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Pd-Catalyzed Hydrodechlorination of Chlorinated Aromatics in Contaminated Waters - Effects of Surfactants, Organic Matter and Catalyst Protection by Silicone Coating

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ABSTRACT

Many chlorinated aromatic and aliphatic hydrocarbons dissolved in water can be rapidly and selectively hydrodechlorinated by means of Pd catalysts. However, if they appear in a complex water matrix, as is common for wastewater treatment or after soil extraction, the protection of the Pd sites against catalyst poisons may become the key step for applicability of this reaction. In the present study, Pd/Al₂O₃ was tested as hydrodechlorination (HDC) catalyst in various soil-washing effluents. As probe compounds 3-chlorobiphenyl (3-CBP), monochlorobenzene (MCB) and trichloroethene (TCE) were chosen. Specific catalyst activities up to $A_{Pd} = 200 \text{ L g}^{-1} \text{ min}^{-1}$ were measured in clean water. The influence of surfactants and co-solvents was studied. In addition, soil slurry supernatant was employed as reaction medium to appraise the influence of soil co-extractants (dissolved organic matter, DOM) on the dechlorination reaction. Results show that commercially available surfactants such as Tween 80, Triton X-100, SDBS, and CTMAOH as well as methanol as co-solvent with concentrations up to 20 vol% did not strongly affect the catalyst activity. However, the catalyst performance was heavily decreased in the presence of a soil slurry supernatant (40 mg L⁻¹ DOM). Hydrophobic coating of the catalyst by silicone polymers was successful in protecting the Pd sites against ionic catalyst poisons such as DOM and bisulphite for at least 24 h.

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1. Introduction

Hydrodechlorination is an emerging chemical reaction in environmental catalysis for treating chlorinated organic compounds (COCs) found in environmental media [1, 2]. In the presence of a catalyst such as Pd/Al₂O₃ and hydrogen or a hydrogen source as reductants, COCs are hydrodechlorinated according to $R-Cl + H_2 \xrightarrow{Pd} R-H + HCl$ and transformed to more benign and more biodegradable compounds. The reaction proceeds quickly and selectively at ambient temperature in clean water. For an assumed catalyst activity of $A_{Pd} = 10 \text{ L g}^{-1} \text{ min}^{-1}$ the half-life of the COC in a fixed-bed reactor (e.g. Pd(0.5wt-%)/Al₂O₃) is in the order of 1 s [2-3]. The selectivity of the HDC reaction may be an advantage, because only halogenated compounds are reduced, whereas many other substance classes are not converted [4]. However, one has to be aware of the fact that the hydrocarbon backbone is not broken down. As an example, benzene is formed from MCB which cannot be considered as cleaning of the water.

The catalyst Pd/Al₂O₃ proved to be efficient for the remediation of relatively less hydrophobic COCs such as chlorinated ethenes and benzenes which are frequently found in contaminated groundwaters [1-10]. More hydrophobic COCs such polychlorinated biphenyls (PCBs), dibenzodioxins (PCDD) and -furans (PCDF) may be sorbed to aquifer materials and their leaching to groundwater is very slow. Thus, they persist in aquifers and soils and cause long-term contamination.

To make such pollutants available to the catalytic HDC reaction they have to be extracted into the water phase. Potential techniques for treating pollutants in the soil are solvent flushing (*in-situ*) or soil washing (*ex-situ*) [11]. In these processes, soil materials are extracted by aqueous solvents which have higher solubilities for the hydrophobic pollutants

than pure water. Typically, co-solvents or surfactants are employed [12-16]. However, soil washing does not destroy pollutants. It generates effluents which need further chemical or biological treatment. A number of studies have shown the effective microbial reductive dechlorination of PCBs in soil, sand and aquifers after their bioavailability was artificially enhanced by the application of biosurfactants, e.g., cyclodextrin and rhamnolipids [17-19]. On the other hand, a more efficient chemical reductive treatment of PCBs using zero-valent iron (ZVI) or Pd-based bimetallic catalysts has also been reported [20-24]. For effluents containing COCs, the catalytic HDC reaction can be considered a promising tool. However, reports on matrix effects, solvent effects and the influence of amphiphiles (i.e. surfactants) on the HDC over Pd catalysts are scarce [25-27]. Most of the studies on the effects of amphiphiles on reductive dechlorination were based on ZVI and palladized ZVI [28-32]. They were mainly focused on enhancing the reaction by modifying the surface properties of the iron particles. In general, the addition of amphiphiles generates rate enhancements for substrates such as chloroform, PCE and chlorinated benzenes [28-29, 31]. The extent of the increase in the reaction rate, however, depends strongly on the type of surfactants and the nature of the catalyst employed. The rate enhancement was attributed to the increase in surface concentrations of the target contaminants, making them more available for the surface-mediated catalytic reactions. To the best of our knowledge, no reports on the influence of amphiphiles on the HDC reaction with Pd/Al₂O₃ have yet been published.

