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Protection of palladium catalysts for hydrodechlorination of chlorinated organic compounds in wastewaters

Rotem Navon[a], Shay Eldad[a], Katrin Mackenzie[b], Frank-Dieter Kopinke[b,*]

[a] *Hebrew University of Jerusalem, Department of Soil and Water Sciences, Rehovot 76100, Israel*
[b] *Helmholtz Centre for Environmental Research – UFZ, Department of Environmental Engineering, 04318 Leipzig, Germany*

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ABSTRACT

Palladium is an efficient catalyst for hydrodechlorination (HDC) of aliphatic and aromatic chlorinated organic compounds in water. However, its applicability in water treatment processes is limited because of its sensitivity to catalyst poisons. In the present study, Pd/Al_2O_3 was modified by various silicone-based fillings and coatings. The modified catalysts proved to be active in the HDC of chlorobenzene with $A_{Pd} = 35–65\,L\,g_{Pd}^{-1}\,min^{-1}$ vs. $570\,L\,g_{Pd}^{-1}\,min^{-1}$ for the unprotected catalyst. It was insusceptible against sulphite as a model catalyst-deactivating ionic water constituent. However, under HDC conditions the silicone appeared to be degraded, becoming gradually permeable for sulphite. Hydrolysis of the silicone polymers, initiated and promoted by the HDC product HCl, is assumed to be responsible for the polymer ageing. Release of chloride from the coated catalyst into the bulk water phase has been revealed as a crucial step in this concept of hydrophobic catalyst protection. It could be shown that with Pd/Al_2O_3, HDC also proceeds in dry organic solvents such as *n*-hexane at significant reaction rates ($A_{Pd} = 18–28\,L\,g_{Pd}^{-1}\,min^{-1}$).

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1. Introduction

Chlorinated organic contaminants (COC) are of particular environmental concern due to their high abundance in wastewater and sewage sludge, surface water, groundwater and soils [1–3]. Hydrodechlorination (HDC) using Pd-based catalysts shows a high potential for the destruction of such contaminants in water. HDC is highly efficient and selective in clean water even at ambient conditions [4–6]. However, the noble metal Pd is very sensitive to deactivation in natural waters and wastewaters due to precipitations, dissolved natural organic matter and in particular poisons such as heavy metals and reduced sulphur compounds [4,7–11]. Hydrogen sulphide (H_2S and HS^-) is ubiquitous in natural waters and is one of the strongest Pd poisons. For these reasons, Pd-based catalysts are rarely used for practical applications in water treatment. Only a few field-scale studies have investigated the use of Pd-based catalysts for the HDC of various COC in groundwater [12–14]. The specific Pd activities A_{Pd} of the catalysts applied for various chlorinated aliphatics were as low as $0.1–0.2\,L\,g^{-1}\,min^{-1}$, estimated from the data reported by the authors. These values are far below the potential performance of Pd catalysts. The highest specific activity of Pd/magnetite nanocatalysts found under optimized laboratory conditions was reported to be up to 5 orders of magnitude higher [15]. Therefore, in order to exploit the high potential activity of Pd better, it is highly desirable to find ways and means to protect the metal from poisoning.

Several methods have been proposed for increasing the resistance of noble-metal gas-phase catalysts against poisons, including the optimization of the catalyst support [16], the use of permselective coatings [17] and the addition of scavengers to selectively bind the deactivating component [18]. However, these methods still fail to provide a full-scale protection against common catalyst poisons for water treatment by HDC. Countermeasures such as applying alkaline scavengers to bind HCl and thus protect the catalysts from chloride poisoning have been investigated [6]. Schueth et al. placed Pd clusters into hydrophobic zeolites in order to repel ionic catalyst poisons [19]. Fritsch et al. [20] and Kopinke et al. [11] demonstrated successfully the use of hydrophobic polymer coatings as a means of preventing catalyst poisoning for the HDC reaction in water. The polymer coating is permeable for the reactants (i.e. H_2, COC and HCl) and impermeable for ionic or bulky molecules, which could deactivate the catalyst. Poly(dimethylsiloxane) (PDMS) was selected as the polymer coating due to its chemical stability and very high diffusivities for small, uncharged molecules. In these studies, the protection of the catalyst was achieved by the embedding of Pd nanoclusters within thin polymer films, or by coating of Pd/Al_2O_3 particles (63–125 μm). The coated catalysts maintained a relatively high activity after 24 h exposure to soil extracts or to

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* Corresponding author.
E-mail address: frank-dieter.kopinke@ufz.de (F.-D. Kopinke).

