal, Cu has been the most studied followed by Sn and In, and in less extent Ni, Ag, Zn and Fe.

The first generation of catalysts, developed in the early 1990s, consisted of bimetallic Pd-Cu catalysts [16,65]. In general, these catalysts showed fairly good activity, although within a relatively wide range

Table 1
Main features of NO_3^- removal techniques from water [1,4,15].

	Ion exchange	Reverse osmosis	Electrodialysis	Biological denitrification	Catalytic reduction
Full-scale system	Yes	Yes	Yes	Yes	No
Multiple contaminant removal	Yes	Yes	Yes	Potential	Potential
Rejected effluent	Waste brine	Waste brine	Waste brine	Bacteria sludge	No
Pre-treatment needs	Yes	Yes	Yes	Yes	No
Water recovery	> 97 %	> 85 %	> 95 %	> 99 %	> 99 %
Movable	Yes	Yes	Yes	No	Yes
Good manageability	Yes	Yes	Yes	No	Yes
Energy demands	Low	High	High	Medium	Low
Space requirement	Low	Medium	Medium	High	Low
Toxic by-product formation	Concentrate ions brine	Concentrate ions brine	Concentrate ions brine	NO_2^-	NH_4^+ , NO_2^-
Other	Use of NO_3^- selective resins			Post-disinfection is required	Catalyst can suffer deactivation

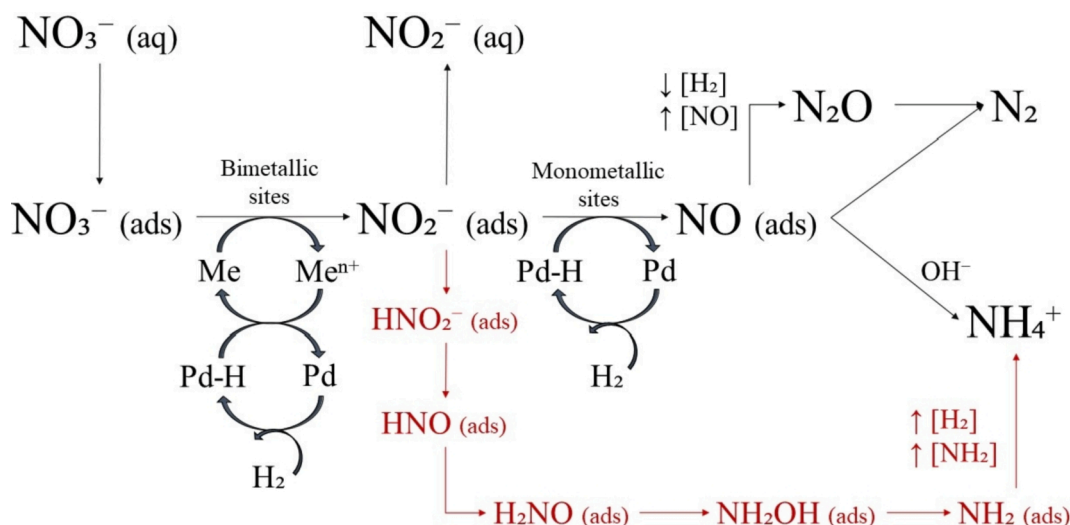


Fig. 1. Scheme of the reaction mechanism for catalytic reduction of nitrate by Pd bimetallic catalysts. Black section represents the most accepted mechanism [26–28,35,38,39,63,64]. Modifications are depicted in red [31,32]. Me represents the promoter metal.

(0.1–3.2 mmol min⁻¹ g_{cat}⁻¹) [42,63,66–70]. The selectivity to N₂ showed important differences, falling between 27 and 84 % [29,48,67,68,71–81] and only in few cases exceeded 90 % [40,82]. A second generation consisting of Pd-Sn and Pd-In catalysts emerged looking for a more efficient alternative to Pd-Cu in terms of nitrate reduction activity, N₂ selectivity and long-term stability [39]. Palomares et al. [83] and Franch et al. [84] compared the performance of Al₂O₃-supported Pd-Cu and Pd-Sn catalysts in the treatment of water from a polluted aquifer in the east coast of Spain and observed that the first one yielded higher selectivity to NH₄⁺ (65 vs 43 %), at similar nitrate conversion (>90 %). Furthermore, comparing the catalytic performance of several catalysts (Pd-Zn, Pd-Cu, Pd-In and Pd-Sn) supported on red mud, Hamid et al. [23] concluded that Pd-Sn was the most active pair (11.6 × 10⁻² min⁻¹ rate constant value), followed by Pd-In (2.3 × 10⁻² min⁻¹), achieving complete nitrate conversion with both catalysts. Meanwhile, under the same conditions, Pd-Cu and Pd-Zn yielded only 78 and 64 %, respectively (0.8 × 10⁻² and 0.5 × 10⁻² min⁻¹).