In the present study, we make two important contributions: First, we quantify how the activity of a commercially available Pd/Al₂O₃ catalyst changes in the presence of four different surfactants, in the presence of methanol as a co-solvent, and in the presence of a soil extract. Second, we propose and verify a new technique by which catalysts can be protected against certain species that might cause catalyst poisoning. We consider 3-CBP as a useful representative of the even more hydrophobic PCBs and PCDD/F because the chemical reactivity of the chlorine substituents at the aromatic rings are similar in all these compounds.

2. Experimental procedures

2.1 Chemicals

The surfactants SDBS (sodium dodecylbenzenesulphonate), CTMAOH (cetyltrimethylammonium hydroxide, $C_{19}H_{43}NO$), Tween 80 (Polyoxyethylene (20) sorbitan monooleate, $C_{64}H_{124}O_{26}$), and Triton X-100 (polyoxyethylene octyl phenyl ether, $C_{14}H_{22}O(C_2H_4O)_{10}$) were obtained from J.T. Baker. The chemicals MCB and 2-methylnaphthalene as well as the solvents methanol, n-hexane and chloroform were purchased from Merck. The 3-CBP, analytical standard, was obtained from Riedel-de Haen. The catalyst Pd on γ - Al_2O_3 (referred to as Pd/ Al_2O_3) was purchased from Commercia, Germany. The catalyst has 0.5 wt% Pd (from EDXRF analysis), a BET surface area of $140 \text{ m}^2 \text{ g}^{-1}$ (N_2 adsorption) and a Pd dispersity of 0.17 (CO adsorption). The original egg-shell impregnated catalyst particles (3 mm pellets) were crushed and sieved. The size fraction of 25-63 μm was employed in all batch experiments.

A silicone-coated catalyst sample was prepared according to the following procedure: 5 g of the Pd/ Al_2O_3 catalyst (fraction 63 - 125 μm) was placed in a 50 mL round-bottom flask, evacuated and spiked with 0.75 g of the methyl silicone SE 30 (poly(dimethylsiloxane); PDMS, Merck, Germany) dissolved in 15 mL of n-hexane. After shaking the suspension for 1 h the solvent was slowly removed in a rotary evaporator ($p \approx 20 \text{ kPa}$, $T = 20\text{-}70^\circ\text{C}$). This procedure was repeated twice until the catalyst material contained about 30 wt-% PDMS. Higher silicone loadings tended to produce a sticky material which is more difficult to handle in aqueous suspensions.

2.2 Dechlorination in the presence of surfactants and co-solvents

Batch dechlorination of 3-CBP in surfactant solution was conducted in a 500 mL serum bottle equipped with a Mininert[®] valve. A 400 mL buffer solution (5 mM $NaHCO_3$ in deionized

water, pH = 8.3) was added into the batch bottle and purged with hydrogen gas. Defined volumes of surfactant stock solutions were spiked into the bottle in order to obtain the desired surfactant loading in the aqueous solution, i.e. at concentrations close to, below, and above their critical micelle concentration (CMC). A methanolic stock solution of 3-CBP was then spiked to the aqueous solution in order to give an initial concentration of $c_0 = 2.5 \text{ mg L}^{-1}$ which is about half of its water solubility ($S_{\text{water}} = 4.7 \text{ mg L}^{-1}$). After shaking the bottle for about 5 min (complete dissolution of 3-CBP) an aqueous slurry of the catalyst (about 50 mg Pd/Al₂O₃, pre-reduced in 10 mL water for 1 h with H₂) was added. This marked the start of the HDC reaction ($t = 0$). The system was continuously shaken (horizontal shaker, 180 rpm) and at certain time intervals 5 mL samples were drawn out through the Mininert® valve by means of a glass syringe and given into a vial which contained sulphide to stop further hydrodechlorination immediately. The sample was extracted with 300 μL of chloroform containing 2-methylnaphthalene as internal standard. After the extraction, the chloroform phase was washed several times with water to remove the surfactants from the extract. The educt 3-CBP and the sole product biphenyl were quantified by GC-MS analysis (Shimadzu GC-MS QP2010). The dechlorination of 3-CBP in water-methanol mixtures was conducted similarly.

