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Application, Protection and Regeneration of Palladium as Hydrodechlorination Catalyst for Chlorinated Organic Pollutants

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Application, Protection and Regeneration of Palladium as Hydrodechlorination Catalyst for Chlorinated Organic Pollutants

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Abstract:

Palladium-catalyzed hydrodechlorination of chlorinated organic pollutants has become an important topic in environmental catalysis. However, the sensitivity of palladium metal to sulfide poisoning and other influences from real-water matrices limits its full environmental application. The presented thesis deals with measures to enable palladium catalysts for their utilization in treatment of environmentally relevant water bodies such as groundwater or wastewaters.

The protection of palladium-based catalysts (e.g. Pd/Al_2O_3) from sulfide-induced poisoning is presented in the first manuscript. This includes protective measures like impregnation of the catalyst with hydrophobic materials to repel catalyst poisons like sulfides. Oxidative water pretreatment is also introduced whereby sulfide poisons are oxidized, prior to contact with the catalytic system, by permanganate which itself does not significantly interfere with the desired hydrodechlorination reaction when kept below a certain threshold concentration. The combination of both strategies: the hydrophobic protection coupled with the oxidative pretreatment allows higher permanganate concentrations and could provide means towards longer catalyst lifetimes under real water conditions.

An alternative approach to regenerate deactivated catalyst charges is likewise presented where permanganate is applied to treat sulfide-deactivated catalysts by oxidizing sulfide species bound to the palladium surface. This successful liquid phase oxidative regeneration of the commercially available catalyst Pd/Al_2O_3 with permanganate is presented in the second manuscript.

Moreover, the possible applicability of palladium to hydrodechlorinate polychlorinated biphenyls in wastewater obtained from soil washing is presented in the third manuscript. The hydrodechlorination is conducted in the presence of a co-solvent and surfactants to mimic the actual wastewater effluents. Matrix effects exhibited by the additives are singly investigated to evaluate their influence on the palladium-catalyzed hydrodechlorination reaction. Silicone coating of the catalyst Pd/Al_2O_3 was found to protect the catalyst from the background matrix such to enhance the catalyst lifetime significantly.

Bibliographische Darstellung

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Application, Protection and Regeneration of Palladium as Hydrodechlorination Catalyst for Chlorinated Organic Pollutants

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Kurzreferat:

Die palladiumkatalysierte Hydrodechlorierung von chlorierten organischen Schadstoffen ist ein wichtiges Thema in der Umweltkatalyse geworden. Jedoch beschränkt die Empfindlichkeit des Palladiums gegenüber Sulfidvergiftung und anderen Einflüssen der realen Wassermatrix seine volle Anwendbarkeit in der Umwelttechnologie. Die vorliegende Dissertationsschrift befasst sich mit möglichen Maßnahmen, das Palladium für die Behandlung von umweltrelevanten Wässern wie Grund- und Abwasser einsetzbar zu machen.
Der Schutz von palladiumbasierten Katalysatoren (z.B. Pd/Al$_2$O$_3$) vor sulfidinduzierter Vergiftung wird im ersten Manuskript dieser Arbeit vorgestellt. Dieses schließt Schutzmaßnahmen wie die Imprägnierung des Katalysators mit einem hydrophoben Material ein, um Katalysatorgifte wie z. B. Sulfide abzuweisen. Daneben wird die oxidative Wasservorbehandlung präsentiert, wobei die sulfidischen Katalysatorgifte vor dem Kontakt mit dem katalytischen System durch Permanganat oxidiert werden, welches in Konzentrationen unter einem gewissen Schwellenwert die Hydrodechlorierung nicht signifikant beeinträchtigt. Die Kombination beider Strategien, der hydrophoben Ummantelung und der oxidativen Vorbehandlung, erlaubt höhere Permanganat-konzentrationen und könnte ein Weg zu längeren Katalysatorstandzeiten unter Umweltbedingungen sein.
Ein alternativer Ansatz zur Regenerierung desaktivierter Katalysatorproben wird vorgestellt, wozu ebenfalls Permanganat angewendet wird, um Katalysatoren durch Oxidation oberflächengebundener Sulfidspezies zu regenerieren. Diese erfolgreiche oxidative Regenerierung des kommerziell erhältlichen Katalysators Pd/Al$_2$O$_3$ in der Wasserphase ist Thema des zweiten Manuskripts.
Im dritten Manuskript dieser Arbeit wird die mögliche Anwendbarkeit von Palladium zur Hydrodechlorierung von polychlorierten Biphenylen in Abwässern von Bodenwäschen behandelt. Die Hydrodechlorierung wurde in Anwesenheit eines Co-Solvents und von Tensiden durchgeführt, um die jeweiligen Abwasserströme zu simulieren. Durch die Additive ausgelöste Matrixeffekte wurden einzeln untersucht, um ihren Einfluss auf die palladiumkatalysierte Hydrodechlorierungsreaktion zu bewerten. Zusätzlich dazu wurde der Katalysator Pd/Al$_2$O$_3$ mit Silikon beschichtet, um ihn vor der Hintergrundmatrix zu schützen, was zu einer deutlichen Standzeitverlängerung führte.

Table of Contents

1   Introduction

1.1   *Chlorinated organic compounds (COCs) in the environment*

Chlorinated organic compounds (COCs) represent an important class of chemicals which are produced and applied in large quantities. Their widespread applications in many industrial and commercial processes make them hardly dispensable to the society, but essentially indispensable as intermediates within the chemical industry. COCs can be classified into major groups such as chlorinated aliphatic and chlorinated aromatic hydrocarbon. Chlorinated aliphatics include chlorinated ethenes like trichloroethene (TCE), tetrachloroethene (PCE), vinyl chloride (VC), and the isomers of dichloroethene (DCE). The saturated counterparts include carbon tetrachloride, chloroform, dichloromethane, and 1,1,1-trichloroethane (TrCA) among others. On the other hand, chlorinated aromatic hydrocarbons include chlorinated benzenes and the polychlorinated biphenyls (PCBs). The presence of chlorine in these compounds makes them more hydrophobic and more resistant to biological degradation and when released to the environment, they may accumulate and persist over the years. Some examples of COCs which have been heavily used in the industry or are still in use are listed in Table 1. They are considered as environmentally relevant chemicals because they are commonly found as pollutants in environmental media such as in surface water, groundwater, soils and sediments.

The heavy industrial and commercial use of chlorinated hydrocarbons as excellent degreasing agents, cutting fluids, solvents and as intermediates for chemical syntheses had led to their production in large quantities worldwide. For example, the world production of TrCA was estimated to be about 600 kt in 1995 [1]. This compound is an excellent solvent for many organic materials and it is also widely used in metal cleaning and in aerosols, adhesives, coatings, dry cleaning and textile processing. Although it is one of the less toxic COCs, its use was banned in the beginning of 1996 according to the Montreal Protocol because of its ozone depletion potential [2]. Nowadays, TrCA is replaced primarily by TCE and PCE. The

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commercial consumption of TCE and PCE had also declined when they were revealed as potential carcinogens [3-8]. But due to their desirable physical and chemical properties, namely they are not flammable, excellent solvents, it has been difficult to replace them completely. Chlorinated aromatic hydrocarbons like chlorobenzene are mainly used as intermediates in organic syntheses such as the production of pesticides, resins, pigments and dyestuffs. Worldwide production of chlorobenzene amounted to 365 kt in 1993 [1]. PCBs have been rather valuable in industrial application due to their chemical inertness, high dielectric constant and resistance to heat. Hence, they were heavily applied as dielectric in transformers and large capacitors and as heat exchange fluids. The industrial production of PCBs started in 1929 and reached a maximum in the 1970s until their production was banned worldwide.

The widespread production and utilization of chlorinated compounds like TCE and PCE and the former application of banned chemicals like TrCA and PCBs have resulted in their abundant and ubiquitous distribution in the environment. In general, chlorinated compounds are lipophilic and they bioaccumulate in living organisms, furthermore, they are potential human carcinogens [3-8, 9-12].

Table 1:   List of chlorinated aliphatic and aromatic organic compounds and their industrial uses.

Compound		Industrial Uses
Tetrachloromethane	CCl_4	Use in dry-cleaning operations, in the manufacture of fire-extinguishers, refrigerants and propellants, and use as solvent.
Chloroform	$CHCl_3$	As a solvent in the laboratory especially in the pharmaceutical industry and for producing dyes and pesticides. As a chemical reagent for synthesizing the dichlorocarbene (CCl_2) group.
Methylene chloride	CH_2Cl_2	In the manufacture of aerosols, photographic films and synthetic fibers, as solvent, degreasing and cleaning agent.
1,1,2,2-Tetrachloroethane	$C_2H_2Cl_4$	As feedstock in the production of trichloroethene, as solvent in paint removers, varnishes and lacquers, as extractant for oils and fats. Use as a biocide has been discontinued.
1,1,1-Trichloroethane	$C_2H_3Cl_3$	Used as cleaning solvent for metals and circuit boards, as a photoresist solvent in the electronics industry, a very good solvent for organic materials and as solvent for inks, paints, adhesives and for coatings.
1,2-Dichloroethane	$C_2H_4Cl_2$	Use in cosmetics, and as fumigant, used in the production of vinyl chloride monomer. Historically, used as an anti-knock additive in leaded fuels.
1,2-Dichloroethene	$C_2H_2Cl_2$	As a chemical intermediate in the production of chlorinated solvents and compounds, as an extraction solvent for dyes, perfumes and lacquers.
Tetrachloroethene	C_2Cl_4	As chlorinated hydrocarbon solvent and as a chemical intermediate. Used in dry-cleaning and textile processing and industrial metal cleaning. Also used as a chemical intermediate in the synthesis of fluorocarbons.
Trichloroethene	C_2HCl_3	Was regarded as the dominant cleaning solvent through the 70's. Widely applied as a degreaser in automotive and aerospace industries. Also used as an ingredient in dyes, rubber and water proofing materials.
Vinyl chloride	C_2H_3Cl	Chiefly used in the manufacture of PVC polymer resins.
Chlorobenzene	C_6H_5Cl	Used as a chemical intermediate in the production of herbicides, dyes and rubber. It serves as a high-boiling solvent in industrial processes. Chlorobenzene is used for the synthesis of nitrochlorobenzenes which are converted to related nitrophenol and nitroanisole by nucleophilic displacement of the chloride with sodium hydroxide.
Polychlorinated biphenyls	$C_{12}H_{10-x}Cl_x$	Widely applied as dielectric fluids in transformers, capacitors and coolants. Also used as stabilizing additives in PVC coating of electrical wiring and electronic components and as plasticizers in paints and cements. Can be found as a component of lubricating oils, hydraulic fluids, sealants, oil-based paints, adhesives, and tapes.

Chlorinated organic compounds may enter the environment during their manufacture, processing and usage. Improper disposals and inappropriate use are the major entry routes of COCs to the environment. Accidents or spillage during transport also contribute to the unwanted release of these chemicals to the environment. The diagram in Figure 1 shows the distribution and frequency of COCs found as contaminants in the aquatic environment

resulting from pollution incidents [13]. Obviously, the compounds TCE and PCE are found to be widely distributed as water contaminants both in the U.S. and Germany. So it was not surprising when the U.S. Environmental Protection Agency (EPA) declared TCE and PCE as priority pollutants. Additionally, U.S. EPA had founded a program called 'Superfund' to clean-up contaminated sites and hazardous waste disposal sites that could continually contaminate soils and water bodies. As of the year 2008, there are 1,255 contaminated sites listed in the program which need remedial action [14].
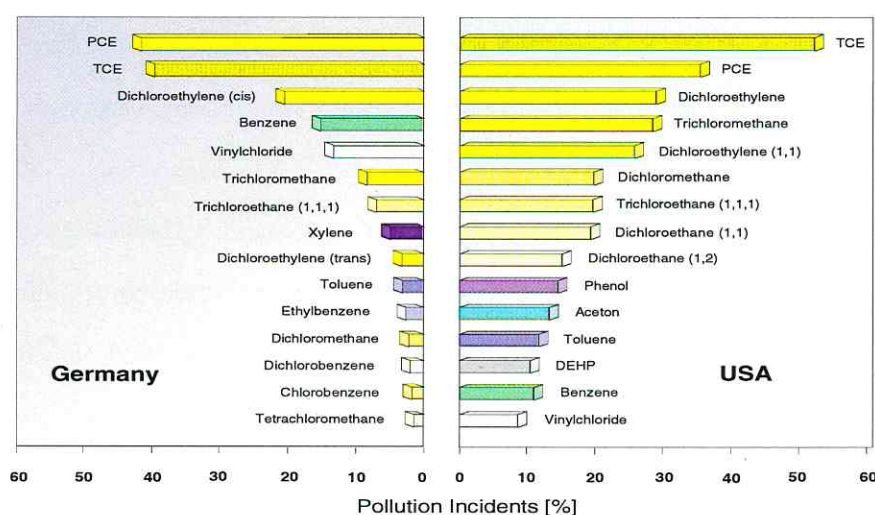
Figure 1: Frequency of chlorinated organic contaminants downstream from pollution incidents [Ref. 13].

Despite of the low water solubility of COCs significant and alarming amounts are found not only in surface water but as well as in the groundwater. In the U.S., for example, survey studies have shown that TCE, PCE, *cis-* and *trans-*DCE and trichloromethane are pollutants commonly found in groundwater samples [15-19]. In particular, TCE was detected to be highly present in the groundwater samples obtained from federal and state surveys. The concentration range of TCE in the collected samples varies from 6 to 635 μg L^{-1} [17]. The high concentrations were detected in the groundwater sources which are in the vicinity of

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landfills or waste disposal sites. Random U.S. survey studies had also shown that the concentration of *trans*-DCE in drinking water derived from groundwater amounted to 120 µg L^{-1} [19]. A rather high or even much higher concentration of COCs (in the range of mg L^{-1}) is found in the contaminated groundwater in Bitterfeld, Germany. Groundwater samples taken from monitoring wells showed that the major contaminants were a cocktail of chlorinated aliphatics (e.g. TCE, PCE, *cis*-DCE, tetrachloroethane) and chlorinated benzenes. Concentrations of these chemicals in groundwater samples were extremely high reaching up to 35 mg L^{-1} for TCE and 15 mg L^{-1} for PCE while measured maximum concentrations for 1,1,2,2-tetrachloroethane reached up to 80 mg L^{-1} [20-22]. It should be taken into account that in the era of pre- and post-war, Bitterfeld was a chemical industry centre and more than 100 years of chemical production in this area have paid their toll to the environment. Chemicals were mainly disposed in unused lignite mining pits and landfills. Through leaching these chemical wastes penetrate and reach the groundwater. This led to the heavy contamination of groundwater area of about 25 km^2 with a water volume of about 4 x 10^8 m^3. Environmental remediation of this contaminated site in Bitterfeld is being considered under the project SAFIRA (Sanierungsforschung in regional kontaminierten Aquiferen) in collaboration with Helmholtz Centre for Environmental Research - UFZ.

It should be noted with emphasis, that highly hydrophobic chlorinated compounds like the PCBs are strongly sorbed in soil and their leaching to groundwater is slow. Remediation of PCB-contaminated soil is a difficult task because PCBs can be transformed into the even more toxic dioxin and furane compounds under certain conditions, especially when treatment techniques like thermal desorption in air are employed. To avoid this problem, contaminated soils are washed with aqueous-based solutions, containing surfactants or co-solvents, to separate and release the polychlorinated aromatic compounds from the soil matrix [23-26]. On the other hand, soil washing generates secondary wastewater effluents containing PCBs which

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still need to be treated and detoxified. But PCBs brought into the liquid phase are much easier to be destroyed than when they are bound to the soil matrix.

