Catalysis Today 151 (2010) 190–194

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Catalytic removal of nitrates from waters

Costas L. Constantinou [a], Costas N. Costa [b,**], Angelos M. Efstathiou [a,*]

[a] Department of Chemistry, Heterogeneous Catalysis Laboratory, University of Cyprus, P.O. Box 20537, CY 1678 Nicosia, Cyprus
[b] Department of Environmental Management, Laboratory of Wastes Management, Cyprus University of Technology, P.O. Box 50329, CY 3603 Limassol, Cyprus

ARTICLE INFO

Article history:
Available online 12 March 2010

Keywords:
Catalytic denitrification
Nitrate reduction
Nitrate removal
Pd-Cu bimetallic catalysts
Mass transport phenomena
Hydrogenation kinetics

ABSTRACT

The selective catalytic reduction of nitrates (NO_3^-) in pure water towards N_2 formation by the use of gaseous H_2 and in the presence of O_2 (air) at 1 atm total pressure and 25 °C has been investigated over Pd-Cu supported on TiO_2-Al_2O_3 pellets (spherical shape). The effects of internal mass transport phenomena, of Pd and Cu loading (wt%), and of reducing feed gas composition on the reaction rate, N_2-selectivity, and the kinetics of the overall reaction in terms of apparent reaction orders with respect to nitrate concentration (mg/L) and H_2 partial pressure (bar) have been investigated. Apparent reaction orders of 0.32 and 1.04 were estimated, respectively with respect to NO_3^- concentration and H_2 partial pressure in the reducing feed gas stream (H_2/He). However, when 20% air is added in the hydrogen reducing feed gas stream, the apparent reaction order with respect to the H_2 partial pressure was increased to 1.7. It is demonstrated for the first time that the presence of internal mass transport phenomena when large catalytic particles (2–3 mm in size) are used in a semi-batch mode reactor operation results in the reduction of the selectivity of reaction with respect to NH_4^+ and NO_2^- products, and at the same time in the increase of N_2 product selectivity, whereas the opposite is true for the rate of reaction. Moreover, it was found that the reaction rate, the NO_3^- conversion (%), and the reaction product selectivity are affected significantly by the presence of oxygen in the reducing feed gas stream, and by the Pd and Cu metal loading used in catalyst's composition.

1. Introduction

Pollution of natural waters with nitrate ions (NO_3^-) is becoming a widespread concern in many countries due to the rapid development of their agricultural and industrial activities [1,2]. High concentrations of nitrates in drinking water are harmful due to their reduction to nitrites (NO_2^-) that combine with haemoglobin in the human blood to form the toxic compound of methaemoglobin [2].

Catalytic reduction of nitrates/nitrites in aqueous media using hydrogen is receiving more and more attention [3–7] since it is an alternative and economically advantageous process to biological treatment (bacteria degradation) as a means of purifying drinking water and wastewater streams without experiencing the drawbacks of conventional methods [1,3]. In particular, denitrification (nitrite and nitrate removal) is one of the most investigated hydrogenation reactions in ground-water treatment [1,5,8]. However, control of the desired N_2-selectivity of reaction (lowest NH_4^+ and NO_2^- formation in water to be obtained) remains *a key issue* in developing a future marketable catalytic reduction of nitrates/nitrites technology [4].

The effects of catalyst chemical composition on the reaction rate and N_2-selectivity have been studied extensively as recently reviewed [3]. It was demonstrated that both nitrate reduction rate and N_2-selectivity of reaction are substantially influenced by the composition of the liquid phase (drinking water), where the efficiency of Pd-Cu and Pd-Sn bimetallic catalysts is markedly influenced by the migration of produced hydroxide ions from the Helmholtz layer to the liquid phase [3,9]. Several attempts have been reported for the improvement of N_2-selectivity of reaction after using additional gaseous, liquid or solid reagents (e.g. CO_2) [10]. Despite these efforts, none of these reagents was proven to be efficient at a reasonable cost and without creating or contributing to any additional problems.

Important mechanistic studies on the catalytic reduction (use of H_2) of nitrates are lacking due to the difficulty in applying *in situ* spectroscopic techniques in water. However, Attenuated Total Reflection Infrared Spectroscopy (ATR-IR) has been recently applied successfully [5,6] to investigate the nature of the adsorbed reaction intermediates formed under reaction conditions in water, information that allowed to draw concrete conclusions for the reaction path and how the N_2-selectivity of reraction might be influenced by the H_2 concentration in the feed stream compared

---

* Corresponding author. Tel.: +357 22 89 2776; fax: +357 22 89 2801.
** Corresponding author.
E-mail addresses: costas.costa@cut.ac.cy (C.N. Costa), efstath@ucy.ac.cy (A.M. Efstathiou).