The dechlorination experiments with MCB and TCE were conducted accordingly, with the exception that the dechlorination kinetics was followed by GC-MS analysis of educts and products via headspace sampling (50 μL).

2.3 Dechlorination in soil slurry supernatant

A soil sample was collected from the surface layer of a field in Steigerwald, Germany. The soil was air dried, mixed thoroughly and passed through a 2 mm sieve. The organic carbon contents of the soil (6.88 wt%) and of the soil slurry supernatant were measured using a TOC analyzer (Stroehlein Instrument). To prepare the soil extract, deionized water was added to the

soil sample (1 : 5 soil to water mass ratio) and shaken overnight on a horizontal shaker at 180 rpm. After shaking the soil slurry and sedimentation of the coarse particles (1 h) the supernatant was decanted and centrifuged (5000 g for 1 h). The soil extract (50 mL) was then used as reaction medium for HDC. The reaction kinetics was followed by taking 0.5 mL water samples from the batch bottle (100 mL), extracting with n-hexane (200 μ L) containing 2-methylnaphthalene as internal standard, and performing GC-MS analysis (Shimadzu GC-MS QP2010).

2.4 Dechlorination with polymer-modified catalysts

These batch experiments were carried out in a similar way to those described in section 2.2. Instead of 3-CBP, MCB and TCE were used as substrates ($c_0 = 20 \text{ mg L}^{-1}$). The course of the HDC was followed by headspace sampling (50 μ L gas-tight syringe) and GC-MS analysis of TCE, ethane, MCB and benzene. In most cases the corresponding substrate and product concentrations correlated well. In cases where significant deviations were observed, the product formation kinetics was selected because it reflects the reaction kinetics more certainly than the educt disappearance, which may be more biased by sorption phenomena.

3. Results and discussions

3.1 Effects of surfactants on the hydrodechlorination kinetics

In order to obtain a baseline activity of Pd/Al₂O₃ for the HDC of 3-CBP, the probe compound was dechlorinated in deionized water buffered by NaHCO₃ at pH = 8.3. The reaction follows a first order kinetics with respect to the substrate concentration up to very high extents of conversion (Fig. 1). This type of kinetics is characteristic for most of our batch experiments. The kinetics can be described by a first-order rate coefficient k_1 . We prefer the specific Pd activity A_{Pd} [$\text{L g}^{-1} \text{ min}^{-1}$] which is defined by Eq. 1

$$A_{\text{Pd}} = k_1 / (\ln 2 \cdot c_{\text{Pd}}) = 1 / (\tau_{1/2} \cdot c_{\text{Pd}}) \quad (1)$$

with c_{Pd} as the applied Pd concentration and $\tau_{1/2}$ as the half-life of the substrate. The data in Fig. 1 deliver a specific catalyst activity of about $190 \text{ L g}^{-1} \text{ min}^{-1}$.

→ Please insert Figure 1 here.

This is in the same order of magnitude as values obtained with other unsaturated COCs such as TCE and MCB [2, 3, 7]. Remarkably, when comparing the activity value with that commonly given for MCB, the additional phenyl substituent in 3-CBP did not significantly affect its HDC reactivity on Pd/Al₂O₃ (cf. Table 1). Apparently, the transition states in the HDC reaction at the Pd sites are similar and the electronic effect of the phenyl group on the reactive benzene ring may be marginal due to its meta-position. An alternative explanation of the observed low selectivity of the heterogeneously catalyzed HDC reaction might be mass-transfer control of the reaction rates. Calculations of mass-transfer resistance such as made in ref. [4] can also be applied to the present catalyst (size fraction 25-63 μm , $A_{\text{Pd}} = 200 \text{ L g}^{-1} \text{ min}^{-1}$). They lead to the following results: the external mass-transfer resistance (film diffusion) can be neglected, whereas the internal resistance (intraparticle diffusion) is significant. An approximate value of the Weisz modulus of $\Phi \approx 3$ means that the substrate inside the pore volume ($\bar{c}_{\text{pore},i} / \bar{c}_{\text{bulk},i}$) is depleted by a factor of 3. This partial mass-transfer control discriminates against high reaction rates, finally giving rise to lower apparent reaction selectivity.