1.2   *Palladium-catalyzed hydrodechlorination as remediation technique for COCs*

Due to the health and environmental impacts of COCs it is necessary to remediate groundwater and also to clean up wastewater effluents (e.g. effluents obtained from soil washing) which are heavily contaminated with COCs. From the chemical perspective, COCs can be treated by chemical oxidation and reduction. Chemical oxidation, unlike the reductive process, is a well-established technology which is capable of destroying a wide range of hazardous wastes. Among the choices of oxidizing agents, permanganate is regarded as having a high potential to be applied *in situ* for the removal of COCs. Some examples of COCs which successfully react with permanganate include TCE, PCE, isomers of DCE and vinyl chloride [27-29]. Fenton's reagent was also shown to oxidize chlorinated ethenes like TCE [30]. The major drawbacks of chemical oxidation as remediation technique for COCs are the non-selectivity of the reaction and the possible formation of byproducts which can be more toxic than the parent compound. An example of this is the oxidation of TCE with Fenton's reagent. When the reaction does not proceed to completion, byproduct like dichloroacetic acid ($Cl_2CHCOOH$) can be formed which is known to have higher toxicity than TCE itself [31-32].

A more promising alternative to remediate chlorinated contaminants is the reductive dechlorination using palladium-based catalysts [33-38]. This chemical reaction, also commonly termed as hydrodechlorination in the literature, involves the removal of chlorine where the C-Cl bond of the parent compound is replaced by a new C-H bond. Together with molecular hydrogen (H_2) or hydrogen donors like formic acid dissolved in the aqueous system, the chlorinated compounds are transformed to non-chlorinated hydrocarbons following the reaction $R\text{-}Cl + H_2 \xrightarrow{Pd} R\text{-}H + HCl$. The chlorinated compound TCE, for

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example, is ultimately transformed into ethane and hydrochloric acid as shown in Figure 2 (Eq. 1.2.1). In this case, the hydrogenation of the double bond also occurs. On the other hand, chlorobenzene is transformed into hydrochloric acid and benzene without further hydrogenation of the aromatic ring (Eq. 1.2.2). Obviously, benzene cannot be considered as a desired reaction product, because it has a high toxic potential as well. This case makes evident that although dechlorination is a selective reaction, it is not in every case the final solution.

The hydrodechlorination in the heterogeneous catalytic system occurs via the surface reaction on the catalyst between the hydrogen and the chlorinated compound. Both species are chemisorbed but do not compete for the same adsorption sites. The hydrogen is activated by dissociative adsorption at the catalyst surface and promotes the C-Cl bond cleavage of the chloroorganic substrate [39-41]. Liquid phase hydrodechlorination with palladium is a clean and direct process and the reaction takes place under ambient condition. Thus, hydrodechlorination is becoming popular in the area of pollution abatement. Such being the case, palladium-catalyzed hydrodechlorination has also become an important topic in environmental catalysis.
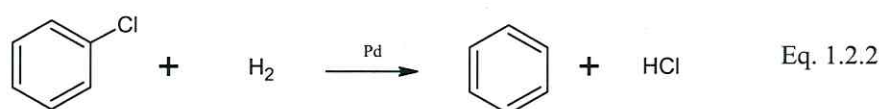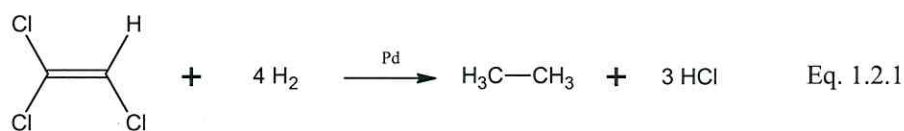
Figure 2: Catalytic reductive dechlorination of TCE and chlorobenzene with palladium catalyst.

It should be noted that zero-valent iron (ZVI) is also capable of reducing COCs via direct electron transfer following the reaction $R\text{-}Cl + Fe^0 + H_2O \rightarrow R\text{-}H + OH^- + Cl^- + Fe^{2+}$.

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The anaerobic corrosion of iron in water ($Fe^0 + 2\ H_2O \rightarrow Fe^{2+} + H_2 + 2\ OH^-$) additionally donates hydrogen. However, Fe^0 is usually not able to use molecular hydrogen for the hydrodechlorination of COCs [42-44]. Since iron is relatively cheap and an environmentally friendly element, it is a popular component of the so called 'permeable reactive barriers' which are applied *in situ* where the contaminant plume of COCs can then pass through [44]. Zero-valent iron, however, does not reduce chlorinated aromatic hydrocarbons. Therefore, the reductive dechlorination of chlorobenzene presented in Eq. 1.2.2 would not proceed using iron-based reagents. In addition, incomplete dechlorination may result in the accumulation of toxic byproducts which can be similarly problematic as the parent compounds. This includes, for example, the dechlorination of COCs like carbon tetrachloride and TCE with ZVI which generates byproducts like CH_2Cl_2, $CHCl_3$ and C_2H_3Cl. These are still chlorinated compounds. Whereas chloroform and VC are still further reducible with ZVI with a much lower rate, dichloromethane is a deadend product which needs an additional treatment. Another major disadvantage of remediation of COCs with iron metal is the consumption of iron during the anaerobic corrosion in water. In this case, the metal as the bulk reagent for reduction must be replaced after a certain time period.

On the contrary, numerous advantages are being offered by palladium-catalyzed hydrodechlorination of COCs. Firstly, it is effective for a wide range of contaminants which include chlorinated aliphatics as well as aromatics. The reaction is catalytic and COCs are dechlorinated at high reaction rates under mild conditions. Furthermore, it allows the re-use of the catalyst. Most importantly, dechlorination with palladium catalysts proceeds to completion and hardly yields partly dechlorinated toxic byproducts, unlike to iron-based dechlorination reactions. Palladium-based technology can also provide *in situ* treatment of chlorinated pollutants present in environmentally related water bodies, such as groundwater. This can be realized, for example, by digging a well bore unit consisting of palladium-based reactors where contaminated groundwater streams can pass through [45-48].

Among the evaluated palladium-based catalysts, palladium supported on γ-alumina (Pd/Al$_2$O$_3$) appears to show high catalytic performance in the reductive dechlorination. In general, high reaction rates with half-lives of only a few seconds are typically realized in fixed-bed reactors (i.e. employing 0.5 wt% Pd on alumina) under ideal conditions, for the dechlorination of chlorinated ethenes like TCE, PCE and VC [35, 37-38]. Similarly, chlorinated aromatics are rapidly reduced over Pd/Al$_2$O$_3$ [36-38, 50-51]. In addition to the high catalytic activity of Pd/Al$_2$O$_3$, the stability and the commercial availability of this catalyst makes it ideal for large-scale technical applications during groundwater remediation or treatment of wastewater. However, real water samples do not only contain the target pollutants but also a complex mixture of dissolved solutes which may affect the activity and stability of the catalyst. Therefore, palladium catalysts are sometimes modified to overcome the matrix effect and protect them from catalyst poisons which are intrinsic to real water samples. In such cases, palladium clusters are embedded in a hydrophobic membrane to make the catalyst resistant to dissolved ionic solutes in water [48, 52]. In this thesis work, the commercially available Pd/Al$_2$O$_3$ is employed as the main catalyst in all experimental studies. In addition, modified versions where palladium is either coated with a hydrophobic membrane or embedded in a zeolite were also employed to test their behaviour and their catalytic property under different experimental conditions.

1.3   Activity and performance of palladium-based catalysts

To be able to assess the performance of various palladium catalysts for the dechlorination of different types of chlorinated contaminants, the parameter specific catalyst activity ($A_{Pd,i}$) is employed [38]. This can be calculated according to Eq. 1.3.1:

$$A_{Pd,i} = \frac{V_{water}}{m_{Pd}\tau_{1/2}} \qquad \text{in } [L\ g^{-1}\ min^{-1}] \qquad \text{(Eq. 1.3.1)}$$

where V_{water} is the volume of contaminated water treated, m_{Pd} is the mass of palladium and $\tau_{1/2}$ is the half-life of the contaminant as obtained from its reaction kinetics. For chlorinated contaminants which react relatively slow, the half-life of the contaminants can be alternatively calculated using Eq. 1.3.2, assuming first-order kinetics:

$$\tau_{1/2} = \Delta t \cdot \frac{\ln 2}{\ln(c_{i,t1} / c_{i,t2})} \qquad \text{(Eq. 1.3.2)}$$

In this case, two data points are taken from the reaction curve. The concentrations of COCs ($c_{i,t1}/c_{i,t2}$) taken from two sampling times (t_1 and t_2) are noted. The time difference between the two sampling times is then considered as $\Delta t = t_2 - t_1$. Alternatively, the observed first-order rate coefficient (k_{obs}) obtained from the plotted reaction curve $-\ln(c_{i,t}/c_{i,0}) = f(t)$ can also be used to calculate the catalyst activity following Eq. 1.3.3:

$$A_{Pd,i} = k_{obs} / (\ln 2 \cdot c_{Pd}) \qquad \text{(Eq. 1.3.3)}$$

In general, the catalyst activity is calculated either from the conversion rates of COCs or from the rates of product formation. For low degree of conversion, catalyst activity is preferably calculated from the formation of dechlorinated product. As long as the dechlorination of COCs follows pseudo-first-order kinetics with respect to educt concentration, the calculated value of $A_{Pd,i}$ is equivalent to the second-order rate coefficient k'_i for the disappearance of COC i according to $k'_i = \ln 2 \cdot A_{Pd,i}$ with $dc_i/dt = - k'_i \cdot c_i \cdot c_{Pd}$.

Unlike to the commonly used parameter 'turnover frequency' (TOF) which represent the number of reactant molecules reacting per catalyst surface site per second, specific catalyst activity is mass-based and, therefore, allows to compare the activity of various catalyst systems with significantly different palladium dispersity under different experimental

conditions. Furthermore, palladium catalyst specific activity readily indicates the volume of contaminated water which can be treated by a certain amount of catalyst for a period of time, a significant criterion from technical and economical point of view.

The graph shown in Figure 3 depicts a typical example of the reaction kinetics of the hydrodechlorination of COCs using palladium catalyst. Based on the data, the liquid phase batch hydrodechlorination of the model compound chlorobenzene over Pd/Al$_2$O$_3$ shows first-order kinetics with respect to the concentration of chlorobenzene up to high conversion degree. The calculated catalyst activity for this reaction according to Eq. 1.3.1 delivered a value of A_{Pd} = 120 L g^{-1} min^{-1}. This also corresponds to a contaminant half-life of 8 min. Half-life in this context is considered as the time period in which 50% of the contaminant is removed.
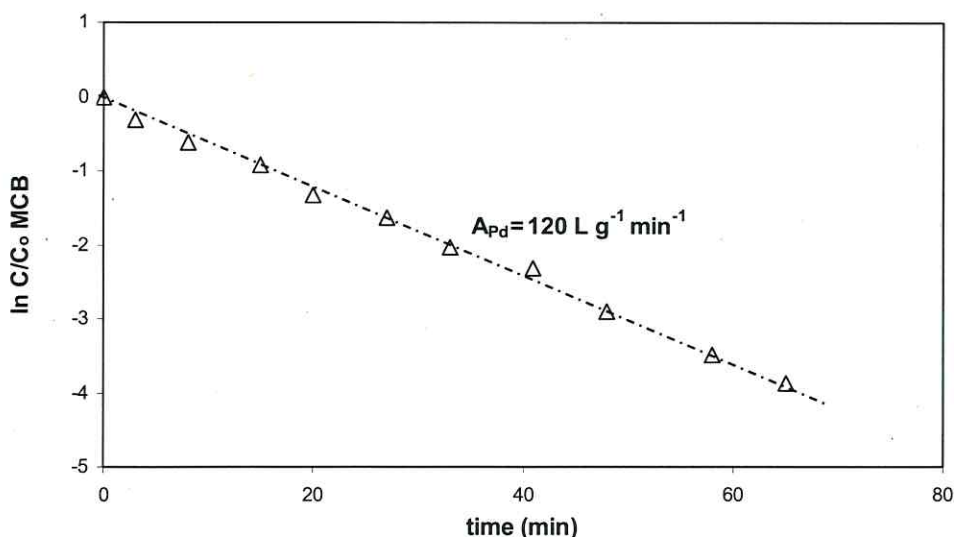
Figure 3:   Kinetics of the liquid phase batch hydrodechlorination of chlorobenzene (MCB) with Pd/Al$_2$O$_3$ (0.5 wt% Pd) conducted under ambient conditions (T = 22 ± 2 °C, p = 0.1 MPa). Applied concentrations: c_{cat} = 150 mg L^{-1}, $c_{0,MCB}$ = 20 mg L^{-1}. The data shown are from own experimental results.

A list of Pd/Al$_2$O$_3$ activities for the hydrodechlorination of various COCs, from simple aliphatics up to the chlorinated two-ring aromatics, is presented in Table 2. The activity data

show that the relative reaction rates of the tested chlorinated compounds differ from each other up to 7 orders of magnitude. The chlorinated ethenes generally show the highest reactivity for hydrodechlorination (e.g. A_{Pd} = 1180 L g^{-1} min^{-1} for vinyl chloride). On the other hand, the hydrodechlorination of chlorinated alkanes delivered moderately low catalyst activities. Chloroform, methylene chloride and 1,2-dichloroethane show extremely low reactivities. Chlorinated benzene as well as the chlorinated biphenyl are both highly reactive with A_{Pd} = 120-190 L g^{-1} min^{-1}. Surprisingly, the chlorinated naphthalene isomers showed significantly lower reactivities for reductive dechlorination as compared to the chlorinated benzenes. Obviously, catalytic hydrodechlorination of COCs seemed to be influenced by several parameters such as (i) the C-Cl bond strength, (ii) the absence or presence of a double bond close to the halogen substituent, (iii) the adsorption or the affinity of the COCs at the palladium surface, and (iv) steric effects. The interplay between these factors may finally determine the reaction pathway, and hence may enhance or retard the hydrodechlorination of COCs [37, 53].

It should be further noted that Table 2 also shows the wide range of chlorinated compounds accessible for dechlorination using palladium catalysts. The data on catalyst activity indicate that the chlorinated aromatics under study, although less reactive as the chlorinated ethenes, are still highly reactive. This is an important aspect to be considered since the alternative iron-based hydrodechlorination is not able to reduce these types of aromatic compounds. In addition, the palladium-catalyzed hydrodechlorination of COCs hardly generates partially dechlorinated intermediates. For example, the dechlorination of chlorinated methanes, ethanes, ethenes and chlorinated aromatics proceeds to the production of non-chlorinated hydrocarbon products in a single step. If a product is formed from partial dechlorination (as e.g. dichloromethane from chloroform), then it is mostly in small or trace amounts. For example, the byproduct methyl chloride from the hydrodechlorination of

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methylene chloride with Pd/Al$_2$O$_3$ was detected to be about 0.2 mol% of the desired product methane [37].

Table 2: Catalyst activity of Pd/Al$_2$O$_3$ (0.5 wt% Pd) for the liquid phase batch hydrodechlorination of various chlorinated organic compounds. Applied concentrations: c_{cat} = 10-100 mg L^{-1}, $c_{0,COC}$ = 1-10 mg L^{-1} and 20 mg L^{-1} for chlorobenzene. Data shown are from own experimental results and from Ref. [37].