Several studies have analyzed the influence of metal load and the noble to promoter metal mass ratio on the performance of the catalysts [18,27–29,36,54,67,74,79,80,85–94]. In most cases the noble metal content was in the range of 0.1–2 wt% and could reach values of 5 wt%. The promoter metal usually ranged from 0.1 to 2.5 wt%. Common noble to promoter metal mass ratios of were 4:1, 2:1 and 1:1. Pizarro et al. [18] observed that increasing the metal loading improved catalyst activity. These authors studied the effect of varying the metal load maintaining constant the noble to promoter metal ratio at 2:1 with Pd-Cu, Pd-Sn and Pd-In catalysts. They concluded that catalysts with metallic contents (Pd-promoter) of 5–2.5 wt% yielded higher activity (0.69, 0.83 and 0.57 mmol min⁻¹ g_{Pd}⁻¹, respectively) than those with 1–0.5 wt% (0.20, 0.31, 0.46 mmol min⁻¹ g_{Pd}⁻¹, respectively). Other authors, however, have reported less significant differences with the same metal ratio. Franch et al. [84] compared alumina-supported Pd-Sn catalysts with 5–2.5 and 3–1.5 wt%, noble-promoter metal contents. Nitrate conversion with the first was only 1.2 times lower than the achieved with the second one at 7 h reaction time. This can be due to the higher amount of promoter, giving rise to a higher coverage of the noble metal surface [54,95,96]. Thus, the H spillover from the noble to the promoter metal site decreases and, therefore the rate of NO₃⁻ reduction. Jung et al. [95] observed, with a Pd-Cu catalyst supported on hematite, that at the highest Cu content tested (2.8 wt%) the surface concentration of Cu²⁺ was 2.2 times higher than that in the sample with 1.6 % Cu, indicating that coverage effect by an excess of Cu.

Regarding NH₄⁺ selectivity, Mendow et al. [54] observed

insignificant differences between Pd-Sn catalysts supported on a macroporous anionic resin with equal amount of Pd (2 wt%) but fairly different of Sn (metallic ratios of 1:1 and 4:1). The respective selectivities were 28 and 29 % at NO₃⁻ conversion of 65 % and 84 %, respectively. However, with a very high ratio (10:1), the selectivity to NH₄⁺ increased to 50 %, decreasing the NO₃⁻ conversion at 18 %. Thus, an excess of noble with respect to the promoter metal increases the hydrogen spillover rate and, consequently, the H:N ratio on the catalyst surface, favoring the formation of NH₄⁺. In addition, that the higher hydrogen spillover enhances NO₂⁻ reduction on the bimetallic sites prior to its desorption, favoring NH₄⁺ formation as well [50,54,91,95–97].

The particle size of the noble and promoter metals has an important effect on the activity and selectivity of the catalysts. However, there is some controversy about the optimum size. Miyazaki et al. [98] achieved complete nitrate conversion with bimetallic Pt-Cu nanoparticles lower than 1.6 nm supported on alumina versus only around 60 % under the same operating conditions when the metallic particles size ranged 4.7–7.0 nm. Marchesini et al. [62] observed that large Pd particles (around 28 nm) could enhance the availability of hydrogen on the catalyst surface and the consequent regeneration of the promoter metal active sites, resulting in a more efficient catalytic reduction of nitrate. Zhang et al. [79] reported that bimetallic Pd-Cu nanoparticles with sizes around 3.5–4.2 nm were suitable for simultaneous adsorption and activation of two N-containing species, obtaining higher selectivity towards N₂. On the other hand, on bimetallic ensembles lower than 3.5 nm, the exposed noble metal particle becomes too small to adsorb and activate two molecules of N species simultaneously for the formation of N₂.

Using a suitable support is important for the catalyst performance [3,4,25]. Both active and passive supports have been used, with zero-valent iron (ZVI) standing out among the first group due to its reduction capacity, in addition to its availability, as well as low cost and environmental impact [99]. Suzuki et al. [100] used ZVI directly as a catalyst in the reduction of NO₃⁻. Electron transfer occurs through the oxidation of Fe⁰ to Fe²⁺ or Fe³⁺. However, some drawbacks have been observed such as particle agglomeration or high NH₄⁺ selectivity [101–103]. These drawbacks can be reduced by using ZVI nanoparticles (NZVI) as support of metals such as Pd or Cu, among others [104–107]. The introduction of a second metal has been studied, improving the rate of NO₃⁻ reduction and the selectivity towards N₂ [50,107–109]. Hamid et al. [106] studied the effect of incorporating Cu to a Pd/NZVI catalyst with different metal loading. They achieved complete nitrate conversion with Cu and Pd at 1.5 and 0.5 wt%, respectively, versus only 21 % with

Pd/NZVI at 0.5 Pd wt.%. Furthermore, the selectivity to NH_4^+ was lower with the Pd-Cu catalyst, although frankly poor values were obtained in both cases. However, it was observed that the addition of a promoter metal increased the selectivity to NO_2^- , due to its low affinity to the catalyst surface, which causes its accumulation as a final reaction product [106,107,110]. This species was negligible with the Pd/NZVI catalyst. Besides, the promoter metal enhances electron transfer, that can affect the lifetime of the catalyst [106].