In the present study, the effects of anionic, cationic, and non-ionic surfactants as well as methanol as co-solvent are studied. The aim of their application is to increase the solubility of highly hydrophobic substrates in the water phase rather than primarily to enhance the catalyst performance. Firstly, the presence of surfactants in solution above their CMC may increase the solubility of the hydrophobic contaminants. Secondly, surfactant monomers or aggregates may attach to the catalyst surface (admicelles) and form hydrophobic layers

around and inside the porous catalyst particles. The interplay between the various sorption and partitioning processes may lead to an increase or decrease of the substrate concentration which is available at the reactive catalyst sites. Additionally, these sites themselves may be affected by sorption of amphiphiles. The high sensitivity of Pd for various classes of catalyst poisons, including many sulphur compounds, is well known [33-36].

Catalyst activities in the presence of the anionic surfactant SDBS at three different concentrations are compiled in Table 1 and Figure 2. The given surfactant concentrations are total concentrations regardless of the speciation within the catalyst suspension (i.e. freely dissolved, as micelles or adsorbed at the catalyst surface). At the lowest surfactant loading ($c_{\text{SDBS}} = 200 \text{ mg L}^{-1} < \text{CMC} \approx 900 \pm 500 \text{ mg L}^{-1}$), the catalyst performance was not significantly affected compared to clean water. When the SDBS loading was increased close to and above its CMC, the catalyst performance was reduced, but kept a significant level of about 30% of its original performance even in the presence of the highest SDBS concentration.

→ Please insert Table 1 and Figure 2 here.

Apparently, micelle formation does not play a dominant role for the catalyst performance. At the highest SDBS concentration most of the substrate is located inside surfactant micelles. This follows from Eq. 2:

$$X_{\text{freely dissolved}} = [1 + K_{\text{micelle}} (c_{\text{SDBS}} - \text{CMC}_{\text{SDBS}})]^{-1} \approx [1 + 10^{4.1} (1.5 - 0.9) 10^{-3}]^{-1} = 0.12 \quad (2)$$

For this estimation it is assumed that (i) the major portion of the surfactant added is dissolved in the water phase rather than adsorbed at the catalyst surface and (ii) the micelle-water partitioning coefficient of 3-CBP (K_{micelle}) is about half of its octanol-water partitioning coefficient (K_{OW}). The fraction of freely dissolved 3-CBP ($X_{\text{freely dissolved}}$) is only about 12%. Hence, the thermodynamic activity of the substrate in the aqueous phase as the driving force for sorption on the catalyst surface is reduced by about one order of magnitude. Nevertheless, the observable reaction rate is only slightly affected, by about 15% ($A_{\text{Pd}} = 55 \text{ vs. } 65 \text{ L g}^{-1}$

min⁻¹). Apparently, sorption of the substrate on the Pd sites does not play a key role in the rate-determining steps. This is in conformity with the similar reactivities of 3-CBP and MCB (cf. above), which are expected to have significantly different sorption affinities from aqueous solution. A plausible mechanistic interpretation of this finding could be site saturation. However, this explanation would not be in conformity with the observed first order kinetics over a wide educt concentration span up to very high conversion degrees (cf. Fig. 1).

In addition, the cationic surfactant CTMAOH (CMC \approx 450 mg L⁻¹) was tested for its influence on the HDC of 3-CBP with Pd/Al₂O₃. At a total surfactant concentration close to its CMC a catalyst activity $A_{Pd} = 80 \text{ L g}^{-1} \text{ min}^{-1}$ was obtained. This is not very different from the activity in the presence of SDBS. Obviously, neither the charge of the surfactant molecule nor the type of the heteroatom in the charged group (S⁴⁺ or N³⁻) plays a decisive role. The positive message is that the Pd sites keep their catalytic activity in the presence of both surfactants.

The non-ionic surfactant Tween 80 has a relatively low CMC (\approx 15 mg L⁻¹). Around this concentration range the catalyst activity is not strongly influenced (Fig. 3). Compared with the reference solution (clean water at pH = 8.3) Tween 80 generates a slight but significant increase in catalyst activity of about 15%. This gain might be even more pronounced if the negative effect of partial mass transfer control could be eliminated. Again, perfect first order kinetics is observed up to very high degrees of substrate conversion.