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.02.019

to the information obtained from kinetic models in combination with steady-state reaction rate measurements.

In a previous work [11] we have demonstrated that the N_2-selectivity of the catalytic reduction of nitrates by H_2 can be significantly improved by introducing oxygen (air) in the reducing feed gas stream. A N_2-selectivity of 97% was obtained [11], which is the highest value ever reported for the reaction at hand. In that study, due to the lack of availability of N_2O and NO gas analysers with a detection limit in the 1 ppb range, it was not possible to check the N_2-selectivity reported which was based on the assumption that if NO and/or N_2O were formed, their gaseous concentrations at the conditions of the experiments described [11] were below the few ppb level. This issue is now resolved in the present work.

In the present work we demonstrate for the first time that the N_2-selectivity of the catalytic reduction of nitrates by gaseous H_2 can be improved in the presence of internal mass transport phenomena when pellets (spherical shape) of Pd-Cu/TiO_2-Al_2O_3 catalyst are used. Moreover, the effects of Pd and Cu loading (wt%) on the reaction rate and N_2-selectivity, and the kinetic orders of the reaction of nitrate hydrogenation with respect to NO_3^-(aq) and H_2 gaseous concentration on the Pd-Cu/TiO_2-Al_2O_3 catalyst have also been investigated.

2. Experimental

2.1. Materials

Coated γ-alumina spheres with TiO_2 (*x* wt% loading) were prepared by immersing commercial γ-alumina spheres (*d* = 2–3 mm) in a solution containing the desired amount of metal oxide precursor. The spheres were left in solution for 24 h under mild stirring. $Ti[OCH(CH_3)_2]_4$ (Aldrich) dissolved in 2-propanol was used as precursor of Ti. The impregnated spheres of alumina were then calcined in air at 600 °C for 4 h before deposition of Pd and Cu took place [11].

The supported Pd-Cu catalysts were prepared as follows. A given amount of Pd was initially deposited within the coated γ-Al_2O_3 spheres by the incipient wetness impregnation method using $Pd(NO_3)_2$ (Aldrich) as precursor of palladium metal. After impregnation and drying (overnight at ∼120 °C) the solid sample was calcined in air at 500 °C for 2 h. The resulting solid was then impregnated with a given amount of aqueous solution of $Cu(NO_3)_2$ (Aldrich) so as to yield the desired loading (wt%) of Cu. After impregnation and drying overnight at ∼120 °C the resulting solid catalyst was calcined in air at 500 °C for 2 h [11].

2.2. Apparatus

Catalytic experiments were conducted in a custom-built autoclave CSTR reactor (Autoclave Engineers, U.S.A., and PID Eng &Tech, Spain) equipped with a Mahoney–Robinson catalyst basket as described elsewhere [11]. All the catalytic experiments were performed in a semi-batch mode: solid and liquid phases were stationary, whereas the gas-phase reducing medium (hydrogen/helium or hydrogen/air gas mixture) was under continuous flow at 1 atm total pressure and 25 °C.

2.3. Catalytic reaction conditions

The volume of the liquid phase (250 mL), the mass of the catalyst (4.0 g), the flow rate of the reducing feed gas stream (100 N mL/min), and the rate of stirring (700 rpm) were kept constant in all catalytic experiments. Nitric acid (HNO_3) solution was the source of nitrate ions used in the present catalytic work.

2.4. Quantitative analyses

UV-kits (Merck's spectroquant) in combination with a UV–vis spectrophotometer (Helios-Beta) were used for the quantification of NO_3^- (code: 1.097313), NO_2^- (code: 1.14776), and NH_4^+ (code: 1.00683). The latter analytical method had an accuracy of 0.15 mg/L for NO_3^-, 0.02 mg/L for NH_4^+, and 0.02 mg/L for NO_2^-. The production of gaseous NO and N_2O was checked using appropriate low-concentration gas analysers (Thermo Scientific (model 42i-HL) and Teledyne (model 7600), respectively). Both gas analysers had a lower detection limit of 1 ppb. Under the reaction conditions specified in Sections 2.2 and 2.3, no formation of either NO or N_2O was observed above the level of 1 ppb at the reactor's exit stream. Based on material balance and considering the initial rate of reaction, a concentration of 1 ppb (NO or N_2O) would correspond to a respective selectivity value of less than 1%.