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the catalyst poison sulphite (50 μM) [11]. However, Fritsch et al. [20] have reported some deactivation of the coated catalyst after several reaction runs, even without the addition of poisons. The authors suggested that this phenomenon could be attributed to partial chloride poisoning. As shown by these studies, the approach of a non-porous hydrophobic polymer coating could be promising for the protection of Pd catalysts against common ionic poisons. However, the long-term stability (i.e. the ability to retain activity over extended time periods) of the coated catalyst still needs to be evaluated.

In the present study, two approaches for protection of Pd/Al_2O_3 catalyst by PDMS were tested. First, a rubbery PDMS wall-coated batch reactor was designed. This reactor was based on Pd/Al_2O_3 powder embedded in a PDMS wall coating. Second, several methods for the coating and/or pore-filling of commercially available pelletized Pd/Al_2O_3 were examined. Usually, the pelletized form of the catalyst is used in established fixed-bed reactors for water treatment [12–14]. Therefore, it is desirable to find ways and means to protect these pellets directly, such that this established reactor type can continue to be operated. For both approaches, the activity and long-term stability of the protected catalysts were evaluated in the absence of poisons. In addition, the ability of the polymer coating to provide a long-term protection against high concentrations of ionic poisons was also tested. It is important to note, however, that this protection method is only efficient for ionic poisons, whereas uncharged molecules such as non-ionic sulphur compounds (H_2S, mercaptanes, disulphides, etc.) could still permeate through the polymer. In order to prevent this, an oxidative pre-treatment of the water is advisable [21].

2. Experimental

2.1. Chemicals

The chemicals monochlorobenzene (MCB, >99% purity), trichloroethylene (TCE, >99.5% purity), benzene, methanol, *n*-hexane, toluene, trimethylchlorosilane (TMCS), sodium bicarbonate ($NaHCO_3$), as well as silicone oil 550, were purchased from Merck, Germany. The two-component PDMS (Wacker SilGel® 612A/B) was purchased from Wacker-Chemie AG, Germany. Sodium sulphite (Na_2SO_3) was obtained from J.T. Baker. The eggshell catalyst G-133D Pd on γ-Al_2O_3 was purchased from Commercia, Germany. A crushed and sieved size fraction of the catalyst (d_p = 63–125 μm) as well as the original 3 mm pellets were used for the HDC experiments. Both the crushed fraction and the original pellets contained 0.5% (w/w) Pd, and had a BET surface area of 161 $m^2\,g^{-1}$ (N_2 adsorption), a porosity of 0.43 $cm^3\,g^{-1}$ (N_2 adsorption) and a Pd dispersion of 0.16 (CO adsorption).

2.2. Preparation of the coated catalysts

2.2.1. Preparation of a rubbery PDMS wall-coated batch reactor

The two components of the PDMS were mixed together at a ratio of 2:1 (components A, crosslinker and B, platinum catalyst respectively). An amount of 2.86 or 9.53 g (corresponding to a 150 or 500 μm film thickness) of the two-component PDMS blend was mixed with 15 mL hexane. The PDMS–hexane mixture and 50 mg Pd/Al_2O_3 (d_p = 63–125 μm) were then added to a 250 mL glass reactor vessel. The vessel was placed in a sonication bath (3 min) in order to achieve complete dispersion of the particles. The solvent was then allowed to evaporate overnight, while the cylindrical vessel was gently rotated horizontally (10 rpm). During this period, the cold-curing silicone rubber was formed by cross-linking polymerization. Subsequently, the polymer was dried (40 °C) for 2 d. This procedure resulted in the formation of a homogeneous polymer film coating at the vessel walls, whereby the catalyst particles were completely embedded within this film. For simplicity, the wall-coated batch reactor will herein be referred to as “batch reactor”.