→ Please insert Figure 3 here.

Triton X-100 is another commercially available non-ionic surfactant, but with a tenfold higher CMC (\approx 150 mg L⁻¹) than Tween 80. Its effect on the catalyst activity when applied with this CMC is similar to that of Tween 80: the catalyst activity is slightly increased ($A_{Pd} = 230 \text{ L g}^{-1} \text{ min}^{-1}$, graph not shown).

Summarizing all findings with ionic and non-ionic surfactants, we can conclude that their presence at relatively low concentrations (\leq 200 mg L⁻¹) only slightly affects the catalytic activity of Pd/Al₂O₃. This might be correlated with the point of zero charge of the

catalyst carrier γ -alumina, which is close to the pH value of the applied buffer solution ($\text{pH}_{\text{pzc,Al}_2\text{O}_3} \approx 8$) [25 and ref. therein]. Therefore, the alumina surface should expose a relatively low net charge. This makes strong electrostatic interactions of ionic surfactants less likely.

3.2 Effects of methanol on the hydrodechlorination kinetics

Co-solvents such as alcohols also enhance the solubility of hydrophobic substrates, but unlike the amphiphiles, co-solvents do not provide sorption-active layers on the catalyst surface. In this study, 20 vol% of methanol was applied. The resulting catalyst activity of $A_{\text{Pd}} = 155 \text{ L g}^{-1} \text{ min}^{-1}$ (graph not shown) is slightly lower than in pure water but still in the same order of magnitude. The decrease in the activity coefficient of 3-CBP in the solvent mixture can be estimated according to the general relationship [37]:

$$\log (\gamma_{i,\text{mixture}} / \gamma_{i,\text{water}}) = -\sigma_{i,\text{solvent}} \cdot f_{\text{solvent}} \quad (3)$$

where $\gamma_{i,\text{mixture}}$ and $\gamma_{i,\text{water}}$ are the activity coefficients of the solute i , $\sigma_{i,\text{solvent}}$ is commonly referred to as the co-solvency power of the solvent, and f_{solvent} is its volume fraction ($0 < f_{\text{solvent}} < 1$) in the aqueous mixture. With $\sigma_{3\text{-CBP,methanol}} \approx 3.0$ and $f_{\text{methanol}} = 0.2$ it follows $\gamma_{i,\text{mixture}} / \gamma_{i,\text{water}} \approx 4$. This means, addition of 20 vol% of methanol decreases the chemical activity of 3-CBP by a factor of 4 compared with pure water. Again, the decrease in chemical activity of the substrate is not reflected in its reactivity.

Fang et al. [27] described a significant decrease in the dechlorination rate of 2-chlorobiphenyl by palladized ZVI when ≥ 10 vol% of methanol as co-solvent was added to the aqueous suspension. This was attributed to two reasons: (i) a shift in the substrate adsorption equilibrium and (ii) a deceleration of the iron corrosion as the source of hydrogen. Since the Pd/Al₂O₃ catalyst is fed with external hydrogen, the second reason can be ruled out. Apparently, substrate sorption equilibria at the Pd-sites do not play a decisive role for the

overall reaction rates. Moreover, the solvation power of the applied solvent mixture ($\text{H}_2\text{O} : \text{MeOH} = 80 : 20$) is sufficient for fast chloride desorption. Thus, no chloride poisoning of the catalyst was observed [38].

Wee and Cunningham studied the Pd-catalyzed HDC of tetrachlorobenzene in water-ethanol mixtures [39]. The reaction rate decreased as the ethanol fraction of the solvent increased. The authors interpret their results in terms of a Langmuir-Hinshelwood kinetic model, wherein the sorption coefficient K_d depends on the solvent composition. The lowest applied ethanol concentration (33 vol%) was above the methanol concentration tested in the present study (20 vol%). No kinetic data are available in [39] for pure water. Thus no direct comparison with the solvent effect measured in the present study is possible. Nevertheless, the specific catalyst activities deduced from the data presented in [39] (catalyst: 1wt% Pd on $\gamma\text{-Al}_2\text{O}_3$) are similar to that measured in our study ($A_{\text{Pd}} = 200\text{-}300 \text{ L g}^{-1} \text{ min}^{-1}$ vs. $155\text{-}190 \text{ L g}^{-1} \text{ min}^{-1}$).