Substance		Catalyst specific activity A_{Pd} = [L g^{-1} min^{-1}]
Tetrachloromethane	CCl$_4$	10
Chloroform	CHCl$_3$	0.8
Methylene chloride	CH$_2$Cl$_2$	1.5 x 10^{-3}
1,1,1,2-Tetrachloroethane	C$_2$H$_2$Cl$_4$	100
1,1,1-Trichloethane	C$_2$H$_3$Cl$_3$	15
1,1,2,2-Tetrachloroethane	C$_2$H$_2$Cl$_4$	3
1,2-Dichloroethane	C$_2$H$_4$Cl$_2$	3 x 10^{-4}
cis-1,2-Dichloroethene	C$_2$H$_2$Cl$_2$	670
trans-1,2Dichloroethene	C$_2$H$_2$Cl$_2$	670
Tetrachloroethene	C$_2$Cl$_4$	210
Trichloroethene	C$_2$HCl$_3$	420
1,1,-Dichloroethene	C$_2$H$_2$Cl$_2$	850
Vinyl chloride	C$_2$H$_3$Cl	1180
Chlorobenzene	C$_6$H$_5$Cl	120
2-Chlorobiphenyl	C$_{12}$H$_9$Cl	190
1-Chloronaphthalene	C$_{10}$H$_7$Cl	45
2-Chloronaphthalene	C$_{10}$H$_7$Cl	45

1.4 Deactivation and regeneration of palladium catalysts

Catalyst deactivation, that is, the loss of activity or selectivity over time, is inevitable and remains an important issue in palladium-catalyzed reaction processes. Different causes have been attributed to the deactivation of the noble metal catalyst and these include poisoning, fouling, crystallite growth and sintering, corrosion and leaching, coking by deposition of carbonaceous materials on catalyst surface or active sites, or modification at the

metal surface such as changes in valency [54-56]. These distinct types of deactivation mechanisms are commonly encountered in palladium-catalyzed reactions such as hydrogenation and thermocatalytic oxidation. In gas phase hydrodechlorination reactions, the poisoning of palladium catalysts is also strongly accounted to the formation of carbonaceous deposits and sintering of the active phase [57-58]. The stoichiometric byproduct HCl, which is inherently produced during the hydrodechlorination, was also found to promote coke residues on the catalyst. This is because HCl contributes to the formation of acid sites on the catalysts favourable for coke formation. In addition, HCl contributes to catalyst deactivation due to the so-called chloride poisoning. In the particular case of aqueous phase hydrodechlorination over palladium catalysts, more relevant causes of deactivation during field-scale applications are pore plugging by precipitation of salts and particulate matter, biofouling and surface poisoning from sulfur-containing compounds (e.g. H_2S, SO_3^{-2}, and organosulfides) present in real waters [22, 38, 59-60].

The biogenic input of sulfur compounds (especially of reduced sulfur species) in natural waters makes them ubiquitous poisons for palladium catalysts during field applications. For example, the prevalent presence of hydrogen sulfide (H_2S and HS^-) in aquatic systems results from the anaerobic respiration of sulfate-reducing bacteria. On the other hand, sulfite (SO_3^{2-}) is produced as an intermediate during the bacterial conversion of sulfides to sulfate and as a result of the disproportionation of sulfur species. These are endogenous microbial processes occurring freely in nature, but being initiated or accelerated by the reductants (H_2 or $HCOOH$) necessary for hydrodechlorination. It should be noted that organosulfur compounds are as strong poisons for palladium as the inorganic sulfides and they too, are endogenously produced in the aquatic environment [61-65]. The presence of volatile organosulfur compounds such as mercaptans and disulfides in the aquatic environment was attributed to the bacterial decomposition of S-containing amino acids and the methylation of H_2S present in the waters. Similarly, H_2S interaction with organic matter is

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a potential pathway for the production of carbon disulfide (CS_2) under natural conditions though anthropogenic sources may be more pronounced. In the work of Kopinke et al. [22, 38] it was shown that the application of Pd/Al_2O_3 as a fixed-bed reactor for groundwater remediation in a pilot test plant in Bitterfeld, Germany was deactivated not only by inorganic sulfides but also by organosulfur compounds such as dimethyldisulfide.

Sulfur species, as catalyst poison, are known to have a strong affinity for noble metals like palladium. They are chemisorbed and form strong covalent bonds with the palladium atom [66-69]. It is important to state, however, that dissolved sulfate is a sulfur species which has been proved to be harmless for palladium. Theoretical mechanistic studies have shown that molecular adsorption of catalyst poisons like H_2S is a non-activated as well as a facile process [67]. This means, that even at ambient temperature, molecularly sorbed H_2S dissociates to give the sulfhydryl SH and H on the surface of the palladium [$H_2S_{(ad)} \rightarrow SH_{(ad)} + H_{(ad)}$]. The sulfhydryl in turn can undergo further dissociation yielding sulfide adsorbed on the palladium surface [$SH_{(ad)} \rightarrow S_{(ad)} + H_{(ad)}$]. The formation of covalent bond between S and palladium results from the substantial overlap of sulfur p-states with the metal surface d-bond. The observed poisoning of palladium by sulfur species may come from the combination of structural and electronic effects [67-68]. Structural effect involves the physical blocking of adsorption sites on the catalyst. The formation of sulfur covered metal surface may block the adsorption of reactants to the catalyst surface, if not, then may at least block the access of reactants to each other and finally prevent or slow down the surface diffusion of the adsorbed reactants. On the other hand, electronic effects arising from the chemical binding of sulfur to palladium may modify the surface charge and reduce the electron density of the d-states of palladium. Consequently, this will lead to the restructuring of the surface and finally lead to the changes in the catalytic properties of the catalyst system.

Reduced sulfur compounds such as H_2S and the like are strong chemisorbers and the covalent bond they form with palladium is strong and difficult to break. Hence, catalyst

deactivation and its possible regeneration remains a challenge. Even so, a more challenging endeavour is to prevent or minimize the deactivation of the catalyst systems during application. Preventive strategies may include the tailoring of the catalyst to improve its stability and resistance to poisoning. Tailored catalysts like palladium on zeolite (Pd/zeolite) and palladium embedded in a hydrophobic membrane like poly(dimethylsiloxane) (Pd/PDMS) were engineered and optimized so that they are more resistant against dissolved solutes and ionic poisons [47-48, 52]. But unfortunately, non-ionic H_2S was found to easily penetrate the membrane of the fabricated catalyst Pd/PDMS. An alternative method to tailor the catalyst is by the addition of another metal to the monometallic palladium catalyst. Alloying of palladium with platinum to produce bimetallic catalysts was found to improve its resistance to sulfur adsorption. This was achieved when the bimetallic Pd-Pt showed higher tolerance to deactivation under the presence of thiophene [70]. Tailoring or modifying catalyst properties may definitely bring out improvement in the stability of the catalysts. But this does not totally protect the catalyst from sulfide poisoning but rather may only decrease its rate of deactivation. Hence, for a long-term perspective a more practical preventive strategy may be sought for to protect the noble metal from sulfide poisoning.

Nonetheless, in the event of catalyst deactivation, may it be accidental or uncontrolled, it is advantageous to have a simple procedure which restores the catalyst activity. In gas phase reactions sulfide-poisoned palladium catalysts are, in principle, regenerated using high temperature treatment with hydrogen [71-74]. This process is, however, energy inefficient and unsuitable for palladium systems used in aqueous phase hydrodechlorination under ambient conditions. So far, the only study which has shown relative success in regenerating sulfide-fouled palladium in the aqueous phase is by oxidative treatment with hypochlorite. This was first introduced by Lowry and Reinhard [60, 75], wherein the catalyst Pd/Al_2O_3 in a column reactor poisoned by HS^- and SO_3^{2-} was periodically regenerated with a dilute solution of hypochlorite. Complementary to this work, Chaplin et al. [76] investigated the pH dependence

of the efficiency of catalyst regeneration using hypochlorite. It was shown that the catalyst Pd/Al$_2$O$_3$ can be best regenerated at near-neutral pH (~ 7.8) rather than at low or high pH values. This was accounted to the uncharged catalyst under neutral pH condition allowing the OCl⁻ ions to approach the sulfide-poisoned site. Successful regeneration can then be achieved when sulfides strongly sorbed on the palladium surface are oxidized to sulfate which is then released to the water phase. Restoration of the palladium activity by hypochlorite treatment seemed to show success. But the major drawbacks of this treatment were that it requires high concentrations of the regenerant and long regeneration times, if not multiple regeneration cycles. The effective concentration of hypochlorite used in rejuvenating sulfide-poisoned catalysts, as mentioned from the two studies, range from 20 to 56 mM NaOCl. The regeneration time usually takes from 2 hours to almost a day. Under optimal conditions, the activity of the strongly-fouled catalyst was restored to about 29% of its original value [76]. In this case, full recovery of catalyst performance was hardly achievable. In addition, it should also be taken into account that hypochlorite is a chlorinating agent and that it can cause new formation of COCs. Therefore, additional care must be taken during its application as regenerant.

1.5   *Aims and objectives of this thesis*

As has been shown and described in the earlier discussion, palladium-catalyzed hydrodechlorination carries a high potential as an alternative remediation technique for treating chlorinated pollutants. However, the high sensitivity of palladium towards poisoning and deactivation induced by reduced sulfur species limits and hinders its full environmental application.

The first principal aim of this thesis is, therefore, to maintain the palladium catalyst stable against poisoning and prolong or maintain its catalytic activity under environmental condition. This can be achieved, for example, by coating the palladium catalyst with a

hydrophobic membrane to exclude the unwanted dissolved solutes and potential catalyst poisons inherent to real water samples. Coating of the catalyst brings out improvement in its stability, but does not totally protect the catalyst from sulfide poisoning. This may only results in the decrease of its rate of deactivation. Hence, a more practical preventive strategy is developed to protect the noble metal from sulfide species. In industrial processes, it is commonly encountered that when the feed contains catalyst poisons appropriate pretreatment is conducted to remove these critical constituents detrimental to the catalyst. In this thesis, a similar approach is undertaken by which the water matrix is freed from sulfides before remediation with palladium is conducted. Hence, in the absence of catalyst poisons the desired reductive dechlorination of COCs on palladium can successfully take place.

Nevertheless, in the inevitable event of catalyst poisoning an efficient regenerative measure would be highly essential. Since palladium belongs to the noble metals which are rare and costly, it is far more economical to restore catalyst performance than to dispose deactivated catalysts. Therefore, the second principal aim of this thesis is to develop an alternative regenerative measure which can re-activate the catalyst when fouled by sulfides. Furthermore, this regenerative measure is optimized so that high regeneration efficiency is realized under ambient conditions.

COCs as pollutants are, however, not only found in groundwaters. In the case of highly hydrophobic COCs like the PCBs, they are mostly found as contaminants in the soil or sediment matrices. PCBs can be subjected to hydrodechlorination after they are extracted into the aqueous phase (i.e. by soil washing). Hence, this thesis further aims to investigate the possible applicability of palladium for the hydrodechlorination of PCBs in soil washing effluents. These effluents, however, exhibit complex matrix effects. This is because they contain not only the target pollutants but also natural organic matter (NOM) and additives like surfactants and co-solvents which are typically applied in soil washing procedures. Therefore, matrix effects caused by surfactants, co-solvents and soil co-extractants (e.g. dissolved

organic matter) on the palladium-catalyzed hydrodechlorination are investigated. This can then evaluate and assess the suitability of palladium for treating wastewater effluents obtained from soil washing.

1.6   References

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2 Overview of the Following Manuscripts

The first manuscript presented in this thesis, which is entitled "Permanganate Oxidation of Sulfur Compounds to Prevent Poisoning of Pd Catalysts in Water Treatment Processes", deals with an experimental approach which aims to prevent the sulfide-induced poisoning of palladium catalysts (e.g. Pd/Al_2O_3). This is a preventive strategy of protecting the catalyst from deactivation whereby sulfides, as potential catalyst poisons, are removed from the water before the desired hydrodechlorination reaction is conducted. To obtain such conditions, oxidative water pretreatment using potassium permanganate is carried out. In batch experimental studies, deionized water was first artificially contaminated with various sulfur compounds such as the inorganic sulfides (H_2S, HS^-, S^{-2}), sulfite (SO_3^{-2}) and organosulfur compounds such as thiophene, carbon disulfide, mercaptan and dimethyldisulfide. Control experiments have shown that complete and irreversible deactivation of the catalyst was immediately induced by the presence of sulfur species in the aqueous bulk phase. The sulfide-contaminated water was treated with permanganate to oxidize and remove the catalyst poison. The pretreated water was then used as the reaction medium for hydrodechlorination. The resulting catalyst activity of Pd/Al_2O_3 in pretreated water was similar to that obtained in clean deionized water. This result reflects the successful removal of sulfides and subsequently prevents the sulfide-induced fouling of the catalyst. It should be noted, however, that the presence of residual permanganate (that is, permanganate which was not consumed during the pretreatment procedure) exhibits an inhibitory effect on the palladium-catalyzed hydrodechlorination. This may possibly results from the competing reaction of permanganate reduction for the activated hydrogen on the palladium surface. Interestingly, this inhibitory effect was observed to be temporary. At extended reaction times dechlorination of COCs takes place again. Further experimental studies have shown that below a certain threshold concentration of about 0.08 mM, permanganate does not inhibit the hydrodechlorination with Pd/Al_2O_3 anymore. The inhibitory effect of permanganate can be

avoided by adjusting the concentration to this tolerable threshold level or by quenching it with hydrazine, which can additionally act as a hydrogen donor for the dechlorination reaction. While excess permanganate inhibits the desired reaction (although only temporarily), its steady presence in water may offer some advantages. Permanganate is known as a biocide and it can prevent undesired microbial activities so that *in situ* production of sulfides and biofouling of the catalyst bed in H_2-fed systems can be prevented. Therefore, additional catalyst systems such as palladium on Y-type zeolite (Pd/zeolite), palladium embedded in a non-porous PDMS membrane (Pd/PDMS) and palladium coated with a silicone polymer (SE30/Pd/Al_2O_3) were tested and showed higher stability and tolerance against permanganate. For such a stable catalyst system, permanganate can then be utilized simultaneously as a selective preoxidant against catalyst poisons and a biocide without inhibiting the high catalytic activity of palladium for the hydrodechlorination of COCs.

The second manuscript entitled "Sulfide-induced Deactivation of Pd/Al_2O_3 as Hydrodechlorination Catalyst and its Oxidative Regeneration with Permanganate", continually adresses the problem of sulfide-induced poisoning of palladium catalysts. Under this section, a regenerative approach is presented in which sulfide-deactivated catalysts are re-activated back to their original performance. At first, experimental batch studies were conducted to assess the stability of Pd/Al_2O_3 in clean water and its deactivation behaviour in the presence of sulfides. Parameters such as the number of reaction cycles, catalyst ageing and pH conditions were varied to evaluate their influence on the catalyst's stability and performance. Primary results have shown that in clean water, the Pd/Al_2O_3 maintains its inherent stability despite of the number of hydrodechlorination reaction cycles conducted on the same catalyst under different pH conditions. Moreover, long standing of the catalyst in the reaction medium (catalyst ageing) under various pH conditions did not appear to dominantly influence the catalyst stability and activity. The addition of hydrogen sulfide to the catalyst suspension resulted in the partial or complete poisoning of the catalyst, depending on the S to

Pd$_{surface}$ atoms ratio. The impact of the pH value on the poisoning effect of sulfide was not significant but nevertheless showed that Pd/Al$_2$O$_3$ tends to be more resistant to poisoning under acidic conditions. Exposure of the catalyst to sulfide at higher doses (e.g. 14 μM sulfide corresponding to S : Pd$_{surface}$ = 12 atoms per atom) resulted in the fast and complete deactivation of the catalyst, regardless of the applied pH value. The completely deactivated catalyst was successfully regenerated by treatment with potassium permanganate. It should be noted that the catalyst Pd/Al$_2$O$_3$, the catalyst poison sulfide and the regenerant permanganate are all susceptible to pH changes. Thus, parameters such as pH value, oxidant concentration and regeneration time were varied to assess the optimum condition for catalyst regeneration. Results from batch regeneration experiments showed that permanganate was most efficient when oxidative regeneration was conducted at low pH value (i.e. pH 3). Under such condition, short regeneration times of 10-30 min were sufficient to completely restore the catalytic performance of Pd/Al$_2$O$_3$.

