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Catalytic denitrification of water with palladium-based catalysts supported on activated carbons

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Abstract

The performance of carbon-supported, Pd bimetallic catalysts for nitrate reduction has been investigated. Pd–In and Pd–Sn catalysts have been tested for a range of nitrate concentration up to 1000 ppm in acidic and close to neutral pH. Pd–Cu was also studied at pH 5 for reference. Nitrate reduction was inhibited strongly by nitrite and moderately by sulphate. Activated carbon catalysts are shown to display an activity similar to metal oxide supported catalysts. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Pollution of water with nitrate ions is a widespread problem arising from the development of agriculture and industrialisation. Conventional techniques such as ion exchange, reverse osmosis and electrodialysis allow effective removal of nitrates, but lead to the production of highly concentrated secondary waste stream. Catalytic reduction of nitrate to nitrogen is a promising process for removal of nitrate from water without the drawbacks of conventional methods [1–5]. Pd bimetallic catalysts, especially Pd–Cu, Pd–Sn, and Pd–In-supported on metal oxides, have proved to be the most effective for nitrate reduction according to the scheme in Fig. 1 [4]. Much effort has been devoted to developing a one-stage treatment process aimed at drinking water using a single catalyst. The reaction scheme of Fig. 1, however, lends itself to a two-stage process with nitrate reduction to nitrite in the first stage [6], and nitrite reduction in the second stage, which allows catalysts optimised for each stage. Such a process may be more appropriate for application to industrial effluent where there may be high concentration of nitrate, other competing ions, and low pH. Under more severe conditions, especially low pH, problems are likely to arise with the stability of the catalyst support. The present study reported here, has explored the utility of activated carbon as a support for Pd bimetallic catalysts for catalytic reduction of nitrate under low pH conditions. High nitrate concentrations and the influence of competing nitrite and sulphate ions are also investigated. Emphasis in this preliminary study has been placed on the activity and selectivity of Pd–In, Pd–Sn, and Pd–Cu for catalytic reduction of nitrate to nitrite, as may be appropriate to a first stage of a two-stage catalytic process.

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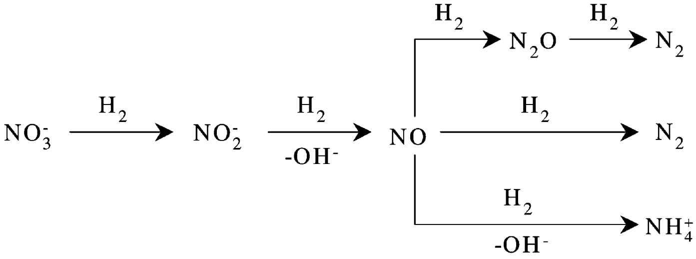

Fig. 1. Hypothetical reaction scheme.

2. Experimental

2.1. Catalyst preparation

A commercially available 5 wt.% Pd on activated carbon catalyst (Aldrich), surface area of $800\,m^2\,g^{-1}$, was used as base for the preparation of the bimetallic catalysts. Prior to impregnation the Pd base catalyst was ground to a particle size distribution with 99% of the particles below 13 μm. The metals associated to palladium (Me) were added to the base catalyst by the pore-filling method to give a nominal ratio Pd:Me of 4:1 by weight, similar to the preparation of Pd bimetallic catalysts on metal oxides supports [7–10]. Aqueous solutions of indium(III) nitrate pentahydrate, 99.999%; tin(II) chloride, 99.99+% and copper(II) chloride, 99.999% (all from Aldrich) were used. Metal chlorides have been reported as the “preferred precursors” [11]. XPS analysis of the present Pd–Sn and Pd–Cu catalysts showed that no chloride remains from the impregnation after calcination and reduction. The amount of water required for the pore filling method was determined by weighing. The impregnated catalysts were dried in a ventilated oven at 373 K until complete dryness. The Pd–Cu catalyst was calcined in a nitrogen flow at 773 K for 3 h, Pd–In and Pd–Sn catalysts were calcined in an air flow at 393 K for 3 h (heating rate $1\,K\,min^{-1}$ in all cases). Calcination temperatures were determined from a TPO study of the catalysts.

XRD of Pd–In and Pd–Sn do not display intense peaks of either Pd or the added co-metal, which is taken to be indicative of a good dispersion of the active metals on the support [7,11]. XPS analysis (VG ESCALAB MkII) supports this conclusion.