3.3 Effect of soil extracts on hydrodechlorination kinetics

When COCs are extracted from contaminated soil or sediment, the HDC catalyst inevitably comes into contact with soil constituents such as water-soluble DOM. This applies regardless of the application of extraction additives such as surfactants or co-solvents. The aqueous supernatant of soil washing employed in our HDC experiments contained a dissolved organic carbon concentration of $c_{\text{DOC}} \approx 20 \text{ mg L}^{-1}$ which corresponds to a DOM concentration of $c_{\text{DOM}} \approx 40 \text{ mg L}^{-1}$. The HDC of 3-CBP was conducted in this supernatant without any dilution or pre-treatment. The resulting initial catalyst activity of $A_{\text{Pd}} = 15 \text{ L g}^{-1} \text{ min}^{-1}$ (graph not shown) is lower by an order of magnitude than the inherent activity in clean water. Moreover, the catalyst showed a decreasing activity over longer contact periods with the soil extract, with complete catalyst deactivation after $\geq 24 \text{ h}$.

The palladized ZVI reagent applied by Fang et al. [40] for the dechlorination of 2-CBP showed a lesser sensitivity to DOM. The reaction rate was decreased in this case only by a factor of 1.6 in the presence of 10 mg L⁻¹ DOM. It is known from the literature that natural organic matter (NOM) can either inhibit or enhance the dechlorination of contaminants with ZVI-based reagents. NOM competes for active surface sites of the reagent and additionally may act as an electron mediator [41-43].

3.4 Protection of Pd-catalysts by polymer coatings

In order to protect the sensitive Pd sites from contact with detrimental water constituents, the catalyst was coated with a thin non-porous polymer layer. PDMS was selected as a coating material due to its chemical stability and its high diffusivity ($D_{\text{MCB}} \approx 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) which is only a factor of about 10 lower than for liquid water. Fig. 4 shows a schematic presentation of a porous catalyst carrier which is filled and coated with a non-porous polymer material.

→ Please insert Figure 4 here.

The non-ionic reactants RCl, RH and H₂ have unlimited access to the Pd sites, whereas ionic compounds are excluded. The reaction product HCl is released from the catalyst particles, but is trapped in the bulk water phase due to its dissociation. The penetration of HCl through the PDMS coating can only proceed if there is no liquid water phase around the catalyst surface, i.e. HCl is present in non-dissociated molecular form. If the Pd sites are in direct contact with the PDMS polymer rather than with a water phase, it is to be expected that their catalytic properties are affected. Moreover, the polymer coating and pore filling create additional mass transfer resistances. On the other hand, the highly diluted organic reactants are enriched in the polymer phase. All these factors may change reaction rates and selectivities in a complex way.

In order to affect the overall reaction rates as little as possible by sorption kinetics we changed the substrate from 3-CBP to MCB and TCE. The reaction kinetics was followed in these experiments by headspace analysis of the products, benzene and ethane.

First, the activity of the silicone impregnated catalyst was tested under standard reaction conditions (distilled water buffered with 5 mM NaHCO₃ at pH \approx 8.3, $c_{0,MCB} = c_{0,TCE} = 20 \text{ mg L}^{-1}$, $c_{\text{catalyst}} = 125 \text{ mg L}^{-1}$) and compared with that of the virgin catalyst. The activities for the HDC of MCB were $A_{\text{Pd}} = 150$ and $50 \text{ L g}^{-1} \text{ min}^{-1}$ and for the HDC of TCE $A_{\text{Pd}} = 200$ and $80 \text{ L g}^{-1} \text{ min}^{-1}$, respectively. Obviously, the coating caused a loss of activity by a factor of about 3 as also found in [6].

Next, the protection efficacy of the silicone coating was tested by applying the ionic catalyst poison bisulphite. 50 μM NaHSO₃ was added to a catalyst suspension without silicone layer containing 5 μM unprotected Pd (S : Pd = 10 moles per mole). After 1 h of mixing and purging the suspension with hydrogen MCB was added, after which there was no measurable HDC activity ($A_{\text{Pd}} < 0.1 \text{ L g}^{-1} \text{ min}^{-1}$). The unprotected catalyst was completely deactivated.