The third manuscript "Pd-catalyzed Hydrodechlorination of Chlorinated Aromatics in Contaminated Waters: Effects of Surfactants, Organic Matter and Catalyst Protection by Silicone Coating", in contrast to the two manuscripts presented above, rather extends and explores the possible wider applicability of palladium-based catalysts for the hydrodechlorination of COCs present in a complex wastewater matrix. It should be taken into account that COCs are not only found as pollutants in water bodies but also in the soil. This is especially true for highly hydrophobic chlorinated compounds like PCBs, which tend to be strongly sorbed to the soil matrix. In order to make PCBs available for hydrodechlorination, they can be brought into the liquid phase by soil washing using co-solvent or surfactant-based solutions. The PCBs can then be detoxified by reductive dechlorination using palladium catalysts. Therefore, the experimental part of this manuscript consists of evaluating the activity of palladium (e.g. Pd/Al$_2$O$_3$) for the reductive dechlorination of a hydrophobic substrate like 3-chlorobiphenyl. The matrix effect of additives like co-solvents and surfactants

and the effect of soil co-extractants on the activity of the catalyst for PCBs dechlorination were additionally investigated. In general, results showed that Pd/Al_2O_3 can efficiently catalyze the reductive dechlorination of the test substrate 3-chlorobiphenyl. The effects of surfactants on the palladium-catalyzed reaction depend on the type and concentration of the amphiphiles in the reaction medium. The presence of co-solvents in the solution matrix did not significantly affect the catalyst activity while the hydrodechlorination of 3-chlorobiphenyl in a soil slurry supernatant resulted in a significant deactivation of the catalyst. Nevertheless, the coating of the catalyst with a polymer silicone had protected the catalyst from the background matrix as well as from ionic catalyst poisons like bisulfite.

3 Permanganate Oxidation of Sulfur Compounds to Prevent Poisoning of Pd Catalysts in Water Treatment Processes

Dalia Angeles-Wedler, Katrin Mackenzie & Frank-Dieter Kopinke

Abstract

The practical application of palladium-catalyzed water treatment processes is impeded by catalyst poisoning by reduced sulfur compounds (RSCs). In this paper, the potential of permanganate as selective oxidant for the removal of microbially generated RSCs in water and as regeneration agent for S-poisoned catalysts is evaluated. Hydrodechlorination using Pd/Al_2O_3 was carried out as probe reaction in permanganate-pretreated water. The activity of the palladium catalysts in the successfully pretreated reaction medium was similar to that in deionized water. The catalyst showed no deactivation behavior in the presence of permanganate at a concentration level ≤ 0.07 mM. With a residual oxidant concentration of ≥ 0.08 mM, a significant but temporary inhibition of the catalytic dechlorination was observed. Unprotected Pd/Al_2O_3 which had been completely poisoned by sulfide was re-activated by a combined treatment with permanganate and hydrazine. However, the anthropogenic water pollutants thiophene and carbon disulfide were resistant against permanganate. Together with the preoxidation of catalyst poisons, hydrophobic protection of the catalysts was studied. Pd/zeolite and various hydrophobically coated catalysts showed higher stability against ionic poisons and permanganate than the uncoated catalyst. By means of combination of oxidative water pretreatment and hydrophobic catalyst protection we provide a new tool to harness the potential of palladium-catalyzed hydrodehalogenation for treatment of real waters.

Introduction

Palladium-catalyzed hydrodechlorination (HDC) is a promising option for the treatment of water contaminated with chlorinated organic compounds (COCs). In comparison with oxidation, reduction of COCs offers a more selective transformation of the contaminants to less or non-harmful and more readily biodegradable substances. The wide range of accessible reactants, together with the outstandingly high catalytic activity under mild reaction conditions, encourages the application of palladium catalysts for groundwater remediation (*1-7*). However, only a few working groups have evaluated the field performance of palladium catalyst systems (*8-11*). All of these remediation studies in the field have suffered from deactivation of the palladium systems during the course of the operation.

Various causes have been suggested for palladium catalyst deactivation and poisoning, including metal sintering, chloride poisoning and strong interactions with sulfur compounds (*12-20*). In the particular case of groundwater as the reaction medium, the most relevant causes of catalyst deactivation are biofouling, strong poisoning from traces of RSCs, blockage by deposition of particulate matter and adsorption of natural organic matter, which may also contain reduced sulfur groups (*21*). Biogenic input of reduced inorganic and organosulfur compounds to the environment makes them ubiquitous poisons for palladium catalysts during field applications. The prevalence of H_2S in aquatic ecosystems results from the anaerobic bacterial respiration, while sulfite is produced as intermediate during the bacterial conversion of sulfides to sulfate and as a result of the disproportionation of sulfur species. Additionally, endogenous production of volatile organosulfur compounds such as mercaptans and disulfides is attributed to the bacterial decomposition of S-containing amino acids and the methylation of H_2S in the aqueous environment (*22-26*). Similarly, H_2S interaction with organic matter was also considered as a potential pathway of carbon disulfide production under natural conditions. However, contributions from anthropogenic sources may also occur. In the work of Kopinke et al. (*27*) it was assumed that in a fixed-bed reactor under field conditions in

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Bitterfeld, Germany the applied Pd/Al_2O_3 catalyst was steadily deactivated not only by H_2S but also by volatile organic sulfur compounds such as dimethyldisulfide.

By its very nature the HDC reaction requires reductants such as H_2 or HCOOH (7). These act as electron donors for the intended catalytic reduction as well as for the undesired microbiological sulfate reduction yielding H_2S. This ambiguous role of reductants cannot be avoided. The addition of electron acceptors such as nitrate, molecular oxygen or hydrogen peroxide (in low concentrations) may help to prevent the undesired microbiological sulfate reduction in the presence of H_2. However, they can be utilized by the microorganisms after relatively short adaptation periods, leading to their fast consumption and to extensive biofouling of the catalyst bed (28). This is the area of conflict that the environmental engineer is faced with when treating contaminated and natural waters.

Despite the practical significance of maintaining a stable and poison-resistant palladium catalyst for water treatment, only a few studies have tried to either protect the catalyst from deactivation or to regenerate the catalyst after loss of activity. For catalyst protection, palladium clusters have been embedded in hydrophobic zeolites as carrier (29) or hydrophobic membranes (11). However, such embedment did not provide sufficient protection against non-ionic sulfides. Some success in prolonging the catalyst lifetime was achieved by frequent flushing with oxidizing agents, such as H_2O_2 or hypochlorite, in order to prevent the growth of sulfate-reducing bacteria (10). But this allowed only a relatively low dechlorination rate to be maintained. Alternatively, sulfur-poisoned palladium catalysts were subjected to flushing with sodium hypochlorite solution for oxidative regeneration (30-31). Such methods may be partially successful but they are not efficient enough to maintain or revive catalyst performance. In addition, hypochlorite is not an environmentally friendly agent and can cause re-chlorination of organic water constituents.

In the present study, the potential of permanganate as an oxidative protective agent for palladium catalysts was investigated. To the best of our knowledge, this concept has never

been described before in the literature: understandably, because the idea of adding a strong oxidant such as permanganate as a co-reactant to a reduction process is not obvious. The concept aims towards a preventive strategy whereby permanganate is used in a preoxidation treatment for the removal of sulfur species in water prior to catalyst contact as well as towards the use of permanganate as a catalyst regeneration agent. Typical inorganic and organic RSCs frequently found in contaminated groundwater were employed as probe substances. The influences of permanganate and its reduction products on the dechlorination process are evaluated in this context.

Materials and Methods

Chemicals

Except where otherwise stated, all chemicals were purchased from Merck or Sigma-Aldrich (Germany) with ≥ 98 % purity and used without further purification. The following catalysts were tested:

i)   A commercially available egg-shell palladium on γ-Al_2O_3 with 0.5 wt% Pd (G-133 D purchased from Commercia, Germany, with a BET surface area of 160 m^2 g^{-1}). The granular catalyst was crushed and sieved. The fraction 25-63 μm with a measured palladium content of 0.51 wt% (determined by EDXRF analysis) was applied in the batch experiments. This catalyst will be referred to as Pd/Al_2O_3.

ii) Pd/Al_2O_3 coated with 19 wt% of a silicone polymer (SE30, methyl silicone, GC grade, Merck) forming a $SE30/Pd/Al_2O_3$ catalyst with 0.42 wt% Pd. The coating with SE30 was carried out as an impregnation process. The catalyst particles (Pd/Al_2O_3 sieve fraction 63-125 μm) were suspended in a hexane-SE30 mixture (20 : 1) and heated under reflux for 2 h. The solvent was then slowly removed from the catalyst grains in a rotary evaporator, whereby the silicone polymer entered into the alumina pores and

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partially filled them. Finally, a non-adhesive catalyst powder was obtained, referred to as SE30/Pd/Al$_2$O$_3$.

iii) Palladium clusters embedded in a poly(dimethylsiloxane) foil (10 wt% Pd in PDMS, thickness 200 μm) which was coated with thin palladium-free PDMS layers on both sides. The triple-layered foil forms a membrane with a mean palladium content of 5.6 wt% and a total membrane thickness of 330 μm. Preparation and characterization procedures are described in (11). This catalyst will be referred to as Pd/PDMS.

iv) Pd/zeolite catalyst (0.5 wt% Pd, wet impregnation) with a hydrophobic Y-type zeolite carrier with a critical pore diameter of 0.74 nm and a Si/Al-ratio of 200. Preparation procedures and characterization of the catalyst are described in (29).

Prior to use in HDC tests, the palladium catalysts were preconditioned by purging the catalyst suspension in water with H$_2$ for 1 h.

Preoxidation of sulfur-rich water with potassium permanganate

All oxidation and HDC reactions were conducted as batch experiments using 250 mL amber screw-cap bottles equipped with Mininert® valves. Stock solutions of RSCs (Na$_2$S, Na$_2$SO$_3$, dimethyldisulfide, thiophene, carbon disulfide, n-butylmercaptan) were prepared by dissolving appropriate amounts of each substance in distilled water. For the preoxidation procedure, the bottle containing 200 mL deionized water was purged with helium in order to strip off dissolved oxygen. A defined volume of the RSC stock solution was added to the bottle in order to give a 5 mg L^{-1} contamination of the RSC under study. In each case, the amount of KMnO$_4$ theoretically necessary for total oxidation to CO$_2$ and SO$_4^{-2}$ was then added from a 0.1 M stock solution. This mixture was allowed to react for various times, ranging from a few minutes up to 12 h. The pretreated water was then spiked with chlorobenzene (MCB) and used as reaction solution in HDC tests.

Catalyst activity in pretreated water

To test the effectiveness of the water pretreatment, a methanolic MCB stock solution and the preactivated Pd/Al_2O_3 catalyst as aqueous slurry were added to the pretreated water prepared according to the procedure described above. The final concentrations of MCB and palladium in the bottle were typically 20 and 0.75 mg L^{-1}, respectively. The 50 mL headspace above the aqueous suspension was filled with H_2 in order to provide excess reductant. The reaction bottle was then shaken (180 rpm) throughout the reaction time (T = 22 ± 2 °C, p = 0.1 MPa). Its reaction kinetics was monitored through educt disappearance (MCB) and/or product formation (benzene) via headspace analysis using a GC-MS QP2010 (Shimadzu).

Influence of potassium permanganate on the catalytic system

The influence of $KMnO_4$ on Pd/Al_2O_3 and hydrophobically protected palladium catalysts was investigated by conducting HDC experiments in the presence of various concentrations of $KMnO_4$ freshly spiked into the batch system. The change in the course of running dechlorination experiments due to the addition of permanganate was noted. For the measurement of permanganate consumption, 1 mL aliquots were taken from the reaction mixture at appropriate time intervals and the MnO_4^--specific absorbance at 545 nm ($\varepsilon_{545} \approx 2$ mM^{-1} cm^{-1}) was measured using a Spekol 1200 UV-vis spectrophotometer (Analytik Jena, Germany). Due to a broad absorbance of the MnO_2 precipitate which is formed as reduction product, the E_{545} value has to be corrected for a variable background (e.g. $E_{545} - E_{600}$).

Results and discussion

The specific catalyst activity $A_{Pd,i}$ for palladium in the HDC of a reactant i is used as a descriptor for the catalyst performance. It is calculated according to $A_{Pd,i} = V_{water} / (m_{Pd} \cdot \tau_{1/2})$ [L g^{-1} min^{-1}] where V_{water} is the volume of treated water, m_{Pd} is the mass of palladium metal

and $\tau_{1/2}$ is the half-life of the probe compound as obtained from its disappearance kinetics. The numerical value for $A_{Pd,i}$ is equivalent to a first-order rate coefficient k_{obs} [s^{-1}] for the disappearance kinetics according to $k_{obs} = \ln 2 \cdot A_{Pd,i} \cdot c_{Pd}$ (32). In case of significant deviations of the observed kinetics from a first-order with respect to the COC, $A_{Pd,i}$ is still defined based on $\tau_{1/2}$, whereas k_{obs} is not. In pure water the HDC of MCB ($c_0 = 20$ mg L^{-1}) using Pd/Al$_2$O$_3$ ($c_{0,Pd} = 0.75$ mg L^{-1}) delivered catalyst activities in the range of 150 to 200 L g^{-1} min^{-1}. Usually, the HDC follows first-order kinetics with respect to MCB.

The expected poisoning effect of the applied RSCs at pH 7 (H$_2$S, HSO$_3^-$, Me-S-S-Me, CS$_2$, Bu-SH, thiophene) on Pd/Al$_2$O$_3$ was found in all cases. Overnight contact of the catalysts with an excess of sulfur species (S : Pd = 8...20 moles per mole) led to complete and permanent poisoning. The mechanism of catalyst poisoning probably includes the formation of strong Pd-S bonds, thus blocking the catalytically active sites and increasing the diffusion barrier for hydrogen by adlayers of S-species (33-35). Regeneration of heavily sulfide-poisoned palladium catalysts using hypochlorite as an oxidant is a difficult procedure with uncertain results (30-31). This procedure is intended to be made redundant by our approach to circumvent catalyst poisoning in the first place.