3. Results and discussion

3.1. Catalysts characterization

The Pd, Cu and TiO_2 loadings in the present Pd-Cu/TiO_2-Al_2O_3 catalyst compositions were determined by ICP-AES analyses [11]. The Pd loading was varied in the 0.1–2.0 wt% range, whereas Cu loading in the 0.01–1.0 wt% range. The TiO_2 loading on γ-alumina spheres was fixed and it was found to be 4.9 wt% [11]. Despite the relatively low metal oxide loading achieved, the coverage of γ-Al_2O_3 spheres with titania was found to be adequate and uniform as proven by SEM-EDX analyses [11].

3.2. Catalytic studies

Fig. 1 presents the effect of Pd (Fig. 1a) and Cu (Fig. 1b) loading (wt%) on the NO_3^-(aq)/H_2/O_2 initial reaction rate (μmol/s g_{metal}) and NO_3^- conversion (%), and N_2, NH_4^+ and NO_2^- product selectivities obtained after 90 min of continuous reaction (semi-batch mode of reactor operation). As shown in Fig. 1, the initial reaction rate, NO_3^- conversion (%), and the reaction product selectivities are affected significantly by the metal loading (Pd or Cu). By increasing the Pd loading from 0.1 to 2.0 wt% the initial specific reaction rate (per gram of Pd) decreased significantly (by an order of magnitude), while N_2-selectivity takes the lowest value at 0.5 wt% Pd loading (Fig. 1a). The largest N_2-selectivity value (60%) was obtained after using 0.1 and 1.5 wt% Pd loadings (0.5 wt% Cu). By increasing the Cu loading from 0.01 to 1.0 wt% (0.1 wt% Pd) the initial specific reaction rate (per gram of Cu) is decreasing, while N_2-selectivity is maximum (78%) at 0.1 wt% Cu loading and minimum (practically zero) at the lowest Cu loading used (0.01 wt%).

The results of Fig. 1 indicate an optimum Cu/Pd ratio (w/w) of 1.0 (0.1 wt% Cu and 0.1 wt% Pd) in terms of N_2-selectivity of reaction. The latter result is in good agreement with the results obtained by Ilinitch et al. [10] and Gao et al. [12], who also reported an optimum Cu/Pd ratio in the 0.5–1.0 range, in terms of NO_3^- conversion and N_2-selectivity of reaction. It was reported [3,4,10,12] that both Cu and Pd or Pd-Cu clusters are necessary for the reduction of nitrates to N_2 gas. However, when the Cu/Pd ratio becomes higher than unity, Cu clusters tend to cover Pd ones, thus decreasing the exposure of Pd to the reaction mixture, the latter necessary for H_2 dissociation into adsorbed H active species for nitrate/nitrite hydrogenation. The opposite occurs when Pd surface concentration is significantly higher than that of Cu. These remarks are in full agreement with the present results of Fig. 1 regarding the strong inhibiting effect of both the Pd and Cu loading (particle size or dispersion) on the initial rate of the present nitrate hydrogenation reaction over Pd-Cu/TiO_2-Al_2O_3 catalyst.

