Catalysis Today 149 (2010) 348–351

Contents lists available at ScienceDirect

Catalysis Today

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

Nitrates removal from polluted aquifers using (Sn or Cu)/Pd catalysts in a continuous reactor

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ARTICLE INFO

Article history:
Available online 27 June 2009

Keywords:
Nitrate catalytic reduction
Continuous process
Natural water
Sn–Pd catalyst

ABSTRACT

The aim of this work is to study the catalytic removal of nitrates in natural water (not the water prepared in the laboratory by adding a nitrate salt to distilled water) from polluted aquifers, using a continuous stirred tank reactor. The catalysts studied are (Cu or Sn)/Pd supported on alumina. The activity and selectivity of these catalysts in different types of polluted waters are analyzed, optimizing the Pd–metal ratio and the reaction conditions. The deactivation of the catalysts, when using different types of water, is studied and discussed.

1. Introduction

Pollution of natural water by nitrates is an important environmental problem. This pollution is due to the increasing use of fertilizers in areas of intensive agriculture, animal excreta and domestic waste. In these areas it is quite common that an important number of water sources surpass the legal limit of 50 mg/L of nitrates. At present, the most used commercial technique for nitrate removal from natural water is reverse osmosis. Although it is quite effective, the post-treatment of the effluent and the exploitation costs are important and high. For these reasons, this is not the most adequate decontamination system from the environmental point of view [1]. Another possibility is the use of biological processes, based on the nitrate reduction by microorganisms into gaseous nitrogen [2]. This process is a well known treatment for wastewater but its use for denitrification of ground water presents multiple difficulties. For this reason, it is necessary to find an alternative technology.

One of the most promising processes is the catalytic reduction of nitrates to nitrogen, using hydrogen or formic acid as a reductant agent [2–10]. The catalysts used combine a noble metal, like Pd or Pt and another no noble metal like Cu, Sn, Ag or In [5–8,11] and they are supported on oxides, mainly alumina. The disadvantage of this process is the formation of subproducts such as ammonia or nitrite. In order to prevent this, different alternatives have been proposed. Some of them are focused on adding different metals in the catalysts composition [2,5,12,13], on the use of different reactor types [14–18], on the use of different catalytic supports [4,19,20] or on the modification of the reaction conditions. The last one shows interesting results when the pH of the media is lowered by the addition of CO_2, HCl, or formic acid, obtaining a better selectivity than when the pH is not controlled [21,22].

It has been reported that this reaction is very much influenced by the presence of other ions in the media, being the most important, the inhibiting effect of the hydrogencarbonates, probably due to a competitive adsorption on the metallic active sites [23–25]. On the other hand it has been recently suggested that the presence of oxygen has a positive influence in the reaction selectivity [26]. Nevertheless it seems that the main problems observed with these catalysts are related with diffusion and mass transfer problems resulting in a low selectivity towards nitrogen [6,7,16,27]. For this reason it is very important to study the activity of these catalysts in real natural water from polluted aquifers in order to design an adequate catalyst.

The objective of this work is to study the activity and selectivity of those catalysts, described as the most actives for the catalytic reduction of nitrates, when using natural water from some nitrate polluted aquifers in a continuous stirring tank reactor.

2. Experimental

The support used for the catalyst was γ-Al_2O_3 supplied by Merck (99.5% purity, surface area 138.5 m^2/g). The bimetallic catalysts were prepared by incipient wetness impregnation with the soluble salts of the desired metals. The sample was initially impregnated with the first salt solution, dried at 423 K and calcined in air at 773 K for 1 h. After that, the second salt was added and the catalyst was dried and calcined again at the same

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doi:10.1016/j.cattod.2009.05.013

Table 1
Chemical and textural composition of the catalysts used.