The most commonly passive supports tested for bimetallic catalysts in nitrate reduction are Al_2O_3 , activated carbon (AC), TiO_2 and SiO_2 . In addition, a wide diversity of some other materials have been used, including CeO_2 [44,70,111–113], ZrO_2 [29,44,67,114,115], hydro-talcites [72,73,116], zeolites [55,96,117], ionic exchange resins [54,82,118,119], carbon nanotubes (CNT) and multiwalled carbon nanotubes (MWCNT) [51,52,120–123], clays, pillared clays [18,77] and glass fiber [124,125].

The porous texture of the supports appears to influence the performance of the bimetallic catalysts [19,126,127]. Krawczyk et al. [126] observed that the textural properties of the support modified the selectivity to N_2 . Pd-In catalysts supported on SiO_2 (BET area of $300 \text{ m}^2/\text{g}$ and mean pore diameter of 45 \AA) and TiO_2 ($50 \text{ m}^2/\text{g}$ and $100\text{--}300 \text{ \AA}$) yielded N_2 selectivities of 55 and 90 %, respectively, at complete nitrate conversion. This result can be explained by the fact that the neutralization of OH^- ions, formed on active sites located in narrow pores, can take place after their diffusion from pores into the reaction mixture. Higher internal porosity would determine slower diffusion so that pH inside the pores may be higher than that of the solution, which would favour the formation of NH_4^+ . However, the point of zero charge (PZC) of the support has been reported as a key factor in the adsorption rate of nitrate ions. Marchesini et al. [61] reported that the high PZC of Al_2O_3 (PZC = 8) seems to improve the performance of Pd-In catalysts compared with SiO_2 (PZC = 2), achieving a > 99 % and 35 % nitrate conversion, respectively. During the reaction, the pH of the solution (pH 5) leads to a net positive charge of the Al_2O_3 surface that would enhance adsorption of nitrate and nitrite ions and so their interaction with the catalyst active phase. Furthermore, the support can be important in connection with potential leaching of the metallic phases. Yoshinaga et al. [29] studied the effect of pH and the support in that respect, comparing Pd-Cu catalysts supported on Al_2O_3 and AC at initial solution pH of 5.4 and 2.3. The highest metal loss occurred with Al_2O_3 at pH 2.3 (30.7 % of Cu), being significantly lower, although still of some importance, at pH 5.4 (6.3 % of Cu). Meanwhile, the catalyst supported on AC did not suffer significant metal loss, which was attributed to the strong interaction between Cu and Pd on this support, giving rise to the of Pd-Cu particles. The stability of the support itself was also in favour of AC, especially at low pH, where 3.7 % of Al was dissolved from Al_2O_3 .

TiO_2 , despite not being the most used support, allow preparing catalysts that have proven higher activity than those supported on other materials [44,68,111,121]. Wada et al. [44] reported significant differences of activity using CeO_2 , TiO_2 , SiO_2 , Al_2O_3 or ZrO_2 as support for Pd-Cu catalysts. They observed that Pd-Cu/ TiO_2 was the most active, yielding up to 10-fold higher reaction rate ($36 \times 10^{-2} \text{ mmol min}^{-1} \text{ g}_{\text{cat}}^{-1}$) than catalysts supported on SiO_2 , Al_2O_3 and ZrO_2 (2.5×10^{-2} , 1.5×10^{-2} , and $5.1 \times 10^{-2} \text{ mmol min}^{-1} \text{ g}_{\text{cat}}^{-1}$, respectively). The authors found that TiO_2 markedly promotes the reduction of surface copper, key issue for the high catalytic activity.

Mixed supports have also been used to improve activity as well as selectivity to N_2 . Kim et al. [70] investigated the behaviour of Pd-Cu catalyst (3–1 wt%) on a mixed $\text{TiO}_2\text{-CeO}_2$ (Ti:Ce 18:1 wt) and found an increased activity of almost 70 % with respect to the TiO_2 -supported catalyst. The modification of the acid-base properties of TiO_2 has also been studied and interesting results have been obtained relative to the reaction kinetics. Bou-Orm et al. [69] analyzed the effect of modifying the TiO_2 support with Nb (1, 2 and 5 wt%) and Mg (7 wt%) as dopant agents, observing a decrease of the crystallinity and increase of the surface area, from $36 \text{ m}^2/\text{g}$ of the raw TiO_2 to $59\text{--}98 \text{ m}^2/\text{g}$ of Nb- TiO_2

and $58 \text{ m}^2/\text{g}$ for Mg- TiO_2 . In addition, the acid-base properties of TiO_2 were strongly modified by including the doping agent, introducing the acidic character of Nb, whereas Mg-doped TiO_2 becomes basic. The Mg doping increased the activity from $0.67 \text{ mmol min}^{-1} \text{ g}_{\text{cat}}^{-1}$ of the original TiO_2 to $0.76 \text{ mmol min}^{-1} \text{ g}_{\text{cat}}^{-1}$, while the Nb catalyst showed lower activity ($0.43\text{--}0.47 \text{ mmol min}^{-1} \text{ g}_{\text{cat}}^{-1}$).