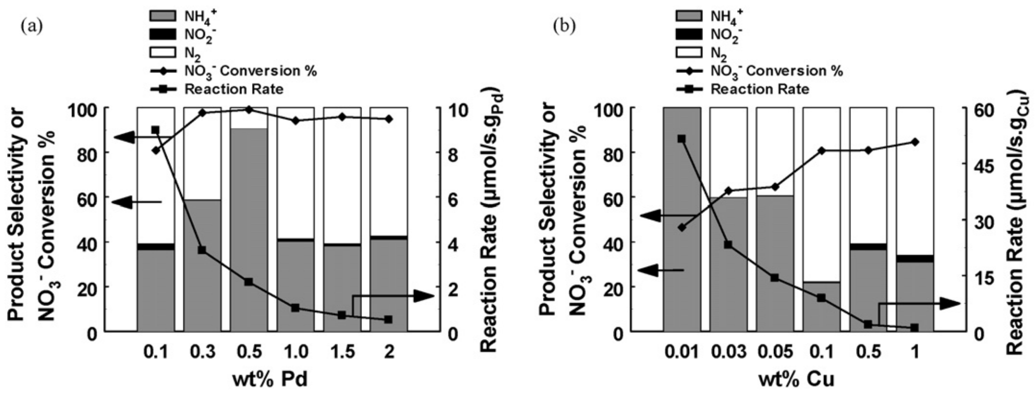

Fig. 1. Effect of Pd (a) and Cu (b) loading (wt%) on the $NO_3^-/H_2/O_2$ specific reaction rate, NO_3^- conversion (%), and product selectivities (N_2, NH_4^+ and NO_2^-) obtained after 90 min of continuous reaction over Pd-Cu/TiO_2-Al_2O_3 catalyst. *Feed gas composition*: 80% H_2/20% air. *Reaction conditions*: $[NO_3^-]^o = 100$ mg/L; $V = 200$ mL; $m_{cat} = 4.0$ g; $P = 1$ atm; $T = 25$ °C; Pd loading 0.1–2 wt% with Cu loading 0.5 wt% (a); Cu loading 0.01–1 wt% with Pd loading 0.1 wt% (b); catalyst particle size, $d = 1.8$ mm (support in the form of spherical particles).

It is interesting to point out that such strong dependence of the rate of nitrate reduction by hydrogen gas *in the presence of oxygen* on the noble metal loading (or dispersion) was recently reported also in the case of H_2-SCR ($NO/H_2/O_2$) over the Pt/MgO-CeO_2 catalytic system [13]. In the latter case, one of the active adsorbed NO_x species was NO_2^- formed on the support at the Pt-support interface [14].

3.3. Internal mass transport phenomena

Fig. 2 presents the NO_3^- concentration (mg/L) (Fig. 2a) and N_2-selectivity (%) (Fig. 2b) profiles as a function of reaction time (semi-batch mode of reactor operation) obtained over the 0.5 wt% Pd-0.5 wt% Cu/TiO_2-Al_2O_3 catalyst using two different γ-Al_2O_3 support particle sizes: $d_p < 0.14$ mm (powder form), and $d_p = 2$–3 mm pellets of spherical shape. As seen in Fig. 2a, nitrates concentration decreases at a smaller rate when using larger alumina support particles, strongly suggesting for the presence of internal (within pellet particle) mass transport resistances. An effectiveness factor, n, of 0.26 was estimated under the present reaction conditions when the rate of reaction is compared to that obtained after using the same amount of catalyst in fine powder form. Note that $n = 1.0$ implies the total absence of internal mass transport resistances. On the other hand, the N_2-selectivity of reaction is improved in the presence of internal mass transport resistances (Fig. 2b). It is important to be noted here that the ultimate N_2-selectivity value of reaction achieved after 3 h of operation, where NO_3^- concentration in solution becomes practically zero (semi-batch mode, see Section 2.2) was about 90% in the case of use of 2–3 mm in size support pellets, to be compared to the value of 80% obtained with support particles less than 0.14 mm in size (powder form).

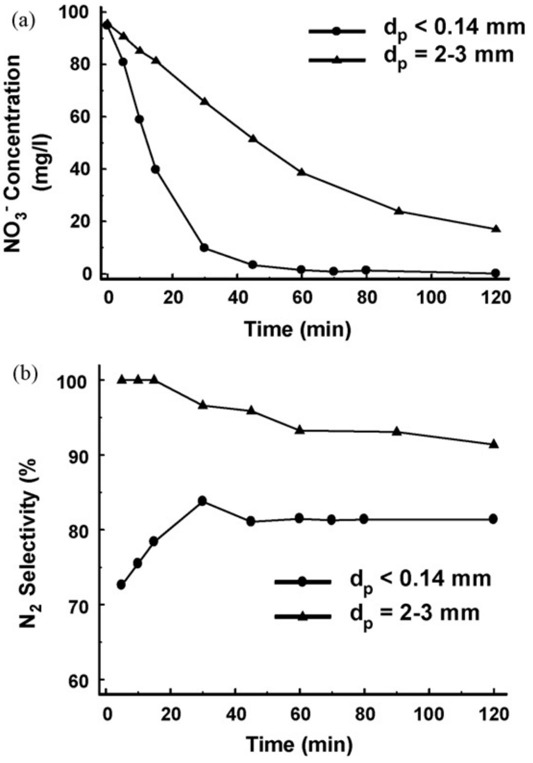

Fig. 2. Nitrate concentration (a), and N_2-selectivity of reaction (b) profiles as a function of reaction time obtained on 0.5 wt% Pd-0.5 wt% Cu/TiO_2-Al_2O_3 catalyst using two different alumina support particle sizes ($d_p < 0.14$ mm (powder) and $d_p = 2$–3 mm). *Feed gas composition*: 100% H_2 (1 bar). *Reaction conditions*: $[NO_3^-]^o = 100$ mg/L; $V = 200$ mL; $m_{cat} = 4.0$ g; $P = 1$ atm; $T = 25$ °C.