Preoxidation of the RSCs with permanganate prior to HDC may prevent catalyst deactivation if their oxidation proceeds up to SO$_4^{2-}$. It is known that sulfate is harmless for the palladium catalyst (21). In order to assess the effectiveness of this method, the HDC of MCB with Pd/Al$_2$O$_3$ was carried out in the pretreated water samples. Results of these experiments are shown in Figure 1. The initial inhibition of the dechlorination reaction is a consequence of the residual permanganate which was not consumed during the pretreatment procedure. The addition of hydrazine (0.5 mM) quenches the surplus of permanganate instantaneously so that the dechlorination of MCB proceeded immediately, thereafter delivering a catalyst activity similar to the initial catalyst activity in clean deionized water. Permanganate inhibits the HDC only temporarily. This behavior also confirms that no intermediates and oxidation byproducts

are generated which could cause similar poisoning of the catalyst. Surprisingly, manganese dioxide as reduction product of permanganate did not exhibit any pronounced deactivating effect on Pd/Al$_2$O$_3$. A similar preoxidation efficiency was achieved with much shorter pretreatment times (t ~ 2 min, c$_{KMnO4}$ = 0.5 mM) especially for sulfide-contaminated water. After this preoxidation procedure and quenching of the residual oxidant with hydrazine (0.5 mM) the Pd/Al$_2$O$_3$ catalyst exposed its full activity. This demonstrates that the oxidation of most RSCs is a very fast reaction.
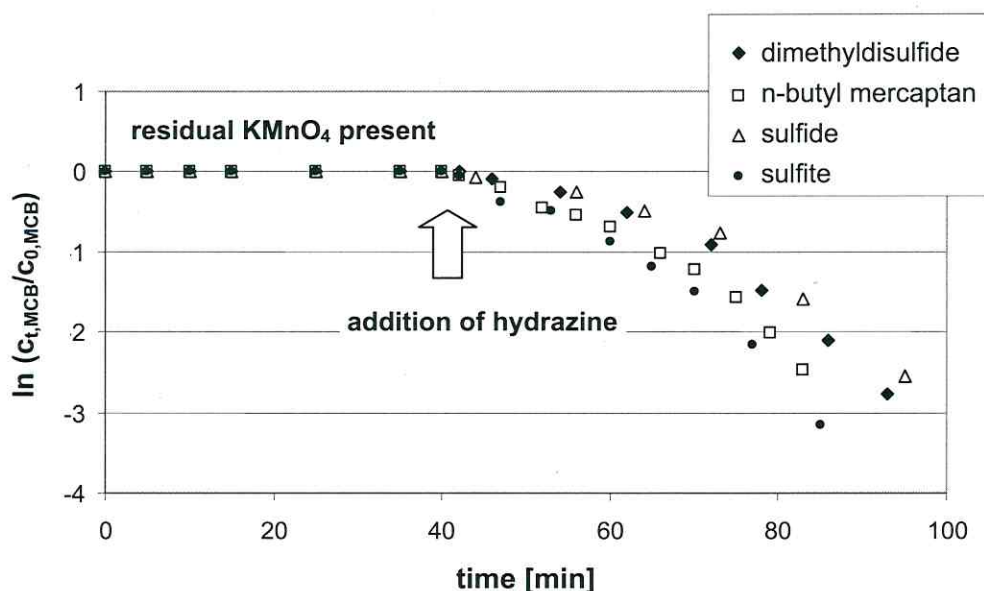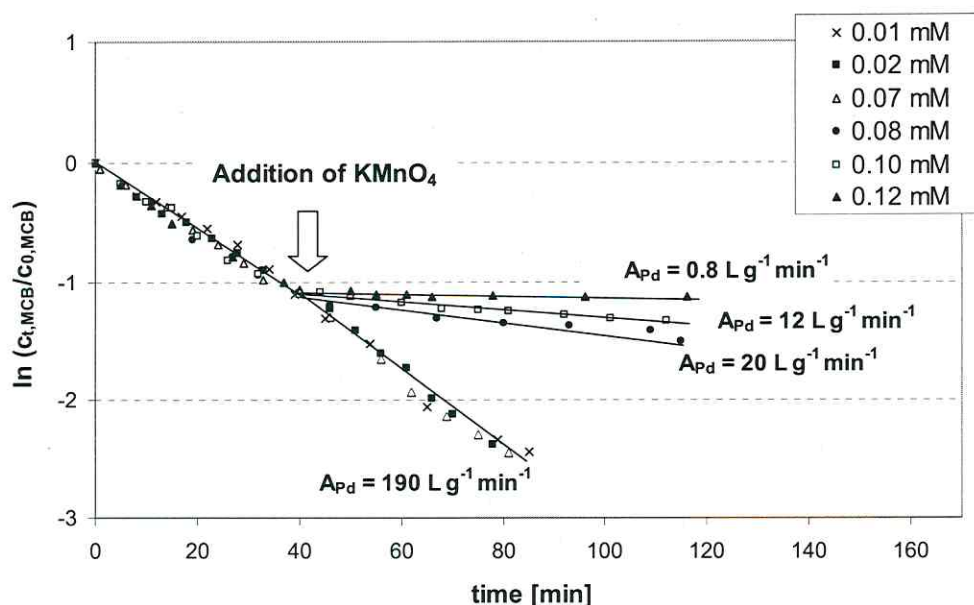

Figure 1: Hydrodechlorination of chlorobenzene over Pd/Al$_2$O$_3$ in permanganate-treated water samples that were contaminated with RSCs, demonstrating the inhibitory effect of excess residual permanganate on the catalyst after RSC oxidation (S : Pd = 8...20 moles per mol, c$_{0,MCB}$ = 20 mg L^{-1}, c$_{Pd}$ = 0.75 mg L^{-1}, c$_{0,RSC}$ = 5 mg L^{-1}, c$_{0,KMnO4}$ = 0.6 to 2.7 mM).

The reaction curves for catalysts contaminated with thiophene and carbon disulfide are not shown in Figure 1 because the oxidation behavior of these compounds differs from that of the other RSCs. Thiophene and carbon disulfide were resistant against permanganate. Thus, permanganate pretreatment could neither prevent catalyst poisoning nor regenerate the

S-poisoned catalyst samples. However, when considering microbial sulfate reduction under natural conditions HS^-/H_2S would be the dominant species produced, as well as mercaptans and organic disulfides. Poisoning by thiophene and carbon disulfide is unlikely to occur unless there is an additional contamination from anthropogenic sources.

The application of permanganate as a preoxidant for the removal of RSCs may also serve another purpose: as a biocide for sulfate-reducing bacteria. Permanganate is an effective biocide which may be even more appropriate than biocompatible electron acceptors such as oxygen or nitrate for long-term inhibition of undesired microbiological activities in the system. It is known from previous work that biological activity in H_2-fed systems can be responsible for the *in situ* production of H_2S which subsequently leads to poisoning of palladium catalysts (*27, 31*). Thus, a steady presence of residual permanganate in the water would be advantageous for the suppression of anaerobic microbial activity. However, the remaining permanganate background concentration must be low enough so as not to inhibit the palladium catalyst. In order to obtain information on tolerable concentrations, various amounts of permanganate were spiked to ongoing dechlorination experiments (Figure 2). At concentration levels of $c_{0,MnO4} \leq 0.07$ mM no inhibiting effect on the dechlorination of MCB using Pd/Al_2O_3 was observed. The concentration levels from 0.08 to 0.12 mM showed a decreasing reaction rate, whereby 0.12 mM of permanganate almost stopped the reaction.

Figure 2: Influence of initial KMnO₄ concentration on the Pd/Al₂O₃-catalyzed hydrodechlorination of chlorobenzene. Defined amounts of KMnO₄ were spiked during the course of dechlorination after a reaction time of 40 minutes to adjust initial permanganate concentrations between 0.01 and 0.12 mM ($c_{Pd} = 0.25$ mg L^{-1}, $c_{0,MCB} = 20$ mg L^{-1}).

Interestingly, the inhibition of the HDC reaction at higher permanganate concentrations appeared to be temporary. At extended reaction times the HDC re-started and the catalyst regained almost its original performance (Figure 3). Also shown in this graph is the kinetics of permanganate reduction in the reaction mixture. Notably, the reduction of MCB is inhibited while the reduction of permanganate takes place. As soon as the permanganate reduction is almost over, there is a significant re-start of the dechlorination reaction. However, the re-start of the dechlorination activity has a significant hysteresis. This means it starts at a much lower residual permanganate concentration than was proved as tolerable (0.07 mM) when freshly spiked.
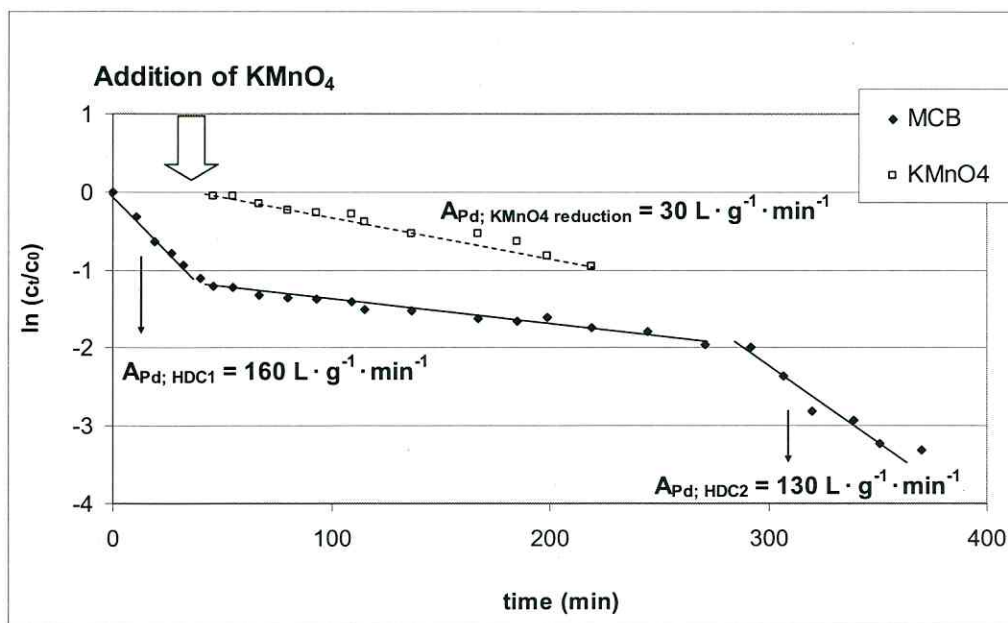
Figure 3: Temporary inhibitory effect of $KMnO_4$ on the Pd/Al_2O_3-catalyzed hydrodechlorination of chlorobenzene ($c_{Pd} = 0.25$ mg L^{-1}, $c_{0,MCB} = 20$ mg L^{-1}, $c_{0,KMnO4} = 0.08$ mM).

The existence of a permanganate threshold concentration and a catalyst re-activation hysteresis are significant observations which require mechanistic explanation. The observed threshold phenomenon may possibly be explained by a competition between permanganate and MCB for activated hydrogen (H*) provided at the palladium surface. The HDC is not significantly inhibited as long as sufficient activated hydrogen can be delivered, but above a certain threshold concentration of permanganate ($c_{KMnO4} \approx 0.07$ mM) this supply may become rate-limiting for the HDC reaction. It appears unlikely that the two competing reactions proceed at the same type of palladium sites, because this would give rise to a steady decrease in the HDC activity with increasing permanganate concentration rather than the observed threshold phenomenon (Figure 2). After the permanganate is consumed, the activated hydrogen becomes available again for the HDC. However, the observed hysteresis of reaction rates cannot be explained by this mechanistic model.

One could speculate that the hysteresis of the catalyst activity is due to the oxidation of Pd^0 to PdO by permanganate. The driving force for this reaction strongly depends on the permanganate concentration which could in principle explain the observed threshold concentration. The estimation of redox potentials supports the existence of a permanganate threshold concentration in the order of 10^{-4} M in neutral catalyst suspension. Since PdO is not an active HDC catalyst, the succeeding reduction of PdO by H_2 (or the activated species H^*) could be kinetically controlled, which may cause the observed hysteresis. The addition of the stronger reductant hydrazine effects a fast reduction of PdO and, hence, a fast re-activation of the catalyst. There is, however, one observation which does not fit the described mechanism: according to the stoichiometry of the surface redox reaction $3 Pd^0 + 2 MnO_4^- + 2 H^+ = 3 PdO + 2 MnO_2 + H_2O$ the effective threshold concentration should depend on the pH value. This was not observed. The permanganate threshold concentration was constant over a broad range of pH values (pH 4 -10, data not shown).

The catalytic reduction of permanganate by hydrogen in the absence of COCs takes place on Pd/Al_2O_3 with rates which are even higher than the HDC of MCB ($A_{Pd, MnO4} \geq 200$ L g^{-1} min^{-1}). The reaction follows mixed-order kinetics (between 0 and 1, data not shown). These rates are probably partially mass-transfer controlled. However, the high catalytic activity of palladium is not inhibited by permanganate concentrations up to at least 0.25 mM, which is clearly above the threshold value of 0.08 mM characteristic of the HDC reaction. This indicates that the active sites or reducing species for the two competing reactions which both use hydrogen as reductant are different. The fast catalytic reduction of permanganate implies that its co-feeding into a fixed-bed reactor with unprotected Pd/Al_2O_3 is not feasible.

The re-activation of sulfur-poisoned palladium catalysts is a difficult task with uncertain results (*30-31*). To the best of our knowledge, the application of permanganate for this purpose has not yet been described in the literature. We tested the reactivation of Pd/Al_2O_3 which had been poisoned with an excess of sulfide ($c_{0,H2S} = 0.15$ mM, S : Pd $\approx$ 20

moles per mol) for 3 days. The catalyst suspension was treated with a 2-fold stoichiometric amount of $KMnO_4$ (0.8 mM) for various reaction times (1 h to 3 days). The residual permanganate was quenched with hydrazine (0.6 mM) before the HDC test reaction. The MCB was hydrodechlorinated at rates of $A_{Pd} = 15$ L g^{-1} min^{-1} after 4 h of permanganate treatment up to $A_{Pd} = 75$ L g^{-1} min^{-1} after 3 days. This is about 50% of the activity of the fresh catalyst. Shorter regeneration times could be realized for catalyst samples poisoned with a stoichiometric sulfide excess ($c_{0,H2S} = 0.015$ mM, S : Pd $\approx$ 2 moles per mol). A regeneration time of 4 h gave an activity recovery of 70%. Although the re-activation is a relatively slow process, these results demonstrate the potential in principle of permanganate to oxidize palladium-bound sulfide.