4. Stability of the catalysts

The possibility of applying catalytic nitrate reduction in real water matrices requires learning on the catalyst stability and understanding the causes of deactivation so to develop effective regeneration procedures. Most of the articles including stability studies report results from continuous flow experiments, mostly using fixed bed (FBR) or continuous stirred-tank (CSTR) reactors [19,21,29,33,48,54,61,78,114,115,118,127–136]. Typically, the FBR used in the experiments thus far are of fairly small size, with an internal diameter between 0.4 and 2 cm and 3–30 cm length [61]. The CSTR are usually also lab-scale, with total volume ranging $250 \text{ mL} - 1 \text{ L}$ and working under continuous stirring at 300–900 rpm, with powdered catalyst. Some studies, evaluate the stability of the catalyst by consecutive semi-batch reaction cycles.

4.1. Catalyst deactivation

Thus far, only few works devoted to the study of catalyst stability have reported truly promising results. Mendow et al. [54] observed a constant nitrate removal efficiency ($\cong 60 \%$) and NH_4^+ selectivity of 5 % upon 80 h on stream with a Pd-Sn (2–0.5 wt%) catalyst supported on an anionic resin working with an aqueous solution of 100 mg/L of NO_3^- . Marchesini et al. [61] reported stable NO_3^- conversion (close to 75 %) with 55 % N_2 selectivity during 120 h of time on stream, in the presence of Cl^- (125 mg/L), HCO_3^- (150 mg/L) and SO_4^{2-} (100 mg/L), with a Pd-In/ Al_2O_3 catalyst (1–0.25 wt%). Hamid et al. [23] reported complete nitrate removal upon 11 consecutive 4 h-batch cycles, with a Pd-Sn catalyst supported on red mud, where the catalyst activity was maintained at a fairly high value ($5.8 \text{ L min}^{-1} \text{ g}_{\text{Pd}}^{-1}$) and > 88 % N_2 selectivity.

However, most of the studies on catalyst stability reported significant deactivation. Table S2 collects those studies, classified according to the causes of deactivation. Together with the catalyst the able contains information on the water matrix and the reactor system. Fig. 2 provides schematic representation of those causes, namely (i) fouling of the catalyst surface (ii) irreversible oxidation of the promoter metal (iii) leaching of the metallic phase and (iv) aggregation of metallic particles. Fouling of the catalyst surface by salts precipitation is the main cause of deactivation with natural waters and synthetic ones spiked with ions other than nitrate [21,22,56,61,83,84,114,116,118,120]. It is mainly caused by sulfur, calcium and magnesium salts, but also by organic matter [21,61,83,137,138]. From adsorption experiments with a Pd-Cu/ Al_2O_3 catalyst, Chaplin et al. [20] established the following order for the fouling capacity: $\text{SO}_4^{2-} < \text{HCO}_3^- < \text{Cl}^- < \text{humic acid} < \text{SO}_3^{2-} < \text{HS}^-$. Palomares et al. [83] tested the stability of a Pd-Sn/ Al_2O_3 catalyst in a long-term experiment using tap water of $1000 \mu\text{S cm}^{-1}$ conductivity, with the following composition (mg L^{-1}) 185 Ca^{2+} , 79 Cl^- , 200 SO_4^{2-} and 90 NO_3^- . They observed complete nitrate conversion upon 8 h on stream, but then, the catalyst started to lose activity, showing monotonical deactivation up to 40 % nitrate conversion after 250 h. The authors discarded metal leaching as a cause of deactivation, which was attributed to precipitation of calcium salts on the catalyst surface and formation of some reduced species of sulfur that slowly deactivate the palladium sites. Theologides et al. [22] reported that fouling of the Pd metal clusters by ions, particularly cations, is directly related to increased selectivity towards NO_2^- . This occurs because reduced availability of Pd sites due to fouling hinders the consecutive reduction of nitrite ions, resulting in their accumulation as a reaction product. Santos et al. [137] integrated catalytic reduction of nitrate and ozonation for