The results of Fig. 2b should be discussed in relation to the kinetics and mechanism of the present reduction of nitrates in water by hydrogen. According to *in situ* ATR-IR spectroscopic data obtained for the reduction by hydrogen of NO_2^-(aq) over a Pd/Al_2O_3 catalyst [5], formation of N_2 proceeds through the formation of adsorbed NO-s species, the dimerization of which leads to adsorbed N_2O-s. The latter is selectively reduced by adsorbed H-s to N_2 gas on the Pd surface [15]. On the other hand, it was found [5] that NH_4^+ ions formation (non-selective product) is the result of a sequential hydrogenation of NO_2^- (formed on the Cu surface) leading to various adsorbed intermediates (e.g. HNO_2^--s, HNO-s, NH_2-s), a reaction path that requires an increased concentration of adsorbed H species.

The surface coverage of adsorbed H species on the Pd surface for the present reaction system under dynamic conditions is expected to be influenced by the rate of diffusion of dissolved di-hydrogen in water within the support's pore structure, which in turn is influenced by the effective diffusivity (D_{eff}) of dissolved di-hydrogen and its concentration within the pores. Under the present reaction conditions and with a constant pressure of H_2 above the liquid phase, the concentration of dissolved di-hydrogen in the bulk of liquid water remains practically constant, and similarly its concentration within the pores of the catalytic system. Furthermore, it should be noted that in the presence of dissolved oxygen (use of H_2/air feed gas mixture) this surface coverage (θ_H) is also expected to be influenced; formation of adsorbed atomic oxygen species on the Pd surface is expected. On the other hand, the transient rate of NO_3^- diffusion from the bulk of liquid water to within the liquid volume of the catalyst's pore system is decreasing with reaction time (batch experiment) and depends also on the effective diffusivity (D_{eff}) of hydrated NO_3^- anionic species in water. These effective diffusivity values depend on the tortuosity parameter (τ) which varies from powders to larger in size particles.

Based on the discussion offered in the previous paragraph, the surface coverage of adsorbed NO_3^- (precursor of the various reaction intermediates [5]) and that of H on the catalyst surface are expected to be controlled by the ratio of D_{eff} of NO_3^- to that of $H_{2,\text{diss}}$ (dissolved di-hydrogen), and by the ratio of the concentration of NO_3^- present in solution at a given reaction time to that of $H_{2,\text{diss}}$. With increasing reaction time it is very likely that a relatively larger concentration of adsorbed H relative to NO_3^- could be found on the catalyst surface. Even though the rate-limiting step to form N_2 is faster than that to form NH_4^+ [5], a decrease in N_2-selectivity with reaction time cannot be excluded. This is what has been observed in Fig. 2b in the case of use of catalyst in pellets form. Based on the same reasoning, at a given reaction time the N_2-selectivity is favored in the case of pellets than of powder catalyst (Fig. 2b) likely because in the former case the surface coverage of H is kept lower than in the latter case (powder catalyst). It was reported [5] that the surface coverage of NO-s was much lower than that of NH_2-s, suggesting for the higher rate of NO-s reduction into N_2(g) than hydrogenation of NH_2-s into NH_4^+(aq) during the NO_2^- hydrogenation over a Pd/Al_2O_3 catalyst. This is relevant also to the present case of nitrate (NO_3^-) hydrogenation, where the generally accepted mechanism involves as a first step the reduction of NO_3^- to NO_2^- that takes place on Cu sites (oxygen scavenger) of the bimetallic Pd-Cu phase, whereas Pd sites are largely responsible for the reduction of NO_2^- to N_2(g) and NH_4^+ [10].