It is not obvious from this experiment whether sulphite itself or its reduction product sulphide is the active catalyst poison. Sulphide is well known as a strong Pd catalyst poison. In order to distinguish between the two possibilities, the catalyst was treated with bisulphite for 1 h in the absence of hydrogen, separated by centrifugation, washed 5 times each with 100 mL of distilled water to remove reversibly bound sulphite, and tested for its HDC activity. The catalyst was also completely deactivated in this case. This experiment shows unambiguously that sulphite and/or bisulphite are the active catalyst poisons in our experiments. The distinction between sulphite and sulphide might be important because sulphide has different penetration properties: due to its protonation equilibria ($pK_{A1} \approx 13$, $pK_{A2} = 7.05$) sulphide is present as H₂S under neutral conditions. H₂S is able to penetrate non-porous silicone polymer coatings even faster than H₂ [44].

Applying the same deactivation procedure to the silicone-coated catalyst (1 h exposure to 50 μM bisulphite under hydrogen purging) resulted in only a slight deactivation. TCE and MCB were completely dechlorinated with $A_{\text{Pd}} = 45$ and $20 \text{ L g}^{-1} \text{ min}^{-1}$, respectively, which corresponds to about 50% of the initial catalyst activity. The dechlorination followed a first order kinetics in both cases. Obviously, a large fraction of the Pd sites were protected against sulphite. An additional experiment with MCB in deionized water without any buffer added (pH shifted from 7 to 4 during the course of the reaction) led to similar results. Therefore, we can extend this conclusion to bisulphite which is the dominating species under slightly acidic conditions ($pK_{\text{A}1} = 1.8$, $pK_{\text{A}2} = 7.0$).

Applying the soil extract as reaction medium, the catalyst activity of the silicone-coated Pd catalyst decreased from $A_{\text{Pd}} = 50$ to 35 and $10 \text{ L g}^{-1} \text{ min}^{-1}$ after 1 h and 24 h of catalyst exposure time, corresponding to 70% and 20% of its original activity, respectively. Nevertheless, the silicone-coated catalyst remained active over extended reaction periods and was able to completely dechlorinate MCB.

Another type of hydrophobically protected Pd catalyst has been described in Refs. [6, 33]. It contains 5.6 wt% of Pd clusters ($d_{\text{cluster}} \approx 5 \text{ nm}$) embedded in a PDMS membrane in a triple-layered arrangement (thickness $\approx 330 \mu\text{m}$) [6]. This membrane-based catalyst (Pd/PDMS) was also tested for the HDC of MCB in the presence of soil extract. Its apparent activity in deionized water ($A_{\text{Pd}} \approx 2.5 \text{ L g}^{-1} \text{ min}^{-1}$) is significantly lower than that of the alumina-supported catalyst. One reason for the lower apparent Pd-specific activity is the marked mass transfer limitation (external film effect and intra-membrane diffusion). The soil extract did not affect this catalyst activity: after 24 h of exposure time A_{Pd} decreased by less than 10%. This gives clear evidence that the Pd sites are steadily protected against particulate and dissolved constituents of a soil extract.

4. Conclusions

Results obtained in this study show that Pd/Al₂O₃ is an efficient catalyst for the reductive dechlorination of hydrophobic contaminants such as chlorinated biphenyls in aqueous solution. Although not tested in the present study, one can assume that PCDD/F are also available for this type of reaction. The catalyst tolerates ionic and non-ionic surfactants as additives as well as methanol as a co-solvent for a better extraction and solubilization of the substrates. Surprisingly, a decrease in the chemical activity of the chlorinated substrate due to these additives did not largely affect the overall reaction rates. However, natural organic matter present in a soil-slurry supernatant poisoned the unprotected Pd catalyst.

The stability of the catalyst was significantly improved by coating it with silicone polymers. This modified Pd/Al₂O₃ catalyst was partly protected against ionic poisons such as bisulphite and NOM. Despite the significantly altered chemical environment around the Pd sites, the HDC reaction proceeds with acceptable rates. This can also be seen when comparing catalyst activities measured with hydrophobically modified catalysts in the present study ($A_{\text{Pd}} \approx 80$ to $2.3 \text{ L g}^{-1} \text{ min}^{-1}$) with those of unprotected Pd/Al₂O₃ catalysts in long-term operation under field conditions ($A_{\text{Pd}} \approx 0.05 \text{ L g}^{-1} \text{ min}^{-1}$ [4, 5, 8, 36]). In particular, it is remarkable that HCl can be released from the catalyst although the water bulk phase is not in direct contact with the catalyst surface.

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