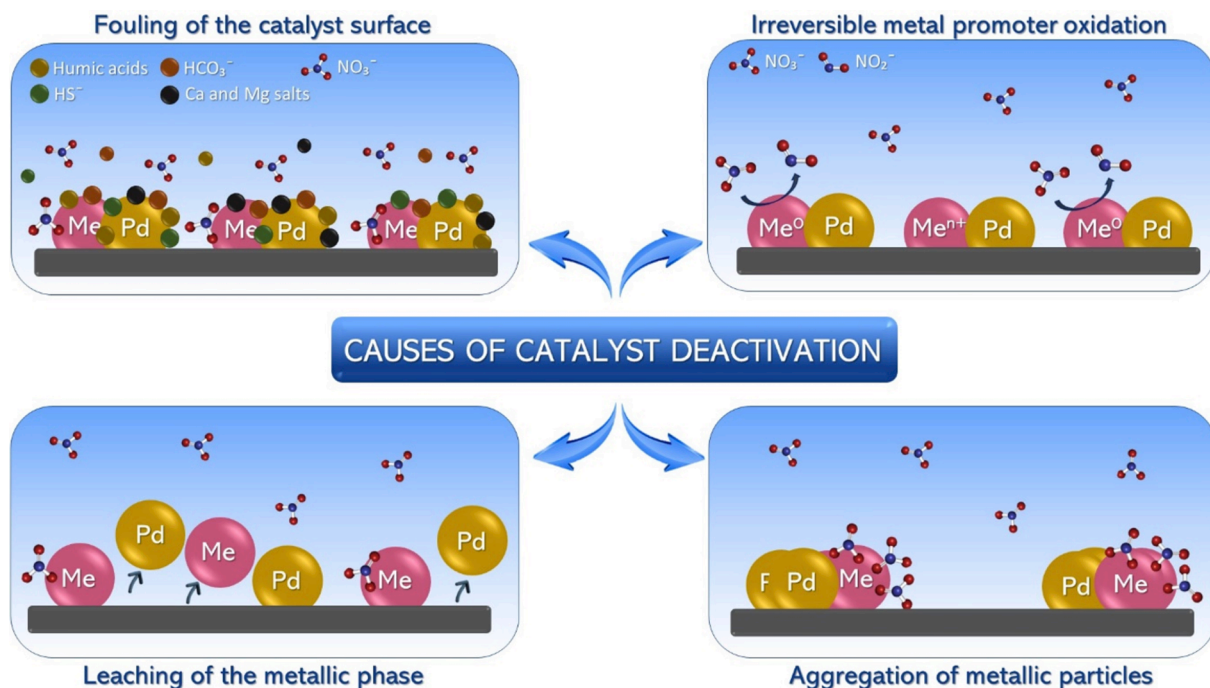


Fig. 2. Main causes of catalyst deactivation. Me represents the promoter metal.

the simultaneous removal of organic and inorganic species from water. They observed that the organic species resulting from ozonation, were responsible of the Pd-Cu/CNT catalyst deactivation upon selective adsorption on the Cu active centres of the catalyst.

Increasing the oxidation state of the promoter metal irreversibly leads to the loss of activity of bimetallic catalyst because of interference in the redox cycle. Franch et al. [84] reported 20–25 % decrease in nitrate conversion with a Pd-Sn/ Al_2O_3 catalyst ($S_{\text{BET}} = 125\text{--}134 \text{ m}^2/\text{g}$, metal dispersion = 1.9–6.4 %, crystal size = 17.6–57.6 nm) after 8 h of reaction. However, using a high surface area alumina (HSA) ($S_{\text{BET}} = 277 \text{ m}^2/\text{g}$, crystal size = 2.9 nm) metal dispersion increased to 38.9 % and deactivation became almost negligible. The activity was also somewhat increased. XPS analyses of the catalysts before and after reaction revealed 24.6–26.7 % of oxidized Sn species (Sn^{2+} and Sn^{4+}) in the used Pd-Sn/ Al_2O_3 catalyst, whereas the one supported on HSA did not show significant variation of the Sn oxidation state. Therefore, using HSA appears a favourable alternative to alumina to avoid oxidation of the promoter metal. Hamid et al. [24] observed that, after a stable period of complete nitrate conversion (60 h), a Pd-Sn/kaolinite catalyst suffered deactivation for 110 h, decreasing NO_3^- conversion by 20 %. Increased Sn oxidation after use was confirmed by XPS, negatively affecting to the catalyst performance.

The loss of metal phase by leaching leads to irreversible deactivation of the catalyst and additionally provokes water pollution by the metal species. The intensity of leaching is pH dependent [17,139] and can be controlled by modifying the characteristics of the catalysts [29,140] or the reaction conditions [17,139]. The calcination temperature during catalyst preparation affects to further metal loss. Bae et al. [139] observed that air-calcination of a Pd-Cu/ TiO_2 (3–1 wt%) catalyst at temperature below 350 °C led to significant loss of Cu and Pd upon reduction with NaBH_4 , indicating that strong Cu and Pd bonding on TiO_2 did not occur at that temperature. Calvo et al. [17] observed that the operating pH affects to the stability of the active phase, especially through the leaching of the promoter metal. The authors tested a Pd-Cu/AC catalyst buffering the reaction solution at different pH values within 5–8. At pH 5 dramatic Cu leaching was observed after 28 h on stream, reaching almost 70 % of the initial Cu load of the catalyst and nitrate conversion strongly decreased upon that time on stream. At pH 6 and 7,