In addition to commercial Pd/Al_2O_3, the stability of hydrophobically protected palladium catalysts in the presence of permanganate was tested. These included palladium on a Y-type zeolite (Pd/zeolite) (29), a membrane-based catalyst (Pd/PDMS) where palladium clusters are embedded in cross-linked poly(dimethylsiloxane) (11), and Pd/Al_2O_3 particles additionally coated with a silicone polymer ($SE30/Pd/Al_2O_3$). No palladium catalyst yet known is resistant against strong catalyst poisons such as sulfide. Since the pK_{A1} value of H_2S is 7.0, under environmental conditions non-dissociated H_2S is always present in sulfide-containing waters. Unfortunately, H_2S can permeate through many polymer phases including silicones. It is not likely that a material will ever be found which rejects H_2S while allowing COCs to pass through. Ideally, a catalytic system should be developed which allows access to the COCs but nevertheless has a maximum stability against water matrix components, such as cations and anions, and which is also permanganate-resistant. In such a system, permanganate can be utilized simultaneously as preoxidant for RSCs and biocide without inhibiting the catalyst activity for the HDC reaction. The resistance and stability of the embedded catalyst (Pd/PDMS) and the palladium catalysts on the hydrophobic porous carrier (Pd/zeolite) against

permanganate is shown in Figure 4, indicating that the catalyst performance can be maintained by a combination of hydrophobic and oxidative protection.
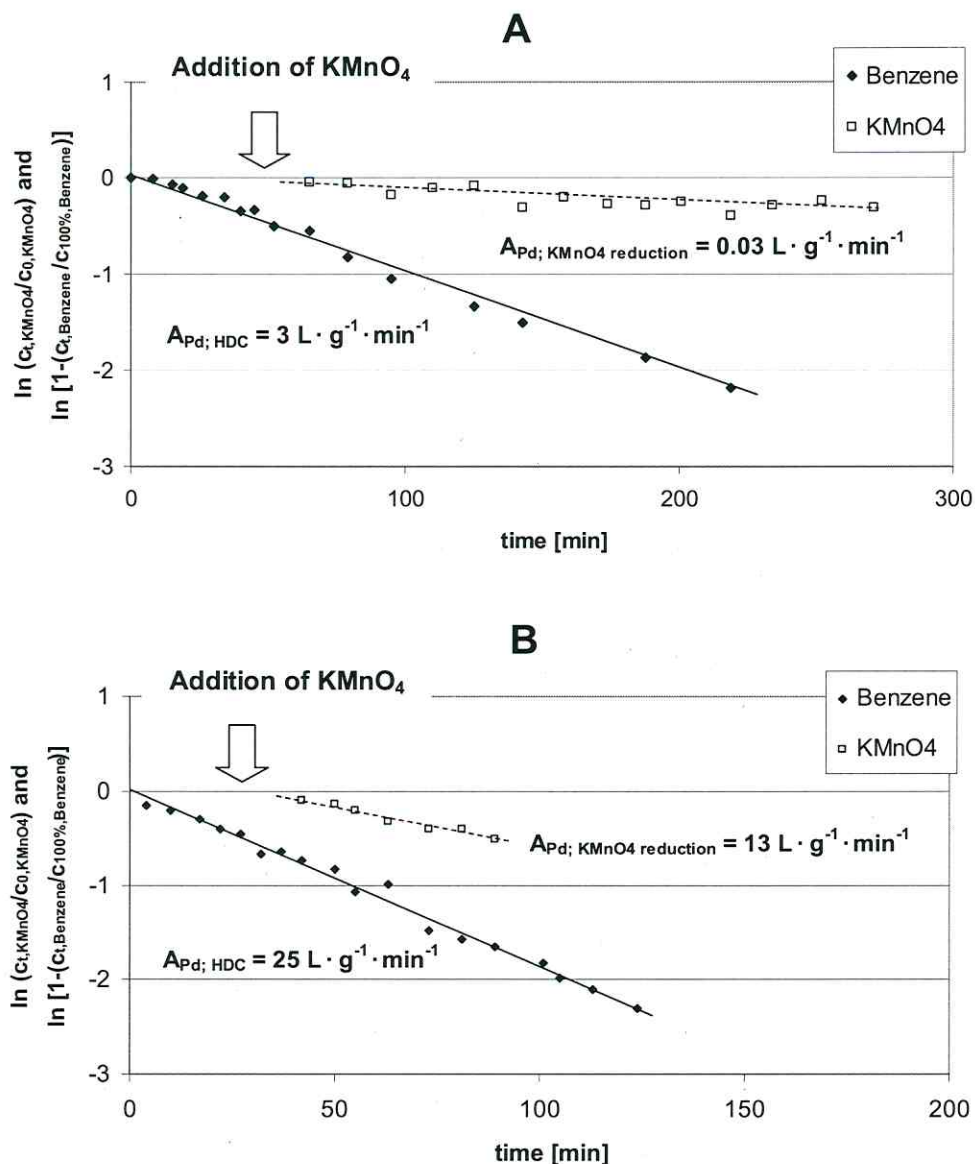
Figure 4: Influence of $KMnO_4$ on the course of the hydrodechlorination (shown as formation of benzene from chlorobenzene) using hydrophobically protected palladium catalysts. **A** = 92 mg L^{-1} Pd/PDMS with 5.6 wt% Pd ($c_{0,MCB}$ = 10 mg L^{-1}, $c_{0,KMnO4}$ = 0.8 mM); **B** = 200 mg L^{-1} Pd/zeolite with 0.5 wt% Pd ($c_{0,MCB}$ = 10 mg L^{-1}, $c_{0,KMnO4}$ = 0.12 mM).

In contrast to the uncoated catalyst (see Figure 2), no inhibitory action on the two protected palladium catalysts was observed when more than 0.08 mM permanganate was present. The membrane-based catalyst Pd/PDMS is resistant even up to the 10-fold concentration. This can be attributed to the impermeability of the non-porous PDMS film for the permanganate ion. However, permanganate reduction still takes place. This may be for two reasons: either a small fraction of the palladium is still available for the ionic species, e.g. at the outer surface of the PDMS membrane, or some reducing species (H*) are sufficiently mobile and long-lived that it reaches the dissolved permanganate (hydrogen spillover). The third type of hydrophobically protected catalysts (Pd/Al$_2$O$_3$ impregnated with silicone SE30, not shown in Figure 4) was less effective. The high initial HDC activity $A_{Pd,HDC}$ = 165 L g^{-1} min^{-1} of SE30/Pd/Al$_2$O$_3$ decreased in the presence of 0.08 mM permanganate by 85%, whereby the permanganate was reduced with $A_{Pd,MnO4}$ ≈ 50 L g^{-1} min^{-1}. Although the permanganate reduction is significantly decelerated in comparison to the unprotected Pd/Al$_2$O$_3$ catalyst ($A_{Pd,MnO4}$ ≥ 50 L g^{-1} min^{-1}), the sensitivity against permanganate is comparable with Pd/Al$_2$O$_3$. Apparently, the silicone film does not fully cover the palladium sites.

Despite a huge driving force for the reaction 1.5 H$_2$ + H$^+$ + MnO$_4^-$→ MnO$_2$ + 2 H$_2$O (ΔG° = - 485 kJ mol^{-1}), permanganate reacts only slowly with H$_2$ in the absence of a catalyst (k ≤ 0.05 M^{-1} s^{-1}). Therefore, a hydrogen-saturated aqueous solution of permanganate can be considered as a metastable redox system. This makes it feasible to spike groundwater with both a strong reductant and a strong oxidant having only minimal mutual interaction. The product of the non-catalytic reduction is not MnO$_2$ but unidentified water-soluble species with a broad absorption band in the near UV range (E$_{max}$ at about 350 nm). Tentatively, this band could be assigned to manganate which has a band at 347 nm. However, none of the characteristic absorption bands of hypomanganate (MnO$_4^{-3}$, 667 nm) and manganate (MnO$_4^{-2}$, 606 nm) were observed in the visible range. The number of experiments conducted in the

course of this study is larger than could be presented in this paper. Original data given in the figures are to be understood as representative examples from a much larger data pool which in all cases confirms the principal findings in the presented examples.

Future Technical Implications

The combination of oxidative water pretreatment and hydrophobic catalyst protection provides a new tool to harness the high potential of palladium-catalyzed hydrodehalogenation for treatment of real waters, such as groundwater. Results from these preliminary experiments can help to define the design of a flow-through reactor (*ex situ* or *in situ*) in which permanganate can be added prior to the palladium catalyst zone in order to prevent S-induced deactivation of the noble metal and biofouling of the catalyst bed.

Although permanganate is a selective oxidant, it oxidizes a large number of COCs such as TCE (*36-37*). It can be used for a selective removal of RSCs only if its reaction rate with the target contaminants is much lower than with the RSCs. Therefore, the relative rate constants for both oxidation reactions have to be considered. The half-life of TCE in the presence of 0.1 mM MnO_4^- can be calculated from the second-order rate constant k_{TCE} (21 °C) = 0.65 M^{-1} s^{-1} (*36*). Thus, $\tau_{1/2,TCE} \approx 10^4$ s $\approx$ 3 h. Under these conditions the oxidation of the target compound H_2S proceeds instantaneously ($\tau_{1/2,H2S} \leq 3$ s, $k_{H2S} \geq 2 \times 10^3$ M^{-1} s^{-1}). This means, H_2S can be selectively oxidized with permanganate even in the presence of a large excess of COCs. Moreover, the half-life of TCE in a fixed-bed reactor filled with the Pd/Al_2O_3 catalyst can be estimated as $\tau_{1/2,TCE} = (A_{Pd} \cdot c_{Pd})^{-1} \approx (10^2$ L g^{-1} $min^{-1} \cdot 5$ g $L^{-1})^{-1} \approx$ 0.12 s. Even if one implies a severe catalyst deactivation under real conditions ($A_{Pd} \approx 1$ rather than 10^2 L g^{-1} min^{-1}) the catalytic hydrodechlorination of TCE would be three orders of magnitude faster than the competing oxidation by permanganate. In contrast to zero-valent iron as reductant, which produces mainly unsaturated hydrocarbons (e.g. ethene from TCE), palladium-catalyzed HDC yields saturated hydrocarbons (e.g. ethane from TCE). Saturated

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hydrocarbons such as ethane are not attacked by permanganate. The same holds for chlorinated benzenes and their HDC product benzene: neither the chlorinated pollutants nor their non-chlorinated products are competitive permanganate consumers under the applied reaction conditions. These considerations make it clear that permanganate can be added into waters that are contaminated with highly chlorinated compounds without significant consumption in undesired reactions with the bulk pollutants or their products. Nevertheless, other permanganate-consuming compounds such as ferrous iron or natural organic matter may be present in real waste or groundwaters.

The reduction of permanganate in neutral solution produces MnO_2 as a colloidal precipitate. This could give rise to blockage of the catalyst bed. If permanganate is applied as a preoxidant, the manganese dioxide can be removed from the water flow simply by sand filtration before entering the catalyst bed. If, however, permanganate is used as a biocide inside the fixed-bed reactor it is essential to protect the catalyst by special measures such as hydrophobic coating in order to prevent extensive palladium-catalyzed reduction of permanganate. From the practical point of view the additional costs of a preoxidation treatment have to be considered. Assuming a price of sodium permanganate of about 5 € kg^{-1} (as 40% solution (38)), a 0.1 mM permanganate concentration would increase the overall treatment costs by 0.07 € per m^3. This is in many cases acceptable for COC-contaminated waters.

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4 Sulfide-induced Deactivation of Pd/Al$_2$O$_3$ as Hydrodechlorination Catalyst and its Oxidative Regeneration with Permanganate

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Abstract

Palladium-based catalysts have become important in environmental catalysis for their ability to hydrodechlorinate a wide range of chlorinated organic contaminants in water under ambient conditions. The success of their application in the remediation practice, e.g. for groundwater treatment, is often hindered by the sensitivity of palladium to poisoning by sulfur compounds. In this study, the stability and sulfide-induced deactivation behaviour of a highly active Pd/Al$_2$O$_3$ catalyst was investigated. The specific activity of palladium for the hydrodechlorination of chlorobenzene corresponds to rate coefficients up to $k_{Pd} = 350$ L g^{-1} min^{-1}. The totally deactivated catalyst, resultant of sulfide poisoning, was regenerated with potassium permanganate. The pH value, as a key parameter which may influence the degree of deactivation as well as the efficiency of catalyst regeneration, was evaluated. Results show that in clean water the Pd/Al$_2$O$_3$ catalyst showed no inherent deactivation regardless of the ageing time and the pH value of the catalyst suspension. The degree of catalyst poisoning effected by 1.8 to 5.4 µM sulfide, corresponding to molar ratios of S : Pd$_{surface}$ = 1.5 to 8.5, was observed to be higher under neutral and alkaline than under acidic conditions. The exposure of the catalyst to higher sulfide concentration of 14.2 µM resulted in complete catalyst deactivation regardless of the pH conditions. However, the efficacy of permanganate as oxidative regenerant for the fouled catalyst showed strong pH-dependence. A regeneration time of 10 to 30 min at low pH was sufficient to recover completely the high catalytic activity of Pd/Al$_2$O$_3$ for the hydrodechlorination reaction.

Introduction

Palladium-based reagents have become important in environmental catalysis whereby halogenated contaminants are transformed to less or non-harmful compounds. Together with an electron donor (e.g. H_2 or HCOOH), palladium catalytically reduces chlorinated organic compounds according to the chemical equation R-X + H_2 $\xrightarrow{Pd}$ R-H + HX. Palladium catalysts, unlike Fe-based dechlorination, can reduce a wide range of chlorinated aliphatic as well as aromatic contaminants with high turnover frequencies in the order of 1 s^{-1} at ambient conditions. This high inherent catalytic activity delivers half-lives of only a few seconds to minutes for the batch hydrodechlorination of C_1- to C_3-halogenated aliphatics and halogenated aromatic compounds such as chlorobenzene [1-4]. The dechlorination reaction proceeds to completion, preventing the accumulation of partly dechlorinated byproducts which are in some cases more toxic than the parent compounds. To date, palladium-based bimetallic catalysts are finding wider application in terms of promoting nitrate reduction and the chemical reduction of emerging water pollutants such as N-nitrosodimethylamine and perchlorate [5-7].

Regarding field application, palladium-catalyzed hydrodechlorination is drawing researchers' attention as a promising alternative for the *in situ* treatment of chlorinated contaminants in water. Palladium-based reactors have been tested in the field, including the construction of a reactive well system, column reactors and palladium-based membrane reactors for the treatment of contaminants such as TCE, PCE and chlorobenzene [8-12]. During these field-test studies, the dechlorination rate of the contaminants was significantly reduced over the time of operation due to poisoning of palladium catalysts by reduced sulfur compounds (e.g. sulfides). Sulfides are known to have a strong affinity for palladium metal and may block the active sites of the catalyst via formation of strong Pd-S bonds and adlayers of sulfide around the palladium clusters [13-15]. Since sulfide is a natural water constituent under reducing conditions produced via microbial sulfate reduction, sulfide-induced catalyst

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deactivation is a crucial issue which hinders the full exploitation of the catalyst potential as a treatment technology for groundwater remediation. One alternative approach to prevent sulfide poisoning is the removal of sulfide prior to any contact with the noble metal. This can be achieved by oxidative water pretreatment with permanganate in order to oxidize sulfides to sulfate, which does not negatively affect the dechlorination reaction [16].

Nevertheless, in any case of catalyst deactivation it is necessary to have a simple and efficient regeneration procedure to recover catalyst performance. The common regeneration procedure for sulfide-fouled palladium catalysts used in gas phase reactions is a high temperature treatment with hydrogen [17-20]. This process is, however, unsuitable for catalysts used in the water phase. So far, the only method which has showed relative success in the liquid phase regeneration of sulfide-fouled palladium catalysts is an oxidative treatment with hypochlorite [21-23]. This procedure requires long regeneration times or multiple regeneration cycles. Other oxidants such as heated air and H_2O_2 have only delivered limited success [21, 23], while the use of Fenton's reagent and Peroxone ($H_2O_2 + O_3$) showed no success (unpublished own results). In the present study, the sulfide-induced deactivation and the permanganate-induced regeneration of Pd/Al_2O_3 were investigated, with a special focus on the pH-dependence of both processes. Obviously, the sulfur speciation also depends on the pH value (for H_2S: $pK_{A1} = 7.05$, $pK_{A2} \approx 13$, with differing values in the literature). The hydrodechlorination (HDC) performance of fresh, poisoned, and regenerated catalysts was tested, whereby monochlorobenzene (MCB) was used as the probe compound.

Experimental section

Chemicals

MCB (99.8%) and $Na_2S \cdot 9H_2O$ (reagent grade) were obtained from Sigma-Aldrich. $KMnO_4$ (extra pure crystalline) was supplied by Merck. A commercially available egg-shell palladium on γ-Al_2O_3 catalyst (G-133 D purchased from Commercia, Germany) with 0.51

wt% Pd (from EDXRF analysis), a BET surface area of 140 m^2 g^{-1} (N_2 adsorption) and a palladium dispersity of 0.17 (CO adsorption) was used. The original 3 mm pellets were crushed and sieved. The 25-63 μm fractions were preconditioned in the aqueous phase by purging with hydrogen gas under atmospheric pressure (i.e. p_{H2} = 100 kPa).