2.2. Catalytic tests

Catalytic tests were conducted in a semi-batch mode in a purpose-built stirred baffled glass reactor (liquid volume = 1 l) at 298 K under atmospheric pressure using a gas flow of $400\,ml\,min^{-1}$ of 50% hydrogen/nitrogen. Distilled and deionised water was used with nitrate ions introduced as potassium nitrate. Prior to the experiment the water was degassed with a flow of $200\,ml\,min^{-1}$ of nitrogen. Reduction was carried out in a dedicated reactor attached to the main reactor for 1/2 h at reduction temperatures obtained from a TPR study. The reduction temperatures used were 373 K for Pd–In and Pd–Sn catalysts, and 423 K for the Pd–Cu catalyst. The reduced catalyst was transferred into the nitrate solution under inert gas flow. The dependence of initial reaction rate on stirring speed was checked using a standard reaction (100 ppm nitrate, neutral pH with Pd–Cu/alumina catalyst). Initial rates were independent of stirring speed above 600 rpm. Consequently, 700 rpm was used in the catalytic tests and was considered a suitable stirring speed to avoid mass transfer limitations for the low catalyst loadings used.

The evolution of the concentration of nitrate, nitrite and ammonium ions was monitored by ion chromatography (Dionex DX-120). For anion detection the column used was an Ionpac AS14 (4 mm × 250 mm) with a guard column AG144 and the mobile phase was a mixture of Na_2CO_3 (3.5 mmol/l) and $NaHCO_3$ (1 mmol/l). The column used for cation detection was an Ionpac CS12A (4 mm × 250 mm) with a CG12A guard column; the mobile phase was a solution of methane sulphonic acid from Fluka (20 mmol/l). In both cases the detection was conducted at room temperature at 1 ml/min. pH was determined with a pH

Table 1
Estimated initial reaction rate of catalytic nitrate reduction for different carbon-supported catalysts, initial pH, and nitrate

Catalyst	Initial concentration nitrate (ppm)	pH	Initial rate constant (min g of catalyst)$^{-1}$	Overall ammonium production rate (ppm/(min g of catalyst))
Pd–In	99	5	0.38	0.5
	498	5	0.12	0.8
	963	5	0.07	1.8
	67	3	0.37	0.3
	538	2	0.12	1.1
Pd–Sn	98	5	0.10	0.1
	537	5.5	0.05	0.1
	122	2	0.33	0.2
	582	2.5	0.16	0.2
Pd–Cu	96	5.5	0.32	0.1
	370	5.8	0.17	0.2

electrode (Cole-Parmer 5992-30) backed up by pH strips; the pH electrode and a PT1000 temperature probe were linked to a Mettler Toledo MA235 pH/ion analyser.

The reactivity of the catalysts has been characterised by the apparent initial rate constant, k_0, for nitrate loss assuming first order kinetics in respect of nitrate. k_0 was estimated from the experimental points in the interval 0–50% conversion fitted to a first order exponential decay. No buffering was applied, hence the pH was observed to rise during the reaction as expected. Typically, the final pH was in the range of 8–9 at the end of the reaction. The change in pH was neglected in the estimate of initial rates as the effect can be expected to be small at low nitrate conversions (vide infra and Table 1). Ammonium production was expressed by the average ammonium production rate over the range of an experiment. Filtered solutions were analysed by atomic absorption spectroscopy to quantify any leaching of the active metals.

3. Results and discussion

An example of the variation of nitrate, nitrite and ammonium concentrations with time is shown in Fig. 2. The main product of nitrate reduction is nitrite in all cases, as expected, with selectivity of up to 90%. At each sampling time the amount of nitrate, nitrite and ammonium sum up to the initial amount of nitrate indicating that nitrite reduction yields only ammonium within experimental error. At lower pH, the mass balance does not sum-up suggesting production of nitrogen with selectivities in the range of 40–65%, although other species in the reaction scheme, Fig. 1, may be present to make the mass balance. For Pd–Sn the nitrate conversion rate became close to zero before total conversion of nitrate was achieved, suggesting some kind of catalyst deactivation.