leaching decreased drastically and the catalyst showed the highest nitrate conversion (80–90 %). Beyond that pH, Cu leaching raised again above 35 % of the initial load. Similar results have been reported by Bae et al. [139], who achieved complete nitrate conversion within the same optimum pH range (6–7) with a significant decrease (up to 58 %) at pH 8 due to the loss of active phase by leaching of Cu (35 %) and Pd (54 %). In this sense, Pd and Cu did not leach when supported on AC, even at low pH (2.3), while a significant amount of Cu, and also appreciable amounts of Pd, were released from the surface of Pd-Cu/ Al_2O_3 , Pd-Cu/ SiO_2 , Pd-Cu/ ZrO_2 catalysts [29]. At pH 5.4, in the Pd-Cu/ ZrO_2 and Pd-Cu/ SiO_2 catalysts, the concentration of Pd decreased by 1.4 and 3.9 %, while the Cu loss reached values of 26 and 10.6 %, respectively. Under the same operating conditions, Pd leaching from the Pd-Cu/ Al_2O_3 catalyst was negligible, and the amount of dissolved Cu was 6.3 %, reaching up to 30.7 % at 2.3 initial pH. The ability of carbon supports to reduce metal leaching could be associated with their functional N-groups. Owing to the lone pair electrons of nitrogen, the N-rich sites in the carbon support can increase the local electron density and promote the formation of active centres which can coordinate with the metallic species thus favoring a more stable anchorage onto the support [141,142].

Aggregation of metal particles affects to the metal dispersion, decreasing the available surface area of the active phase and thus the adsorption of hydrogen onto the noble metal [91,96,119,143]. Hamid et al. [96] observed >50 % activity loss after five consecutive batch reaction cycles with a Pd-Sn/Nanocrystalline ZSM-5 catalyst. They reported an increase of the metal mean particle size from 4.5 to 9.8 nm, with the subsequent loss of dispersion (from 20.8 to 11.4 %), active metal surface area (from 92 to 51 m^2/g) and cumulative hydrogen uptake (from 0.35 to 0.19 $\text{cm}^3 \text{ g}^{-1}$). Mendow et al. [118] observed a decrease somewhat above 10 % of nitrate conversion after 3 reaction cycles with a Pd-Cu catalyst supported on anion exchange resin, attributed to a loss of metal dispersion of almost 15 %.

Some other less common causes of deactivation have been observed related to the deterioration of the catalyst during the washing process. For instance, Bae et al. [107] attributed a slight loss of activity of a Pd-Cu/NZVI catalyst (from complete to 95 % nitrate conversion after 5 successive batch reaction cycles), attributed to the continuous exposure

to NO_3^- and the contact with O_2 in the washing step following each reaction cycle. Similarly, Zeng et al. [144] observed that the active sites on the outer and internal surface of Fe, Cu/Fe and Mn/Fe nanoparticles were partly depleted after the third batch reaction cycle. In addition, they reported that the dissolved oxygen in the aqueous solution could provoke the formation of a less reactive oxide layer on the surface of the nanoparticles.

4.2. Catalyst regeneration

The literature also reports on the regeneration of catalysts used for nitrate reduction, as summarized in Table 2. Partial recovery of the activity has been reported in cases where deactivation is attributed to fouling of the catalyst surface or promoter metal oxidation [24,137,145,146]. However, loss of metal phase by leaching and

aggregation of metal particles cannot be reversed. Chaplin et al. [145] applied an oxidative treatment to Pd-In/ Al_2O_3 and Pd-Cu/ Al_2O_3 catalysts affected by sulfide deactivation. The authors used several agents of different strength (NaOCl , H_2O_2 , dissolved oxygen, air) and under different conditions of concentration, pH and temperature. The Pd-In/ Al_2O_3 catalyst was partially regenerated to 60 % of the initial activity with NaOCl (28–56 mM, pH = 7.8) or air at 120 °C. The S fouling increased the undesired selectivity to NH_4^+ , which was not restored to the original value. They applied the same treatments (except for pH, now 11) to the used Pd-Cu/ Al_2O_3 catalyst, which partially recovered its initial activity, increasing the nitrate conversion from 51.7 % to 78 and 72 %, respectively. Santos et al. [137] recovered the activity of a Pd-Cu/CNT catalyst whose Cu sites were partially covered by adsorbed organic species (loss of 61 % of the catalytic activity) by thermal treatment at 200 °C for 1 h under N_2 flow, followed by reduction under H_2 flow for 3

Table 2
Results reported in the literature on the regeneration of bimetallic catalysts for nitrate reduction.