Catalyst activity and stability

The HDC of MCB over Pd/Al_2O_3 was conducted as batch experiments using 250 mL amber screw-cap bottles equipped with Mininert® valves. The general procedure for preparing a batch reaction included the addition of 30 mg of prereduced Pd/Al_2O_3 into the batch bottle containing 200 mL deionized water (DW), HCl-amended DW (for pH 3) or NaOH-amended DW (for pH 13). The resulting catalyst suspension was then purged with He for 1 h, after which the headspace was exchanged with hydrogen gas without mixing the water phase. A defined volume of MCB stock solution was spiked into the batch bottle, giving a concentration of 20 mg L^{-1}. The bottle was shaken (180 rpm in a horizontal shaker) to start the HDC reaction. Repeated batch runs were conducted on the same catalyst suspension after 0 to 16 days standing (catalyst ageing). Before each run, the benzene product of the preceding reaction was purged-out with He. Hydrogen gas and MCB were then freshly added into the reaction bottle. The kinetics of the HDC reaction was followed via educt disappearance and product formation. Both were monitored via headspace analysis (25 μL gas tight syringe) using a GC-MS QP2010 (Shimadzu). In all cases, the MCB disappearance and the benzene formation followed identical kinetics. It is worth mentioning that for low conversion degrees (especially utilized for experiments with low catalyst activities) tracing the benzene yields more accurate data, whereas for high conversion degrees tracing the MCB gives more reliable results.

Catalyst poisoning and regeneration

The catalyst suspension prepared as described above (30 mg Pd/Al$_2$O$_3$ in 200 mL DW with the corresponding pH) was purged with He for 1 h. Afterwards, a defined volume of Na$_2$S stock solution was spiked into the batch bottle to give the desired sulphide concentration, ranging from 1.77 μM to 14.2 μM. These concentrations correspond to S : Pd = 0.25 and 2 moles per mole, respectively. Taking into account the palladium dispersity of 0.17 and that S is exclusively bound to the outer Pd surface, the corresponding ratios are S : Pd$_{surface}$ = 1.5 and 12. The batch bottles were shaken overnight in order to effect sulfide-induced catalyst deactivation. The fouled catalysts were tested for their remaining activities by adding hydrogen and MCB. For the totally deactivated catalyst (S : Pd = 2), oxidative regeneration was conducted by spiking an aqueous solution of KMnO$_4$ into the bottle, giving the desired initial concentration of 0.18 mM. The bottle was left to shake on a horizontal shaker at 180 rpm for a defined time period. Afterwards, unconsumed permanganate in the bulk solution was quenched by adding hydrazine until the pink colour had disappeared completely. Hydrogen and MCB were then added in order to test catalyst activities. The changes in pH values during the periods of poisoning, regeneration and HDC reaction were all noted.

Results and discussion

Catalyst baseline activity and stability in clean water

The catalyst performance for the HDC reaction of a contaminant i is expressed in terms of the specific palladium activity $A_{Pd,i}$ according to the following equation [24]:

$$A_{Pd} = \frac{V_{water}}{m_{Pd}\,\tau_{1/2}} = \frac{\ln(c_{t1}/c_{t2})}{\ln 2 \cdot c_{Pd} \cdot (t_2 - t_1)} \quad \text{in [L g}^{-1}\text{ min}^{-1}] \quad (1)$$

where V_{water} is the volume of contaminated water applied, m_{Pd} is the mass of Pd and $\tau_{1/2}$ is the half-life of the contaminant as obtained from its disappearance kinetics. The chosen sampling

times t_1 and t_2 correspond to the contaminant concentrations c_{t1} and c_{t2}. In the case of simple kinetics, the numerical value for $A_{Pd,i}$ is equivalent to a second-order rate coefficient according to $k'_i = \ln 2 \cdot A_{Pd,i}$ with $dc_i/dt = - k'_i \cdot c_i \cdot c_{Pd}$.
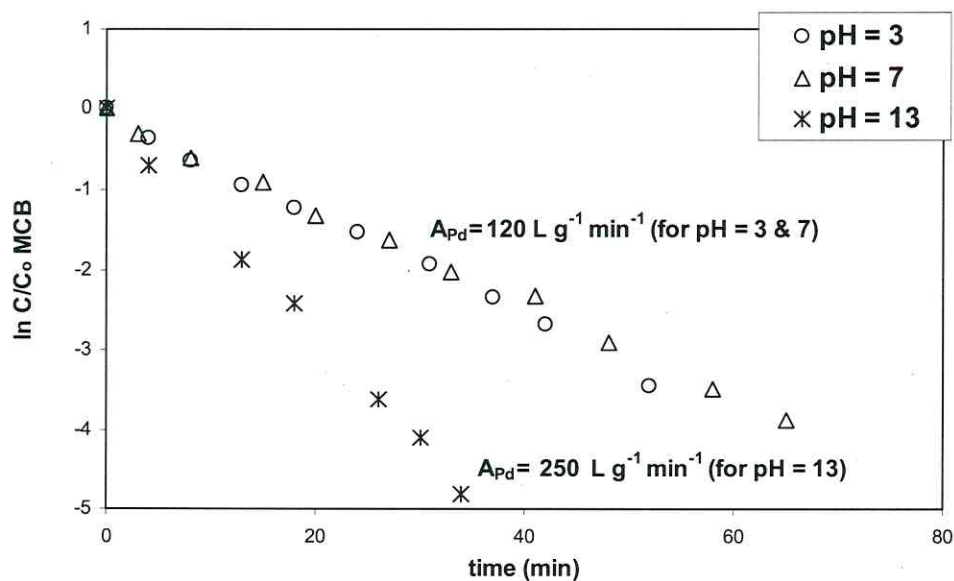
Figure 1. Kinetics of the hydrodechlorination of chlorobenzene, and catalyst activities (A_{Pd}) under various pH conditions. Deionized water (DW) was used for pH 7, HCl- and NaOH-amended DW for pH 3 and pH 13, respectively ($c_{cat} = 150$ mg L^{-1}, $c_{0,MCB} = 20$ mg L^{-1}).

Typical HDC kinetics of MCB over Pd/Al$_2$O$_3$ are shown in Figure 1. All the reactions, conducted under various pH conditions, follow first-order kinetics with respect to the concentration of MCB up to high conversion degrees (> 99%). The catalyst activity is higher under basic conditions ($A_{Pd} = 250$ L g^{-1} min^{-1} at pH 13) compared to acidic conditions ($A_{Pd} = 120$ L g^{-1} min^{-1} at pH 3). However, the difference is only a factor of 2. This is significant, but not drastic. Due to the lack of an appropriate buffer system which does not disturb the catalytic system, the HDC reaction under neutral start conditions gave rise to slightly decreasing pH values (pH$_{end}$ ≈ 4). A fraction of the released protons was buffered by the

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catalyst carrier alumina. The catalyst activities calculated from these reaction kinetics are taken as the reference or 'baseline' activities of Pd/Al_2O_3 in clean deionized water. The beneficial effect of elevated pH values or adding a base (e.g. NaOH) during the HDC reaction is known and has been described in various studies [4, 25, 26], but this effect is outside the scope of the present study.

A stable activity of the Pd/Al_2O_3 catalyst for repeated batch HDC runs in a broad pH range (from 3 to 13) is demonstrated in Figure 2. It should be noted here that the repeated batch runs were conducted on the same catalyst samples and in the same reaction mixtures. Additionally, the catalyst was left to stand in the bulk solution for 0 to 16 days (catalyst ageing) before each experiment. There are several factors that might deactivate the catalyst due to ageing and prolonged use, e.g. dissolution of palladium under strongly acidic conditions or unfavourable morphological changes in the palladium clusters. Obviously, such inherent deactivation phenomena are not significant in clean water, irrespective of the applied pH value. This is an important technical implication when the Pd/Al_2O_3 catalyst is to be applied for long-term operation in water treatment processes.

Sulfide-induced deactivation of Pd/Al_2O_3

The addition of sulfide to the catalyst suspension resulted in the expected poisoning of the catalyst. Table 1 gives a compilation of the deactivation effects observed. A trace level of sulfide (1.77 μM, S : $Pd_{surface}$ = 1.5 moles per mol) already significantly reduced the catalyst activity in all experiments conducted . The degree of catalyst deactivation depends on the pH value: it is a factor of 10 to 12 at pH $\geq$ 7 vs. a factor of 3.6 at pH 3. When the sulfide concentration in the catalyst suspension was increased, the degree of catalyst deactivation also increased. Again, the effects are more pronounced at pH $\geq$ 7 than under acidic conditions. This points to a stronger poisoning effect of HS$^-$ (and possibly of S^{2-}) than of H_2S. The exposure of the catalyst to high sulfide concentrations (i.e. 14.2 μM, giving S : $Pd_{surface}$ = 12)

resulted in the total and permanent deactivation of the catalyst regardless of the pH value during the poisoning procedure.

(a)

(b)

(c)
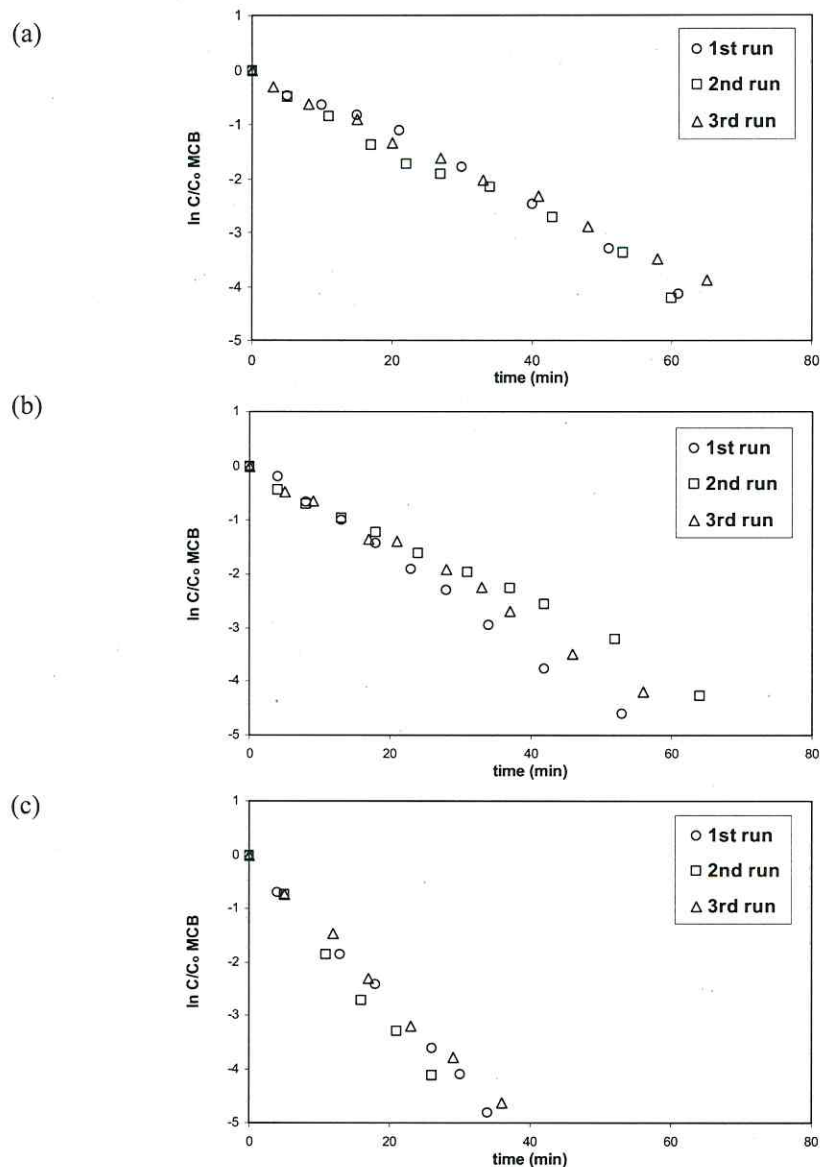
Figure 2.   Stability of the Pd/Al$_2$O$_3$ catalyst performance during repeated runs of hydrodechlorination of chlorobenzene under various pH conditions. The 1st, 2nd, and 3rd runs were conducted on the same catalyst sample after 0, 6, and 16 days of catalyst ageing, respectively, in the aqueous reaction medium. (a) pH 7 (DW) (b) pH 3 (HCl-amended DW) (c) pH 13 (NaOH-amended DW). Applied concentrations: c_{cat} = 150 mg L^{-1}, $c_{0,MCB}$ = 20 mg L^{-1}.

Table 1.   Specific catalyst activities (A_{Pd}) for the hydrodechlorination of chlorobenzene in the presence of sulphide under various pH conditions. Deionized water (DW) was used for neutral conditions (pH 7), HCl- and NaOH-amended DW for pH 3 and 13, respectively (c_{cat} = 150 mg L^{-1}, $c_{0,MCB}$ = 20 mg L^{-1}).

conc. of sulphide (µM)	A_{Pd} (L g^{-1} min^{-1})		
	DW	pH 3	pH 13
0	120 ± 20[a]	120 ± 20	250 ± 40
1.77	10	33	26
3.55	4	20	10
5.35	0.1	3	0.6
14.2	< 0.01	< 0.01	< 0.01

[a] Average deviation of the single values from the mean value originating from three parallel batch experiments.

The influence of the pH value on the sulfide-induced deactivation of palladium on γ-alumina has been reported in Ref. [23]. Munakata and Reinhard observed a faster deactivation at lower pH (i.e. 4.8) and a non-zero steady state activity under alkaline conditions (i.e. pH 9.6 -10.4). The influence of the pH value on the deactivating effects of sulfide species can be discussed in the light of two phenomena: the sulfur speciation and the surface charge of the catalyst. The sulfur speciation is determined by the two pK_A values of H$_2$S (7.05 and ca. 13), whereas the surface charge of alumina is characterized by its pH-dependent zeta-potential and its point of zero charge (pH$_{pzc}$). For the Pd/Al$_2$O$_3$ under study we found pH$_{pzc}$ = 8.2 by means of potentiometric titration [27]. Reported values of pH$_{pzc}$ of γ-alumina range between 7 and 9, depending on thermal activation and impurities [28]. From the point of view of electrostatic interactions, higher pH values are unfavourable for sulfide binding, because the catalyst surface and the sulfur species (HS$^-$ and S^{2-}) are both negatively charged. However, the deactivation experiments showed the opposite tendency. Therefore, we conclude that bisulfide

(and possibly sulfide) has a stronger affinity to palladium than the non-charged H_2S, which is the exclusive sulfur species at pH 3.
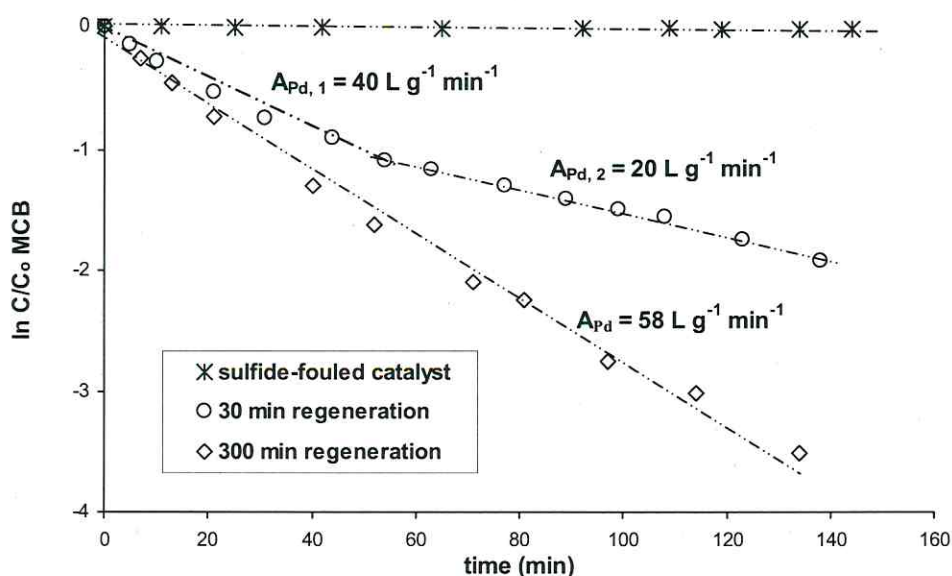
Regeneration of sulfide-fouled Pd/Al₂O₃ with permanganate

For the regeneration of the fully sulfide-deactivated Pd/Al_2O_3 catalysts (S : Pd = 2), permanganate was utilized. An efficient regeneration is only possible when the surface-bound sulfide is accessible by the regenerant and oxidation to sulfate occurs. Sulfate in turn has no affinity to palladium metal [16, 21, 22] and, therefore, is released to the aqueous phase, freeing the active sites of the catalyst. Permanganate as a powerful regenerant for sulfide-deactivated palladium catalysts was recently reported by our group in Ref. [16]. This report did not, however, consider the pH value as a key parameter for the efficiency of the regeneration procedure. In the present study, Pd/Al_2O_3 was subjected to sulfide poisoning (S : Pd = 2 moles per mole) and subsequently to oxidative regeneration under various pH conditions. The poisoning was conducted under neutral, acidic, and alkaline conditions which resulted in the complete loss of catalyst activity. Permanganate was added to the catalyst suspensions at the corresponding pH values. The addition of sulfides and permanganate did not significantly change the pH values in the catalyst suspensions. It is important to note that after a given regeneration period, the unconsumed permanganate was quenched with hydrazine (instantaneous decolourisation of the suspension) before HDC tests were conducted. This is due to the inhibitory effect of permanganate on the HDC when present at higher than a threshold concentration of about 0.08 mM, as described in detail in Ref. [16]. The addition of hydrazine for quenching the unconsumed permanganate caused the pH value of the suspension to increase to pH $\approx$ 8 (for $pH_{regeneration}$ = 3) and pH $\approx$ 10 (for $pH_{regeneration}$ = 7), while under alkaline conditions the pH remained alkaline (pH $\approx$ 13). Therefore, these pH values were then taken as the starting pH of the bulk solution when the performance of the regenerated catalysts was probed.