Catalysts	Cu (wt%)	Sn (wt%)	Pd (wt%)	Surface area ($m^2\ g^{-1}$)
1.5/2.5 Cu–Pd	1.5	–	2.5	–
2.5/5 Cu–Pd	2.5	–	5	–
1.5/5 Cu–Pd	1.5	–	5	–
0.5/2.5 Cu–Pd	0.5	–	2.5	–
2.5/1 Cu–Pd	2.5	–	1	–
3/2.5 Cu–Pd	3	–	2.5	–
5/2.5 Cu–Pd	5	–	2.5	127.2
1.5/1 Cu–Pd	1.5	–	1	–
2.5/5 Sn–Pd	–	2.5	5	125.3

temperature. Different combinations of palladium with tin or copper were prepared. The metallic salts used to prepare the impregnation solutions were $Pd(NO_3)_2{\cdot}H_2O$, $SnCl_4{\cdot}5H_2O$ and $Cu(NO_3)_2{\cdot}3H_2O$. The catalysts were reduced with hydrogen at 773 K for 4 h before reaction. The composition and the textural properties of the tested catalysts are shown in Table 1. As it can be seen, the surface area of the catalysts is quite similar to that of the alumina, indicating that the impregnation of the alumina with the different salts does not result in an important decrease of the catalysts surface area.

The catalysts were tested in a continuous flow stirred tank reactor (1 L), where the reactant solution was fed into the reactor at atmospheric pressure. The start-up procedure consists in filling the reactor with natural water that is bubbled with hydrogen during 30 min. After that, the catalyst was introduced into the tank and a liquid flow rate of 5 ml/min was maintained during the reaction. The mass of the catalyst was 3 g and a mixture of CO_2 and H_2 (1:1) with a total flow of 500 cm^3/min was introduced into the reactor during the reaction. The experiments were carried out at 293 K, and the reactor was stirred at 900 rpm. The reaction progress was followed by taking, at defined periods, small aliquots for the photometric determination of nitrate, nitrite and ammonia concentration. The measurements were done in an UV/VIS spectroscopy (Jasco UV/VIS spectrophotometer, model V-530) combined with reagent kits for the determination of nitrate (Spectroquant® nitrate test from Merck, measuring range 1–90 mg/L at 515 nm), nitrite (Spectroquant® nitrite test from Merck, measuring range 0.02–3 mg/L at 525 nm) and ammonia (Spectroquant® ammonia test from Merck, measuring range 0.01–3.5 mg/L at 690 nm).

3. Results and discussion

The initial studies were made with water coming from a polluted aquifer located in the Comunidad Valenciana (Spain). The characteristics of this water are described in Table 2 (water B), being the most significant parameters, the hardness of the water, the high content in sulfates and chlorides and the high conductivity. The catalytic reduction of nitrates was studied with this water using different catalysts, with different Pd:Cu ratio supported on alumina. These catalysts are described as one of the most active catalysts for this type of reactions [3,27,28]. The catalysts were tested during 3 h in a continuous flow stirred tank reactor. As it can be seen in Fig. 1, the activity of the catalysts increases while increasing the Pd:Cu ratio up to a Pd:Cu ratio of 1.7–2, showing a slow decrease in the activity for higher Pd:Cu ratios. These results indicate that in this water, an active catalyst for the nitrate reduction, needs the presence of two phases, Pd and Pd–Cu. These results agree with the reaction mechanism proposed by Vorlop [22], suggesting that the Pd–Cu centers are necessary for the reduction of nitrate to nitrite, being the Pd isolated centers necessary for the activation of the hydrogen and for the reduction of the nitrites formed.

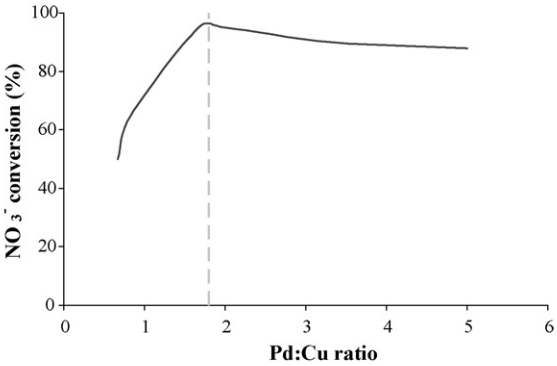

Fig. 1. Influence of the Pd:Cu ratio in the activity of the catalyst for the reduction of nitrates using natural water from a polluted aquifer (water B).