D'Arino et al. [16] have investigated the effect of pore size of SnO_2 support used in the reduction of nitrates by hydrogen at 25 °C over Pd/SnO_2. They found that by increasing the mean pore size of support from 50 to 250 Å the initial reduction rate increased significantly (by more than a factor of two), and at the same time the maximum concentration of NH_4^+ formed (batch mode of operation) was reduced significantly. The authors explained these experimental observations by the existence of a gradient in pH formed due to mass transport diffusional limitations of -OH species produced by the reaction network. In other words, local pH in the pores of the catalyst within which catalysis takes place may be significantly higher than the one measured in the water bulk solution. The authors concluded that intrinsic selectivity properties of the catalyst might be severely masked by mass transport phenomena.

It is noted that the positive effect of internal mass transport phenomena on the N_2-selectivity of the present reaction (Fig. 2b) is reported for the first time over Pd-Cu/TiO_2-Al_2O_3 in pellet form. The latter result is of great importance for the industrial application of the present denitrification process.

3.4. Kinetic studies

Kinetic studies in determining the apparent reaction order with respect to nitrate concentration (NO_3^-(aq)) and hydrogen partial pressure were performed over the 0.5 wt% Pd-0.5 wt% Cu/TiO_2-Al_2O_3 catalyst (particle size <0.14 mm) in the presence and absence of oxygen (air) in the feed gas stream. Figs. 3 and 4 present the logarithm of the *initial* kinetic rate (μmol/s g_{cat}) of nitrate conversion into N_2, NO_2^- and NH_4^+ as a function of the logarithm of the *initial* NO_3^- feed concentration (mg/L) (Fig. 3) and partial pressure of H_2 (bar) in the presence (Fig. 4a) and absence (Fig. 4b) of air in the reducing feed gas stream. The apparent reaction orders with respect to NO_3^- and H_2 were calculated from the slopes of the straight lines shown in Figs. 3 and 4, respectively, after considering an empirical power-law rate expression: Rate $(NO_3^-) = k[NO_3^-]^x P_{H_2}{}^y$; a least square correlation coefficient, R^2, larger than 0.95 was obtained for the results of Figs. 3 and 4. The apparent reaction order with respect to nitrates was found to be 0.32, whereas that of hydrogen in the presence and absence of 20% air in the reducing feed gas stream, respectively, was found to be 1.7 and 1.04.

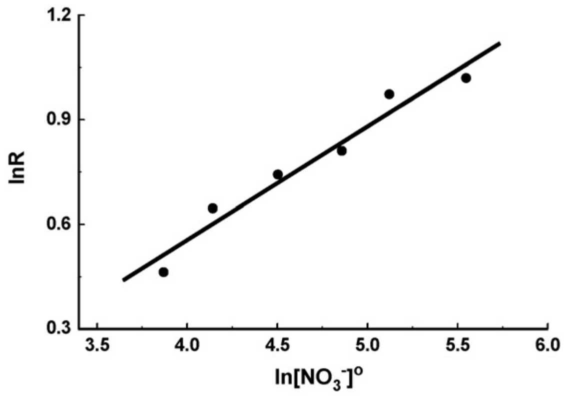

Fig. 3. Logarithm of the initial kinetic rate of nitrate conversion into N_2, NO_2^- and NH_4^+ as a function of the logarithm of the initial NO_3^- feed concentration obtained on the 0.5 wt% Pd-0.5 wt% Cu/TiO_2-Al_2O_3 catalyst. *Reaction conditions*: $[NO_3^-]^o$ = 50–300 mg/L; V = 200 mL; m_{cat} = 4.0 g; $P_{H_2} = 1$ atm; T = 25 °C.

The relatively small reaction order with respect to NO_3^- suggests strong interaction of the latter anions with the catalyst surface, leading to high adsorption rates. Pintar et al. [17] reported a small reaction order (close to zero) at high initial feed concentrations of NO_3^-, and a significantly higher reaction order (close to unity) at low NO_3^- feed concentrations. A Langmuir-type adsorption of nitrate to the respective active catalytic site could explain

