Efforts for long-term protection of palladium hydrodechlorination catalysts

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ABSTRACT

Nano-sized palladium (Pd) catalysts are known for their high intrinsic hydrodechlorination (HDC) activity towards many chlorinated water pollutants, converting them into non-harmful compounds. Optimization of catalyst protection by embedding various types of Pd catalysts (Pd on oxidic supports and *in-situ* generated Pd clusters) into poly(dimethylsiloxane) (PDMS) layers was studied together with their use in HDC reactions. The catalyst performance in standard batch and long-term experimental set-ups was used to better understand and optimize the Pd-PDMS system. The phenomenon of polymer deterioration by entrapped HDC-generated HCl is studied for various systems and found to be the main reason for limited life times of Pd-PDMS systems.

Pd-PDMS composites were found to provide long-term protection from ionic catalyst poisons. This gain in prolonged catalyst protection goes along with an inevitable decrease in specific catalyst activity which is unhesitantly accepted for the benefit of a longer-lasting catalytic activity. However, when comparing the relative loss of the specific Pd activity due to embedding, it is found to be much lower for initially less active catalyst particles (e.g. a factor of 2 for Pd/Al$_2$O$_3$) compared to about two orders of magnitude for the highly active nanoscale Pd particles. It could be shown that embedded catalysts in continuously operated long-term set-ups have enhanced resistance and longevity compared to those tested in repeated batch-type reaction cycles. PDMS-embedded Pd/Al$_2$O$_3$ maintains its full initial activity up to turnover numbers of >750 (for trichloroethene as probe substance), whereas the catalyst system loses more than 50% of its initial activity for a comparable catalyst utilization (TON $\approx$ 750) operated in batch cycles.

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1. Introduction

Traditional chlorinated hydrocarbons (CHCs) and emerging chlorinated contaminants are among the most widely distributed pollutants in water. Their dechlorination to environmentally harmless compounds is a significant contribution towards cleaner water resources. Together with hydrogen donors, such as molecular hydrogen (H$_2$), Pd catalysts are able to perform under ambient conditions fast hydrodechlorination (HDC) of a broad range of chlorinated contaminants, converting them to non-harmful products [1–4]. Compared with other transition-metal-based catalysts, such as Rh, Pt or Ni, Pd catalysts are characterized by higher selectivity, activity, stability and a lower toxicity, and are therefore particularly appropriate for a rapid and effective water treatment [4–6]. In the case of chlorinated ethenes, of which PCE and TCE are widely distributed groundwater pollutants, Pd catalyses the substitution of

chlorine by hydrogen atoms and the saturation of the double bond, forming ethane and hydrochloric acid. The high intrinsic specific activity of Pd A_{Pd} in terms of L of water per g of palladium per min (L g^{-1} min^{-1}), which is equivalent to a second-order rate coefficient k_i [7], becomes evident when using nanostructured catalysts [8–10]. For example, a specific Pd activity of 22,500 L g^{-1} min^{-1} was reached for TCE hydrodechlorination using Pd on nanomagnetite (Pd/Fe$_3$O$_4$) in clean waters [8]. This was the highest activity ever recorded for a Pd catalyst in a HDC reaction. Nevertheless, the few tests under field conditions led to much lower specific Pd activities of about 0.1 L g^{-1} min^{-1} in real groundwaters [11–13]. The dramatic loss in reaction rates compared with laboratory-scale experiments is caused not only by common external (bulk to surface) and internal (diffusion into pores) mass-transfer limitations, but especially by the deactivation of the catalytic functions due to the high sensitivity of Pd towards a broad range of groundwater constituents [15–18]. Naturally-occurring reduced sulphur species, such as dimethyl sulphide, diethyl sulphide, SO$_3$$^{2-}$, HS$^-$, S^{2-} and H$_2$S, can strongly bind to Pd, inducing structural and electronic effects which result in loss of activity or shift in selectivity—so-called catalyst

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poisoning [19,20]. Even though Davie et al. [14] came to the conclusion that Pd-based catalysis is already economically competitive with other detoxification methods (such as air stripping, permeable reactive barrier or active-carbon sorption), the problems associated with catalyst regeneration [13,16–18,21] strongly hinder its use in environmental practice. The currently accepted opinion is that further research efforts have to be made in the direction of catalyst protection rather than focusing on intrinsic activity improvements [22]. Promising protection approaches include the use of Pd-doped hydrophobic zeolites or polymeric membranes to shield the catalyst from poisons [23–26]. In theory, hydrophobic non-porous polymeric membranes are able to enrich the organic compounds in the vicinity of the catalyst centres by partitioning from the water phase. Thus, the catalytic surface is protected from ionic compounds, metal ions and macromolecules. Poly(dimethylsiloxane) (PDMS), a well-known and extensively used rubbery polymer [27], has been chosen by our group as protecting material due to its outstanding properties, such as chemical stability, non-toxicity, high hydrophobicity and easy handling. In particular, the flexibility of the O–Si–O backbone structure, its low glass transition temperature ($\approx -125\,°C$) and its high diffusivity make PDMS extremely well permeable to non-ionic compounds [28,29]. In previous reports on our research, the batch catalytic properties of PDMS membranes containing Pd/Al_2O_3 [25,26] or Pd clusters [24] have been studied, showing promising results in performance and stability. However, although the batch system is useful for screening of the catalyst's basic properties, it cannot be reliably used to predict the behaviour in treatment plants, where the catalyst is presumably stressed by high and varying concentrations of CHC and poisons. Subject of the present work are the further development of the discontinuous batch system and the understanding of the properties of supported and unsupported Pd catalysts embedded in PDMS layers for continuously operated semi-batch mixed-flow-reactors (MFR). The catalytic Pd-PDMS material has been applied as coating on reactor walls or covering the surface of glass rings, which then can be used as packing material in fixed-bed reactors. Special attention has been given here to the long term performance of embedded Pd catalysts, their stability against internal and external poisons and to the influence of mass-transfer effects in different reactor configurations. The outcomes of this research represent a useful and necessary step towards the implementation of PDMS-protected Pd systems in water treatment facilities.