2.2.2. Coating and pore-filling of Pd/Al_2O_3 pellets

i. *Pore-filling with silicone oil.* An amount of 10 g pellets was added into a 2-neck round-bottom flask and evacuated for 2 h to remove air and water from the pores. About 20 mL of degassed hot silicone oil (70 °C) was then injected into the flask and the mixture was shaken under vacuum for an additional 1 h, after which the excess oil was removed. Due to this impregnation, the pellets gained 25% weight, which corresponds to about 55% pore filling. This procedure was applied to the original commercial pellets and to pellets hydrophobized by pre-treatment with TMCS. For hydrophobization the pellets were treated in a solution of 1% (v/v) TMCS in toluene at 75 °C overnight and afterwards rinsed twice with methanol.
ii. *Pore-filling with silicone oil and external rubbery PDMS coating.* Pore-filled pellets (see *i*) were coated with an additional layer of the rubbery two-component PDMS. The two liquid PDMS components were first mixed together (2:1, without any solvent), then 15 g of the mixture was added to a flask containing 10 g of pore-filled pellets. After 30 min, the excess liquid PDMS was discarded. The coated pellets were dried (40 °C) for 2 d. The weight gain was 8.7%, which corresponds to an average external film thickness of about 140 μm.
iii. *Double-layer rubbery two-component PDMS coating.* Approximately 10 g of the two-component PDMS mixture was dissolved in 15 mL of *n*-hexane and added to a flask containing 10 g Pd/Al_2O_3 pellets. The mixture was purged with N_2 for 1 h in order to evaporate some *n*-hexane, and the pellets were then separated from the solution. Subsequently, the pellets were dried (40 °C) for 2 d. An additional external two-component PDMS coating was implemented as described above in *ii*.

2.3. Procedures for catalyst testing with HDC reactions

The catalyst testing was performed as batch experiments. Both for the wall-coated reactors and for the 3 mm pellets, the HDC of MCB was conducted in 250 mL glass vessels equipped with a Mininert® valve with 200 mL buffer solution (1 mM $NaHCO_3$ in deionized water; pH 8.7). The solution was first purged with hydrogen gas and then spiked with a stock solution of MCB in methanol ($C_{0,MCB} = 10\,mg\,L^{-1}$). This marked the start of the HDC reaction ($t = 0$). During the reaction, the vessel was continuously shaken (120 rpm). The HDC kinetics was monitored by means of headspace sampling (25 μL, gas-tight glass syringe) with GC–MS (Shimadzu GC–MS QP2010) or GC–FID (Shimadzu GC-14B) analysis. At the end of the reaction, the release of chloride to the bulk solution was measured by means of ion chromatography (IC25, Dionex).

In the case of the uncoated pelletized catalyst, a cage-like arrangement of a perforated PTFE tube was used in order to protect the pellets from mechanical damage and dispersion of the particles while avoiding additional mass-transfer resistance. The PDMS coating of the coated pellets provided mechanical protection, no cage was necessary here.

The protection of the PDMS coating against ionic catalyst poisons was tested by adding Na_2SO_3 (1–120 mM) to the catalyst suspension. For each reaction cycle, the interaction time between the catalyst and the poison was at least 3 d. In alkaline solution, sulphurous acid is mainly deprotonated ($pK_{A2} = 7.21$), i.e. SO_3^{2-} is the dominating sulphite species.

The stability of the coated catalyst systems against internal HCl formation (i.e. self-poisoning) was tested using TCE at higher concentrations ($C_{0,TCE} = 26–37\,mg\,L^{-1}$, $C_{NaHCO3} = 10\,mM$).

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