Values of k_0 for different initial concentrations of nitrate for the three catalysts studied are given in Table 1. Pd–Cu was studied mainly for comparison purposes and so fewer nitrate concentrations were investigated. For all the catalysts, an increase of the initial nitrate concentration is accompanied by a decrease of the apparent initial rate constant for nitrate conversion. The data are consistent with a Langmuir–Hinshelwood (L–H) rate equation [10], with a nitrate adsorption constant, $K_{\mathrm{NO_3^-}}$, of $12 \times 10^{-3}\,\mathrm{ppm}^{-1}$ for the Pd–In catalyst, which is independent of nitrate concentration in the range studied. Values of $K_{\mathrm{NO_3^-}}$ are 4×10^{-3} and $5 \times 10^{-3}\,\mathrm{ppm}^{-1}$ for Pd–Sn and Pd–Cu catalysts, respectively. These are in reasonable agreement with published values obtained with alumina supported Pd bimetallic catalyst ($4.5 \times 10^{-3}\,\mathrm{ppm}^{-1}$) [10].

Values of overall ammonium production rates are given in Table 1. Ammonium production remains low, and as a consequence it is not possible to relate the time dependence of the ammonium concentration to nitrate conversion for nitrate concentrations below 500 ppm. However, in the case of high nitrate concentrations the ammonium does appear to arise from conversion of the nitrite product from nitrate reduction, which is consistent with the reaction pathway of Fig. 1. Low

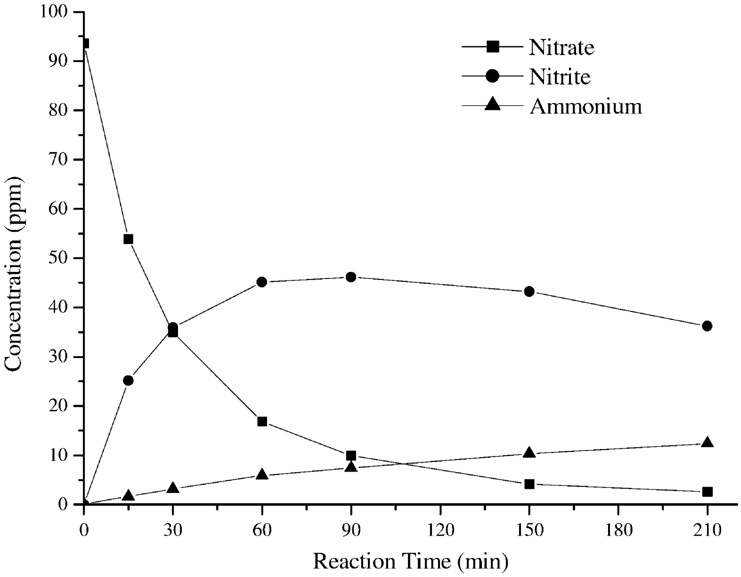

Fig. 2. Typical experimental results showing the evolution of nitrate, nitrite and ammonium ions concentration with reaction time. Pd–In-supported on activated carbon, pH 5.

overall ammonium production rates are, therefore, a consequence of the low activity of the catalysts for reduction of nitrite, which is desirable in a first stage catalyst.

Data showing the influence of initial pH on nitrate reduction is also given in Table 1. The Pd–In catalyst does not display any noticeable change of reactivity with decreasing pH, which is in line with published work on nitrate reduction over alumina-supported catalysts (see [1,3] and references reported therein). Rather surprisingly, the Pd–Sn catalyst has an increased activity at low pH. This could be associated with an inhomogeneous nature of the catalyst, a point discussed further below. For all the catalysts, a decrease in pH does not lead to increased production of ammonium ions, Table 1, but as noted above results in some nitrite reduction to nitrogen.

Leaching of palladium is low giving rise to a measured solution concentrations of 0.1–0.4 ppm. This corresponds to a maximum of about 4% of the total amount of Pd initially present on the catalyst. Leaching of indium gives solution concentrations in the range 0.3–0.6 ppm, which is more significant because of the lower loading, and corresponds to a maximum of about 20% of the total amount of indium loaded onto the catalyst. On the other hand, XPS analysis shows hardly any effect on Pd dispersion and only a small reduction of the In/Pd ratio (see Table 2). Indium is expected to alloy easily with palladium under reducing conditions at ambient temperature or just above forming the intermetallic Pd_3In. The high value of the In/Pd ratio determined by XPS (0.67) points to significant surface enrichment of bimetallic particles with indium as expected on surface energy considerations, and/or the presence of poorly dispersed free indium oxide. The percentage of leached indium suggests that any free oxide and the enriched layer may be removed. Leaching of Pd from Pd–Sn was similar to the Pd–In case, but the leached Sn was difficult to detect because of the lower sensitivity of AAS for Sn. However, we assume it to be at least