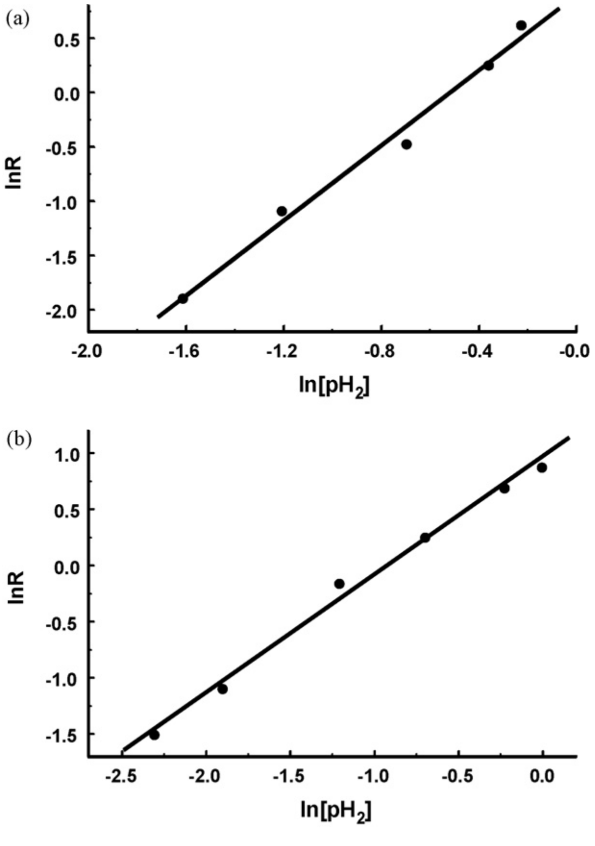

Fig. 4. Logarithm of the initial kinetic rate of nitrate conversion into N_2, NO_2^- and NH_4^+ as a function of the logarithm of the partial pressure of H_2 obtained on the 0.5 wt% Pd-0.5 wt% Cu/TiO_2-Al_2O_3 catalyst in the presence (a) and absence (b) of 20% air in the hydrogen feed gas stream. *Reaction conditions*: $[NO_3^-]^o$ = 100 mg/L; V = 200 mL; m_{cat} = 4.0 g; P = 1 atm; T = 25 °C.

this behavior [17]. Similar reaction orders with respect to nitrates were also reported over a similar in composition Pd-Cu/Al_2O_3 catalyst [17,18].

The high reaction order with respect to H_2 (both in the presence and absence of air in the feed gas stream) suggests that reduction of nitrates strongly depends on the concentration of adsorbed H species (θ_H) formed by dissociative hydrogen chemisorption on Pd surface sites. This surface concentration of H, θ_H is determined by the rate of hydrogen transfer from the liquid phase to the solid surface, the rate of H_2 chemisorption, and the rate of hydrogenation of NO-s and NH_x-s intermediates as previously discussed. At a first glance, a likely slow reaction step might be considered that of diffusion of dissolved di-hydrogen from the bulk water liquid phase inside the catalyst's pores as compared to the corresponding step of solvated nitrate ions. As previously mentioned, these diffusion rates will depend on the ratio of D_{eff} for the two diffusing species, their concentrations in the bulk water phase, and of course on the intrinsic kinetics of nitrate hydrogenation on the Pd/Cu catalytic surface. Given the fact that the initial nitrate concentration in water was 16.1×10^{-4} mol/L, that of dissolved hydrogen was less than 4×10^{-4} mol/L (1 atm H_2 pressure, 25 °C) [19], and the ratio of $D_{H_2,diss}/D_{NO_3^-}$ (25 °C) in water had the value of about two [20,21], it cannot be excluded under the present experimental kinetic studies that hydrogen diffusion could become a rate-limiting step for nitrate hydrogenation. This then could explain the higher than one apparent reaction order with respect to the hydrogen partial pressure (hydrogen in contact with the liquid water phase). It is noted that on a Pd-Cu/AC (active carbon) catalyst a reaction order with respect to hydrogen in the 0.2–0.3 range was reported [22], result opposite to that found in the present work. As mentioned above, if both mass transport of dissolved hydrogen from the liquid phase to the catalyst surface inside the pores of support and kinetics become important, then apparent reaction orders lower than unity could be experimentally observed.

The significantly higher reaction order with respect to H_2 obtained in the presence of air as compared to that observed in the absence of air suggests that oxygen partially reacts with adsorbed H species on the catalyst surface, the latter formed after dissociation of molecular H_2 on Pd, resulting in a lower surface coverage of adsorbed hydrogen, θ_H. The latter leads to a stronger dependence of θ_H and reduction rate of nitrates/nitrites on the partial pressure of H_2 in the gas phase. The strong dependence of θ_H on the hydrogen partial pressure is in agreement with results previously reported by us [11], where it was found that the presence of air in the gaseous reduction feed stream favors the production of N_2 gas. In that work [11] it was also suggested that the positive effect of the presence of air is due to the ability of oxygen to regulate the coverage of adsorbed hydrogen (θ_H) on the Pd catalyst surface towards values that optimize the N_2-selectivity of reaction.