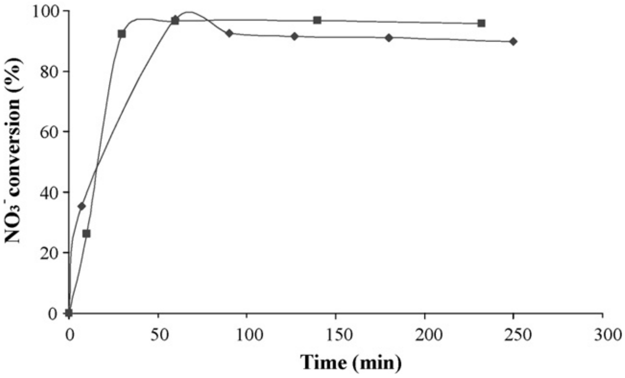

Fig. 2. Catalytic hydrogenation of nitrates on Pd–Cu (■) and Pd–Sn (◆) catalysts supported on alumina, using natural water (water B) from a polluted aquifer (Pd:metal ratio = 2).

Recent reports suggest [7,22,29,30] that Pd–Sn catalysts could be so active as the Pd–Cu catalyst for this type of reaction. For this reason we prepare both catalysts with a Pd:(Cu or Sn) ratio of 2 and we compare their activity for the catalytic reduction of nitrates using polluted natural water (water B). As it can be seen in Fig. 2, both catalysts show a similar activity, although the Pd–Sn catalyst has a higher initial reaction velocity than the Cu–Pd catalyst. Nevertheless after 50 min of reaction the conversion keeps constant showing both catalysts a similar behavior, without any deactivation of the catalysts after 4 h of reaction. The most significant difference is related to the selectivity of the catalysts (Fig. 3). As it can be seen, with this type of water, a better selectivity

Table 2
Chemical composition and precedence of the polluted water used in the catalytic experiments.

Water	Precedence	Conductivity (μS/cm)	Ca^{2+} (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	NO^{3-} (mg/L)
A	Ruidera Lake (Castilla la Mancha)	570	85	35	160	30
B	Sink in Picassent (Comunidad Valenciana)	1,000	185	79	200	90
C	Sink in Puzol (Comunidad Valenciana)	1,580	280	232	173	150
D	Chemical Industrial wastewater	24,000	1.2	5	4.2	1300

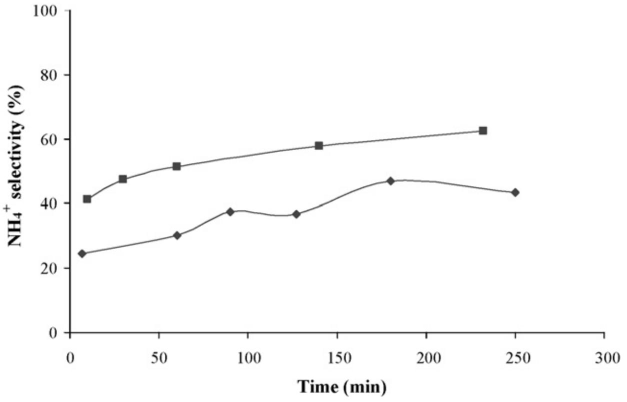

Fig. 3. Selectivity towards ammonia in the catalytic hydrogenation of nitrates, using natural water (water B) from a polluted aquifer, on Pd–Cu (■) and Pd–Sn (◆) catalysts supported on alumina (Pd:metal ratio = 2).

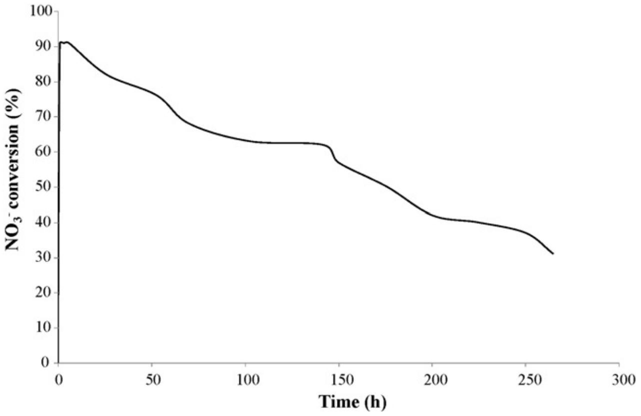

Fig. 5. Nitrate reduction long-term reaction with a Pd–Sn catalyst supported on alumina using natural water from a polluted aquifer (water B).

towards nitrogen is obtained with the catalyst containing tin than with the catalyst containing copper. These results are different from those previously described by Pintar et al. [17] and this is probably related with the different characteristics of this water if compared with the water used in those experiments.