Deactivation cause	Catalyst	Fresh catalyst	Used catalyst	Regeneration agent/process*	Regenerated catalyst	Ref.
Oxidation of the promoter metal	Pd-Sn/ kaolinite Pd-Sn/ Al_2O_3 - diatomite	X- NO_3^- = 100	X- NO_3^- = 80	DDIW washing and H_2 reduction	X- NO_3^- = 100	[24]
		S- N_2 = 77 %	S- N_2 = 42 %	NaOH washing	S- N_2 = 70 %	[146]
			S- N_2 = 60 %		S- N_2 = 63 %	
			Catalytic activity = 0.30 $\text{mg/L g}^{-1} \text{min}^{-1}$		Catalytic activity = 0.32 $\text{mg/L g}^{-1} \text{min}^{-1}$	
				HCl washing	S- N_2 = 74 %	
					Catalytic activity = 0.46 $\text{mg/L g}^{-1} \text{min}^{-1}$	
Fouling of the catalyst surface	Pd-Cu/CNT		Catalytic activity = $1.6 \cdot 10^{-5} \text{ mmol min}^{-1} \text{g}_{\text{cat}}^{-1}$	Thermal treatment with N_2 at 200 °C during 1 h and 3 h of H_2 reduction	Catalytic activity = $2.3 \times 10^{-4} \text{ mmol min}^{-1} \text{g}_{\text{cat}}^{-1}$	[137]
	Pd-In/ Al_2O_3	Catalytic activity = $190 \times 10^{-3} \text{ L min}^{-1} \text{g}_{\text{cat}}^{-1}$	Catalytic activity = $38.1 \times 10^{-3} \text{ L min}^{-1} \text{g}_{\text{cat}}^{-1}$	Air-saturated water washing	Catalytic activity = $39.9 \times 10^{-3} \text{ L min}^{-1} \text{g}_{\text{cat}}^{-1}$	[145]
		X- NO_3^- = 100 %	X- NO_3^- = 52.2 %		X- NO_3^- = 48.7 %	
		S- NH_4^+ = 29.7 %	S- NH_4^+ = 12.1 %		S- NH_4^+ = 19.3 %	
		S- NO_2^- = 0 %	S- NO_2^- = 0 %		S- NO_2^- = 0.7 %	
		S- NH_4^+ (X- NO_3^- = 50 %) = 3.8 %	S- NH_4^+ (X- NO_3^- = 50 %) = 23.2 %		S- NH_4^+ (X- NO_3^- = 50 %) = 39.4 %	
		H_2O_2 washing	Catalytic activity = $41.5 \times 10^{-3} \text{ L min}^{-1} \text{g}_{\text{cat}}^{-1}$			
			X- NO_3^- = 55.7 %			
			S- NH_4^+ = 17.6 %			
			S- NO_2^- = 0.8 %			
			S- NH_4^+ (X- NO_3^- = 50 %) = 31.4 %			
			Air (120 °C) for 4 h	Catalytic activity = $91.4 \times 10^{-3} \text{ L min}^{-1} \text{g}_{\text{cat}}^{-1}$		
				X- NO_3^- = 93.7 %		
				S- NH_4^+ = 28.6 %		
				S- NO_2^- = 0.1 %		
				S- NH_4^+ (X- NO_3^- = 50 %) = 17.3 %		
			NaOCl washing	Catalytic activity = $96.9 \times 10^{-3} \text{ L min}^{-1} \text{g}_{\text{cat}}^{-1}$		
				X- NO_3^- = 100 %		
				S- NH_4^+ = 14.7 %		
				S- NO_2^- = 0 %		
				S- NH_4^+ (X- NO_3^- = 50 %) = 11.5 %		
	Pd-Cu/ Al_2O_3	Catalytic activity = $187 \times 10^{-3} \text{ L min}^{-1} \text{g}_{\text{cat}}^{-1}$	Catalytic activity = $38.1 \times 10^{-3} \text{ L min}^{-1} \text{g}_{\text{cat}}^{-1}$	NaOCl washing	Catalytic activity = $64.1 \times 10^{-3} \text{ L min}^{-1} \text{g}_{\text{cat}}^{-1}$	
		X- NO_3^- = 51.7 %	X- NO_3^- = 51.7 %		X- NO_3^- = 77.9 %	
		S- NH_4^+ = 28.0 %	S- NH_4^+ = 14.7 %		S- NH_4^+ = 9.8 %	
		S- NO_2^- = 0 %	S- NO_2^- = 0.2 %		S- NO_2^- = 0.1 %	
		S- NH_4^+ (X- NO_3^- = 50 %) = 14.9 %	S- NH_4^+ (X- NO_3^- = 50 %) = 28.4 %		S- NH_4^+ (X- NO_3^- = 50 %) = 9.4 %	
				Air (120 °C) for 4 h	Catalytic activity = $65.0 \times 10^{-3} \text{ L min}^{-1} \text{g}_{\text{cat}}^{-1}$	
					X- NO_3^- = 72 %	
					S- NH_4^+ = 19.3 %	
					S- NO_2^- = 0 %	
					S- NH_4^+ (X- NO_3^- = 50 %) = 20.6 %	

* Ambient conditions unless other indicated.

h.