Table 2
Metal to palladium atomic ratios determined by XPS

Catalyst	Me/Pd atomic ratio
Pd–In reduced	0.67
Pd–In spent pH 2	0.58
Pd–Sn reduced	0.53
Pd–Sn spent pH 2	0.44

similar to In (see XPS data Table 2) and it could be an explanation for increased activity of Pd–Sn at low pH. XPS shows significant surface enrichment of Sn (consistent with surface energies) and the presence of Sn oxide. The method used to prepare the catalysts may not lead to complete alloying of the two metals, nor to complete reduction of the Sn. Leaching may give rise to exposure of the underlying bimetallic surface and increased activity for nitrate reduction.

Studies of nitrite reduction on Pd/alumina show that the activity of the catalyst increases sharply with decreasing pH from 10 to 4. [6] The present carbon-supported catalysts show increased selectivity to nitrogen at low pH consistent with increased nitrite reduction and possibly the leaching observations, although more detailed characterisation of the spent catalysts is clearly required.

The influence of competing ions has been studied by addition of nitrite and sulphate to the initial solution. Typically, experiments were conducted in the presence of 500 ppm nitrite or sulphate. At pH 5 and with about 100 ppm starting concentration of nitrate, the apparent initial rate constant for Pd–In decreases to 0.28 and 0.06 (min g of catalyst)$^{-1}$ in the presence of 500 ppm of sulphate and nitrite respectively. The L–H rate equation reported for alumina-supported catalyst [10] can be modified to take into account the influence of nitrite and sulphate ions

$$r=\frac{k_{\mathrm{s}}K_{\mathrm{NO_3^-}}C_{\mathrm{NO_3^-}}}{1+K_{\mathrm{NO_3^-}}C_{\mathrm{NO_3^-}}+K_{\mathrm{NO_2^-}}C_{\mathrm{NO_2^-}}+K_{\mathrm{SO_4^{2-}}}C_{\mathrm{SO_4^{2-}}}}$$

The present results for Pd–In catalysts yield an adsorption constant for nitrite (27×10^{-3} ppm^{-1}) which is about three times that of nitrate (12×10^{-3} ppm^{-1}). Experiments conducted with 500 ppm nitrite and Pd–Sn supported on carbon show the nitrate disappearance rate to be very low, suggesting either a large nitrite adsorption constant or significant variation in the nature of the catalyst, or perhaps both. The results imply that even a relatively low initial concentration of nitrite has a strong influence on the nitrate disappearance rate. The sulphate adsorption constants are relatively low, 2×10^{-3} and 1.3×10^{-3} ppm^{-1} for Pd–In and Pd–Sn, respectively, so that sulphate has a significant influence only at high concentration.

The activity of activated carbon-supported catalysts compares well with the published activity of metal oxides supported catalysts. The apparent initial rate constant of 0.36 (min g of catalyst)$^{-1}$ determined for Pd–Cu at pH 5.5, with 100 ppm nitrate, is about twice that determined for Pd–Cu supported on alumina under the same set of experimental conditions [12]. Under similar conditions, Prüsse et al. [3] found a k_0 of about 0.01 (min g of catalyst)$^{-1}$ with Pd–Cu on alumina. In the same paper, Prüsse et al. report a k_0 of about 0.04 (min g of catalyst)$^{-1}$ for Pd–Sn supported on alumina which is lower than the value of 0.15 (min g of catalyst)$^{-1}$ we determined for carbon-supported Pd–Sn under the same conditions. While the activities of the present carbon-supported catalysts appear promising for nitrate reduction, especially under conditions where oxide supports would be unsuitable, we note that Strukul et al [11] have reported activities in the order of 2 (min g of catalyst)$^{-1}$ for Pd–Cu on ZrO_2 catalysts.

4. Conclusions

The activity of carbon-supported Pd bimetallic catalysts for nitrate reduction, especially Pd–In, is comparable to metal oxide supported bimetallic catalysts. The results suggest that carbon-supported catalysts would be suitable for nitrate reduction in acidic environments. The selectivity of the catalysts to nitrite is high with low ammonium production rates measured over the entire course of the reaction. This has attractions for application in the first stage of a two-stage process for nitrate reduction.

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