The Pd–Sn catalyst was chosen to study the influence of the reaction pressure in the activity and selectivity of the catalyst and to study the catalytic behavior when using different polluted waters. The studies performed at different pressure inside the reactor indicate that the same activity and selectivity (not shown) are obtained when the reaction is performed at atmospheric pressure, 1.5 bar, 2 bar or 3 bar. The pressure of the reactor is directly related with the quantity of H_2 and CO_2 dissolved in the water. It has been indicated in previous works that the activity and selectivity of this reaction [6,7,16,27] is seriously affected by mass transfer problems. Nevertheless, the results obtained in our experiments indicate that these problems do not depend on the hydrogen transfer towards the active sites. They also show that performing the reaction at atmospheric pressure there are enough hydrogen dissolved to reduce the nitrates present in water.

The activity of this catalyst for the nitrate reduction was studied using different types of water coming from different sources (see Table 2). As it can be seen in Fig. 4, there are some differences in the catalyst activity depending on the water conductivity, this is depending on the water ions concentration. Although in the natural waters (waters A, B and C) the differences are not so important, it seems that the catalyst activity in the waters with a high conductivity is lower than the activity of the same catalyst when it is tested with water that present a low conductivity. This difference is very significant, when comparing these results with those obtained with an industrial water with a very high conductivity (water D). This can be attributed to the competitive adsorption of the different ions present in this water on the active sites [23–25] or more likely to a partial deactivation of the catalysts due to some species present in water.

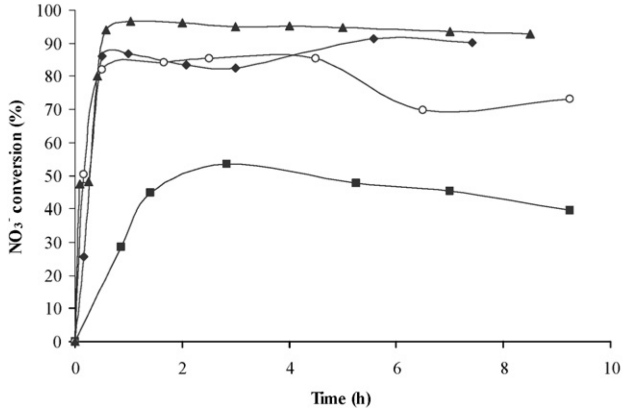

Fig. 4. Catalytic hydrogenation of nitrates on a Pd–Sn catalyst supported on alumina, using different natural waters from polluted aquifers, water A (▲), water B (◆), water C (○) and water D (■).

The stability of the Pd–Sn catalyst was checked in a long-term experiment, using the water B. As it can be seen in Fig. 5, the catalyst shows almost a 100% conversion only during the first 8 h of reaction, afterwards the catalyst starts to deactivate. The velocity of the deactivation is quite slow and even after 250 h of reaction a 40% conversion is observed. The content of Pd and Sn was measured in the treated water and no metals were detected in it, for this reason we assume that the leaching of the catalyst is not produced during the reaction. On the other hand, an elemental analysis of the catalyst after deactivation shows the presence of traces of calcium and sulfur in the catalyst. These species are probably the responsible of the catalyst deactivation. As the water used in the experiments has a high calcium content, it is very likely the precipitation of calcium salts on the catalyst surface. This will cause a deactivation of the catalyst masking the active metallic sites of the catalyst. On the other hand the high sulfate content of the water and the reducing ambient of the reaction are probably forming some reduced species of sulfur that slowly deactivate the palladium sites. Nevertheless more studies are necessary in order to elucidate the mechanism of the deactivation.

4. Conclusions

The results obtained in this work show that the activity of the catalysts in the water nitrate reduction depends on the type of water used. In a water with a high conductivity and hardness, as that used in this work, the best results are obtained when using a Pd:Sn catalyst with a Pd:Sn ratio of 2. The activity and the selectivity of the catalyst do not depend on the pressure of the reaction indicating that the diffusion of hydrogen towards the active sites is not the limiting step of the reaction. The results obtained also show that the catalyst deactivation in water with a high conductivity and hardness is probably related with the masking of the catalyst because the precipitation of calcium salts on the catalyst surface and with the poisoning of the palladium centers by the sulfur compounds present in the water.

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