Regeneration of catalysts suffering of promoter metal oxidation has been investigated by several authors. Chen et al. [138] used NaBH_4 and H_2 as reducing agents with a Cu-Pd/Titanate nanotubes catalyst. Around 60 % of the initial activity was restored but not the N_2 selectivity. Regeneration of a Pd-Sn/ Al_2O_3 -diatomite catalyst was performed by acid washing (HCl 2 M), which favoured the reduction of SnO_2 to Sn [146]. Hamid et al. [24] used H_2 to regenerate a sn-Pd-kaolinite catalyst that suffered oxidation of Sn to Sn^{+2} and Sn^{+4} after 60 h on stream. After 1 h under continuous H_2 flow the initial activity for NO_3^- reduction was completely recovered together with 70 % of the selectivity to N_2 . Jung et al. [91] and Hamid et al. [23,117] developed a treatment for the catalyst to prevent the loss of activity. That treatment consisted of washing with deaerated deionized water (DDIW), drying at 100 °C, air-calcination at 350 °C and reduction with NaBH_4 . It was tested with several catalysts (Cu-Pd/maghemite, sn-Pd-red mud, In-Pd/N-Beta zeolite, Cu-Pd/N-Beta zeolite, sn-Pd/N-Beta zeolite), which showed no significant loss of activity after eleven 75 min-batch cycles. However, some sintering of Cu particles was observed in the Cu-Pd/maghemite catalyst, which slightly reduced the catalytic activity but increased the selectivity to NO_2^- .

5. Conclusions

The results reported in the literature on the topic of this review allow summarizing the following conclusions:

(i) Pd-Sn and Pd-In based bimetallic catalysts have emerged as competitive alternative to Pd-Cu pair in terms of nitrate reduction activity, N_2 selectivity and long-term stability.

(ii) Regarding the metallic phase, an excess of promoter metal can provoke adverse effects on catalytic denitrification, due to partial blockage of the noble metal active surface, thus decreasing the rate of hydrogen adsorption and spillover, essential for continuous regeneration of the promoter oxidation state. On the other hand, excess of noble metal increases the H concentration on the catalyst surface and the H:N ratio, favoring the formation of undesired NH_4^+ . The optimum metal content in bimetallic catalysts appears to be in the range of 0.5–2 % of each metal, with a noble:promoter metal ratio between a fairly wide range of 1:1 to 4:1.

(iii) PZC of the support affects to the catalyst performance. A value above that of the solution pH, leads to a net positive charge of the catalyst surface, favouring the attraction of negative nitrate and nitrite ions and, thus, their interaction with the metallic active phase. Among the metal oxides, TiO_2 , despite not being the most used support, has proven to enhance the activity more than other materials. Activated carbon has shown a better stability in terms of metal loss by leaching. It is worth to highlight the growing interest for the use of waste materials, such as red mud or biomass residues-derived materials, like biochars and hydrochars.

The main catalyst deactivation causes identified in the literature are.

Fouling of the catalyst surface by salt precipitation and organic matter, the main cause of deactivation with natural and synthetic waters spiked with ions other than nitrate.

Irreversible oxidation of the promoter metal.

Metal loss by leaching, with the additional adverse effect of water contamination.

Aggregation of metal particles, decreasing the available surface area of the active metal phase.

Different regeneration procedures have been investigated in the literature. Sulfide-fouled catalysts have been partially regenerated by oxidative treatment with NaOCl or air at 120 °C. The adsorption of organic compounds on the catalyst surface could be reduced by thermal treatment at 200 °C under N_2 flow followed by reduction by H_2 . For catalysts deactivated by oxidation of the promoter metal combined treatments of washing followed by calcination at 350 °C and reduction by NaBH_4 have been used, as well as more simple methods based on H_2 -

reduction.

6. Challenges and future outlook

Catalytic reduction is not yet a demonstrated technology to be implemented as a full-scale solution for effective removal of nitrate from drinking water sources. In principle it has potential advantages over the currently employed methods, based on the use of membranes or ion-exchange resins, which produce residual streams with high nitrate concentrations, requiring proper disposal. Biological denitrification is mostly used for wastewater treatment and produces waste sludge to deal with. Its application to water for human consumption would require deep disinfection. Catalytic reduction emerged to avoid those drawbacks but needs to solve important challenges related to the catalyst selectivity to N_2 and lifetime. Nitrite and ammonium are undesired byproducts from nitrate reduction, which need to be almost completely avoided given their harmful character, which determines highly stringent allowed limits. That demands a very high selectivity towards N_2 , which must be compatible with the high levels of nitrate conversion commonly required. Growing research efforts addressed to the development of novel catalytic systems fulfilling those requirements are expected in the next future. This has to go in parallel with the stability of the catalysts, a crucial issue regarding potential application in cost-effective terms with natural waters, commonly containing other accompanying ions that have proven to provoke deactivation of the catalysts tested thus far. Long-term continuous experiments must be an extended practice associated to the stability studies. Gaining in-dept knowledge on the causes of deactivation is also a main task for the future. That knowledge can be comprehensively applied to the development of effective regeneration procedures capable of enlarging the catalyst lifetime. The design of reactors advantageously adapted to the characteristics of the catalyst is also a challenge requiring resolute research efforts including pilot-scale studies.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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