2. Materials and methods

2.1. Chemicals

Reagents, Pd salts and CHCs were purchased in the highest available grade from Merck, Sigma–Aldrich or Chempur (Germany) and used as received. SilGel® 612 A/B, a two-component PDMS precursor, was purchased from Wacker-Chemie, Germany. Activated carbon (PKD, grain size ca. 75 μm) was purchased from Carbotech, Germany. The eggshell catalyst G-133D with nominal 0.5 wt-% Pd on γ-Al_2O_3 was purchased from Commercia, Germany, crushed and sieved prior to use; the size fraction d_p <25 μm was used for the HDC experiments and analysed for its BET surface area (161 m^2/g, N_2 adsorption), porosity (0.43 cm^3/g, N_2 adsorption), Pd content and dispersion (x_{Pd} = 0.51 wt-% by XRF and d_{Pd} = 0.16 by CO chemisorption, respectively).

2.2. Polymer-coated catalysts

2.2.1. Wall-coated reactors

For Pd particles embedded in PDMS (PDMS-Pd), (i) 4.0 g of the PDMS blend (A and B components 2:1) were mixed into 15 mL hex-

ane and placed in a cylindrical glass vessel, which (ii) was allowed to rotate in horizontal position overnight (final treatment at 40 °C) in order to assure uniform distribution and curing of PDMS at the inner wall of the vessel. Then (iii) an aliquot of a solution of $Pd(ac)_2$ in THF (50 mg in 15 mL) was introduced into the vessel under continued rotation. After complete evaporation of the solvent, (iv) the incorporated Pd(II) was reduced to the catalytic active Pd(0) by flushing the system with N_2/H_2 for 30 min. The fast reduction is visible by colour change from yellow to black. For Pd/Al_2O_3 embedded in PDMS (Pd/Al_2O_3-PDMS) the procedure consists of steps (i) and (ii). In step (i), 50 mg of Pd/Al_2O_3 was added to the PDMS-hexane mixture. The average thickness of the resulting PDMS membranes was 200 μm for 250-mL vessels and 190 μm for 300-mL vessels.

2.2.2. Packed-bed reactors

Two different sizes of Raschig glass rings providing different surface area per bed volume were used as membrane carrier in a packed bed. The average mass per piece & geometric surface area were 270 mg and 12 cm^2/g for type A and 39 mg and 15 cm^2/g for type B, respectively (see Fig. SI2 for details). In a typical coating procedure, the rings were dip-coated in a glass flask containing a homogeneous mixture of 2 volumes PDMS precursors and 1 volume hexane together with a given amount of suspended Pd/Al_2O_3 particles. The rings were then removed from the flask and dried at 70 °C. Rings of type A were coated with three different thicknesses of PDMS (7, 40 and 80 μm) having 7.3×10^{-5}, 4.9×10^{-4} and 4.8×10^{-4} wt-% of Pd, respectively. Rings of type B were coated with a PDMS layer of 33 μm having a Pd content of 8.4×10^{-4} wt-%. The batch tests and the long-term mixed-flow tests were performed in a reactor equipped with a perforated Teflon plate as spacer, thereby preventing the membranes on the rings from being damaged by the stirrer (see Fig. SI1 for details).

2.3. Characterization of membranes

Physical and qualitative characterization of the membranes was performed by means of scanning electron microscopy (SEM, Zeiss, DSM982 Gemini) and energy-dispersive X-ray spectroscopy (EDX, NORAN Instruments, 984A-1SUS Pioneer Norvar SUN/Voyager).

2.4. Hydrodechlorination (HDC) experiments

The performance of the various types of Pd HDC catalysts (as particles, wall coated reactors and coated packed bed materials) was tested in closed batch systems (for screening of catalyst activities) and continuous mixed flow reactors (MFR) (preferably used for continuous longer-term experiments). Chlorobenzene (MCB), trichloroethene (TCE) and chloroform (CF) were chosen as model contaminants representing three classes of substrates: fast-reacting aromatic CHCs, fast-reacting aliphatic CHCs and slow-reacting CHCs, respectively [7]. The reaction kinetics was monitored by means of headspace analysis of educts and products using GC–MS (QP 2010, Shimadzu Corp., equipped with a 25 m DB1 capillary column) or GC-FID (GC 2010, Shimadzu Corp., equipped with 30 m HP5-MS and GS-Q capillary columns) devices. The chloride concentration in the reaction solution was regularly monitored via ion chromatography measurements (IC25, Dionex, IonPac AS11/AG15).

2.4.1. Batch reactivity screening

250-mL clear screw-cap bottles equipped with Mininert® valves were chosen as reaction vessels. After filling the vessels with 200 mL of slightly buffered reaction solution ($NaHCO_3$ 9 g/L) and purging with gaseous hydrogen for 15 min (pH = 8.7), the HDC was started by adding a methanolic CHC stock solution. The system was kept under continuous shaking (210 rpm on a horizontal shaker)