4. Conclusions

The main conclusions derived from the results of the present work are as follows:

(a) The positive effect of internal mass transport phenomena on the N_2-selectivity of NO_3^-(aq)/H_2/O_2 reaction is reported for the first time, to our knowledge, over Pd-Cu/TiO_2-Al_2O_3 catalyst in pellet form (2–3 mm in size). The latter result is of great importance when considering industrial applications of the present de-nitrification process.

(b) The apparent reaction order with respect to nitrate was found to be 0.32, whereas that of H_2 was 1.04 when using H_2/He gas mixture as reducing agent. These apparent reaction orders seem to depend on the initial concentration of nitrate in solution and whether or not mass transport of dissolved di-hydrogen and hydrated nitrate species are considered important for the prevailed experimental conditions.

(c) The presence of air (oxygen) in the reducing feed gas of hydrogen stream significantly increases the reaction order with respect to H_2 (1.7) possibly due to the partial oxidation of adsorbed hydrogen species on Pd, result to be reported for the first time.

Acknowledgements

The Cyprus Research Promotion Foundation (project TEXNO/1104/05) and the Research Committee of the University of Cyprus are gratefully acknowledged for their financial support.

References

[1] A. Kapoor, T. Viraraghavan, J. Environ. Eng. 123 (1997) 371–380.
[2] L.W. Canter, Nitrates in Groundwater, CRC Press, Boca Raton, FL, 1997.
[3] A. Pintar, Catal. Today 77 (2003) 451–465.
[4] K.-D. Vorlop, T. Tacke, M. Sell, Eur. Patent DE 3,830,850 A1 (1998).
[5] S.D. Ebbesen, B.L. Mojet, L. Lefferts, J. Catal. 256 (2008) 15–23, and references therein.
[6] S.D. Ebbesen, B.L. Mojet, L. Lefferts, J. Phys. Chem. C 113 (2009) 2503–2511.
[7] J. Sá, J. Montero, E. Duncan, J.A. Anderson, Appl. Catal. B: Environ. 73 (2007) 98–105.
[8] U. Prüsse, M. Hähnlein, J. Daum, K.-D. Vorlop, Catal. Today 55 (2000) 79–90, and references therein.
[9] A. Pintar, M. Šetinc, J. Levec, J. Catal. 174 (1998) 72–87.
[10] O.M. Ilinitch, L.V. Nosova, V.V. Gorodeskii, V.P. Ivanov, S.N. Trukhan, E.N. Gribov, S.V. Bogdanov, F.P. Cuperus, J. Mol. Catal. A: Chem. 158 (2000) 237–249, and references therein.
[11] C.L. Constantinou, C.N. Costa, A.M. Efstathiou, Environ. Sci. Technol. 41 (2007) 950–956.
[12] W. Gao, N. Guan, J. Chen, X. Guan, R. Jin, H. Zeng, Z. Liu, F. Zhang, Appl. Catal. B: Environ. 46 (2003) 341–351.
[13] C.N. Costa, A.M. Efstathiou, Appl. Catal. B: Environ. 72 (2007) 240–252.
[14] P.G. Savva, A.M. Efstathiou, J. Catal. 257 (2008) 324–333.
[15] A.C.A. de Vooys, M.T.M. Koper, R.A. van Santen, J.A.R. van Veen, J. Catal. 202 (2001) 387–394.
[16] M. D'Arino, F. Pinna, G. Strukul, Appl. Catal. B: Environ. 53 (2004) 161–168.
[17] A. Pintar, J. Batista, J. Levec, T. Kajiuchi, Appl. Catal. B: Environ. 11 (1996) 81–98.
[18] K.D. Vorlop, U. Prüsse, Environmental Catalysis, Imperial College Press, London, 1999.
[19] R.C. Weast (Ed.), Handbook of Chemistry and Physics, 48th ed., The Chemical Rubber Co., Cleveland, OH, 1970.
[20] D.L. Wise, G. Houghton, Chem. Eng. Sci. 21 (1966) 999–1010.
[21] E. Karawacki, Rev. Sci. Instrum. 51 (6) (1980) 789–791.
[22] I. Mikami, Y. Sakamoto, Y. Yoshinaga, T. Okuhara, Appl. Catal. B: Environ. 44 (2003) 79–86.