The evaluation of the recovered catalyst performance shows a strong correlation between the applied pH values and the regeneration efficacy of permanganate. After 24 h of permanganate (0.18 mM) treatment at neutral conditions, the recovered catalyst activity for the complete dechlorination of MCB was around 71 L g^{-1} min^{-1}, corresponding to about 60% of the original activity. Shorter regeneration times (e.g. 4 h) only delivered an unstable catalyst state. The HDC of MCB proceeded incompletely, i.e. the catalyst lost its activity during the course of the HDC reaction. This behaviour was typical of incompletely regenerated catalyst samples. It suggests a re-poisoning of the catalyst under the reducing reaction conditions. In Ref. [23] a long-term sulfur reservoir in the catalyst was discussed. The authors speculate on the diffusion of sulfur into palladium clusters where the sulfur would be protected against short-term oxidation.

A different scenario was observed for the catalyst regenerated under acidic and alkaline conditions. 0.5 h of permanganate treatment at pH 13 resulted in the recovery of an initial catalyst activity of about $A_{Pd,1}$ = 40 L g^{-1} min^{-1} (Figure 3). After 50 min the HDC rate slowed and the catalyst activity was reduced to $A_{Pd,2}$ = 20 L g^{-1} min^{-1}. When the regeneration time with permanganate was increased to 5 h, the obtained catalyst activity was increased to A_{Pd} = 58 L g^{-1} min^{-1} and the HDC reaction proceeded to completion without any further activity loss (Figure 3). This magnitude of catalyst activity was also obtained for Pd/Al$_2$O$_3$ regenerated under neutral conditions, but this required a full day of regeneration as was mentioned above.

Figure 3. Recovered catalyst activity (A_{Pd}) after oxidative regeneration of sulfide-fouled Pd/Al$_2$O$_3$ under alkaline conditions (pH 13). Regeneration was conducted using 0.18 mM KMnO$_4$ for 30 and 300 min (c_{cat} = 150 mg L^{-1}, $c_{0,MCB}$ = 20 mg L^{-1}).

The most efficient regeneration of sulfide-fouled Pd/Al$_2$O$_3$ was obtained under acidic conditions (pH 3). This is demonstrated in Figure 4, where short regeneration times of 10 min and 30 min completely recovered the catalyst activity (A_{Pd} = 132 and 466 L g^{-1} min^{-1}, respectively). It is remarkable that after 30 min of permanganate treatment and hydrazine quenching the catalyst exposed even higher activities than the baseline activity of the fresh catalyst (A_{Pd} = 120 L g^{-1} min^{-1}). This phenomenon was reproduced several times (A_{Pd} = 450 $\pm$ 100 L g^{-1} min^{-1}). It should be emphasized again, that dechlorination was conducted in the same reaction mixtures where the catalyst samples were first poisoned and then regenerated. This means that the observed exceptionally high reaction rates can be due either to the catalyst state or to the composition of the reaction medium. In order to distinguish between these two reasons another set of dechlorination experiments was conducted. This time, after the regeneration process, the catalyst was separated from the suspension by centrifugation and washed with deionized water. This catalyst sample was then added to a fresh reaction solution

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(DW with pH 7-8) containing H_2 in the headspace and MCB in the water phase. The catalyst delivered activities ($A_{Pd} = 120 \pm 10$ L g^{-1} min^{-1}) in the range of the baseline activity of the fresh catalyst under neutral condition (cf. Table 1). Thus, the very high dechlorination rates with the regenerated catalyst under the employed conditions appeared only when the reaction was conducted in the regeneration matrix. The key components or parameters of this matrix responsible for the accelerating effect are not obvious. Hydrazine is known to be active as a reductant for the palladium-catalyzed HDC reaction. However, it was found to be effective only under alkaline conditions [29].
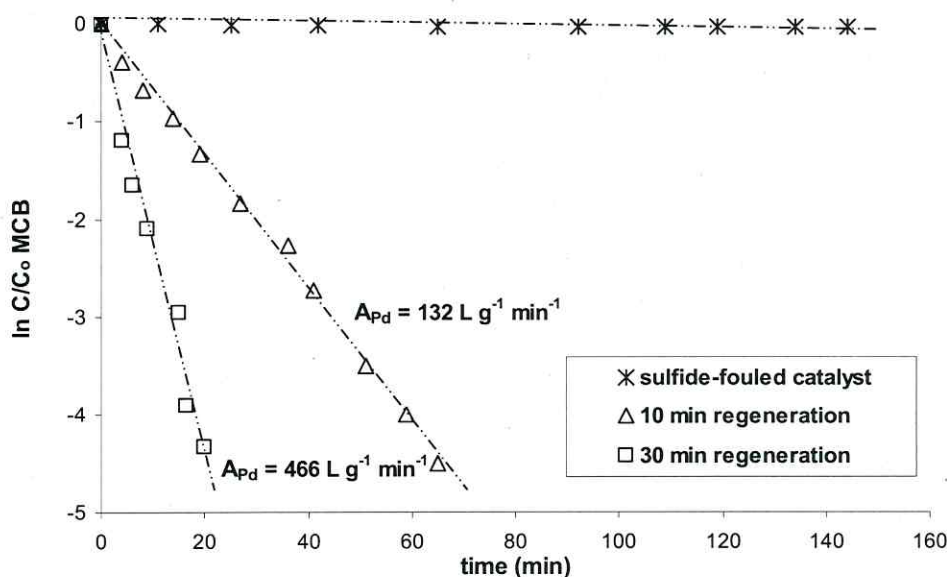
Figure 4. Recovered catalyst activities (A_{Pd}) after oxidative regeneration of sulfide-fouled Pd/Al$_2$O$_3$ under acidic condition (pH 3). Regeneration was conducted using 0.18 mM KMnO$_4$ for 10 and 30 min ($c_{cat} = 150$ mg L^{-1}, $c_{0,MCB} = 20$ mg L^{-1}).

In order to further confirm the hypothesis that low pH values are a key requirement for efficient catalyst regeneration, an additional experiment was conducted. This time the catalyst was poisoned with sulfide (14.2 μM) under neutral and regenerated under acidic conditions (pH 3; 0.18 mM KMnO$_4$). The results from this experiment showed again the recovery of a

very high catalyst activity of about 400 L g^{-1} min^{-1} after only 30 min of regeneration time, similar to the data shown in Figure 4. This confirms the strong pH-dependence of permanganate efficacy as regenerant for sulfide-fouled Pd/Al$_2$O$_3$ catalysts.

The fast and effective regeneration of sulfide-fouled Pd/Al$_2$O$_3$ under acidic conditions, as shown in Figure 4, needs further elucidation. It should be taken into consideration that the active component palladium, the carrier Al$_2$O$_3$, the sulfur and manganese speciation are all susceptible to pH changes. Permanganate itself is reactive in a wide pH range. Under acidic conditions, the oxidation half-reaction is MnO$_4^-$ + 8 H$^+$ + 5 e$^-$ → Mn^{2+} + 4 H$_2$O with a standard oxidation potential of E° = 1.51 V. The reduction proceeds to the formation of Mn^{2+}, which is soluble in water. On the other hand, water-insoluble manganese dioxide (MnO$_2$) is the end product of the reduction of permanganate under neutral and basic conditions (MnO$_4^-$ + 2 H$_2$O + 3 e$^-$ → MnO$_2$ + 4 OH$^-$ with E° = 0.60 V). There are two plausible reasons for the observed pH effects: (i) the higher redox potential ('oxidation power') of permanganate under acidic conditions and (ii) the positive surface charge of alumina (pH$_{pzc}$ = 8.2) which may facilitate the access of the permanganate anion to the palladium sites. This is the kinetic aspect of the reaction, which may be even more significant than the thermodynamic aspect considered above. Apparently, both permanganate reduction products (i.e. dissolved Mn^{2+} at acidic pH and MnO$_2$ at neutral to alkaline pH) do not significantly deactivate the palladium catalyst.

Additional experiments were conducted in order to assess an optimal permanganate concentration at pH 3. According to the reaction stoichiometry 5 H$_2$S + 8 MnO$_4^-$ + 2 H$_2$O → 5 SO$_4^{2-}$ + 8 Mn^{2+} + 14 OH$^-$, the reagent concentrations usually applied (14.2 μM S^{2-} and 0.18 mM MnO$_4^-$) are equivalent to an 8-fold surplus of the oxidant, provided there are no other permanganate consumers in the catalyst suspension. When the permanganate concentration was reduced to 0.09 mM, an activity recovery of only 14% after 10 min regeneration was achieved but the full activity was regained after 60 min regeneration time. On the other hand,

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an increase of the oxidant concentration (e.g. to 0.36 mM) did not give rise to any significant improvement of the regeneration efficiency. That is, it neither shortens the regeneration time requirement nor increases the recovered catalyst activity. This implies that the permanganate-based regeneration procedure can be realized at a low concentration level (about 0.1 mM), depending mainly on the stoichiometric demand. For comparison, in the oxidative regeneration of sulfide-fouled catalysts using hypochlorite, much higher regenerant concentrations (in the range of 20 to 50 mM NaOCl) are usually employed [21-23]. In one study [21], the 'highly poisoned catalyst' (S to Pd molar ratio of 0.66, surface S content of Pd as determined by X-ray photoelectron spectroscopy), 56 mM NaOCl was used in order to restore the catalyst activity to about 29% of its original value. In this case, full recovery of catalyst reactivity was not easily achievable. It is worth mentioning that in the study of Munakata and Reinhard [23] on various catalyst regenerants, the applied Pd/Al$_2$O$_3$ catalyst with 1 wt% Pd had an apparent baseline activity ($A_{Pd} \approx 0.1$ L g^{-1} min^{-1}) which is three orders of magnitude lower than that of our catalyst. Therefore, it might be easier to achieve a partial regeneration there than for a highly active catalyst such as used in the present study. Furthermore, hypochlorite is a chlorinating agent and additional care must be taken during its employment as catalyst regenerant.

Conclusions

The presented paper describes the stability and sulfide-induced deactivation behaviour of a Pd/Al$_2$O$_3$ (0.5 wt% Pd) hydrodechlorination catalyst and its response to oxidative regeneration using potassium permanganate. Primarily, in sulfide-free clean water the catalyst did not show any inherent deactivation during repeated batch reaction cycles in the pH range 3 to 13. The addition of sulfides to the catalyst suspension led to the expected poisoning of the catalyst. The impact of the pH value on the deactivating effect of sulphides was relatively small but nevertheless showed that Pd/Al$_2$O$_3$ was more resistant to poisoning under acidic

conditions. The exposure of the catalyst to higher sulfide doses (e.g. 14.2 μM, S : Pd$_{surface}$ = 12 moles per mole) resulted in a complete catalyst deactivation regardless of the applied pH conditions. The oxidative regeneration of the totally deactivated catalyst with permanganate showed consistently strong pH-dependence. Regeneration under neutral and basic conditions showed a complete but slow recovery of catalyst activity. When oxidative regeneration was conducted under acidic condition (pH 3) the fouled catalyst could be re-activated within a short time of 10 to 30 min with the complete recovery of its performance. Thus, we point out in our study the superiority of permanganate as regenerant for sulphide-fouled Pd/Al$_2$O$_3$.

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5 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 palladium catalysts. However, if they appear in a complex water matrix, as is common for wastewater treatment or after soil extraction, the protection of the palladium sites against catalyst poisons may become the key step for applicability of this reaction. In the present study, Pd/Al$_2$O$_3$ 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 L g^{-1} 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 palladium sites against ionic catalyst poisons such as DOM and bisulfite for at least 24 h.

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/Al_2O_3 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 $A_{Pd} = 10$ L g^{-1} min^{-1} the half-life of the COC in a fixed-bed reactor (e.g. Pd/Al_2O_3 consisting of 0.5 wt% Pd) 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/Al_2O_3 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), polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (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 palladium-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 palladium 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/Al_2O_3 have yet been published.

In the present study, we make two important contributions: First, we quantify how the activity of a commercially available Pd/Al_2O_3 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-chlorobiphenyl (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 is similar in all these compounds.

Experimental procedures

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 palladium 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 m^2 g^{-1} (N_2 adsorption) and a palladium 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 kPa, T = 20-70 °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.

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 $c_0 = 2.5$ mg L^{-1} which is about half of its water solubility ($S_{water} = 4.7$ 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/Al$_2$O$_3$, prereduced in 10 mL water for 1 h with H$_2$) 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).

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 was allowed to stand (about 1 h) and the

supernatant was decanted and centrifuged (5000 x 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 µL) containing 2-methylnaphthalene as internal standard, and performing GC-MS analysis (Shimadzu GC-MS QP2010).

### *Dechlorination with polymer-modified catalysts*

These batch experiments were carried out in a similar way to those described above. Instead of 3-CBP, MCB and TCE were used as substrates (c_0 = 20 mg L^{-1}). The course of the HDC was followed by headspace sampling (50 µL 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.

Results and discussions

Effects of surfactants on the hydrodechlorination kinetics

In order to obtain a baseline activity of Pd/Al$_2$O$_3$ for the HDC of 3-CBP, the probe compound was dechlorinated in deionized water buffered by NaHCO$_3$ at pH 8.3. The reaction follows first-order kinetics with respect to the substrate concentration up to very high extents of conversion (Figure 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} [L g^{-1} min^{-1}] which is defined by Eq. 1 with c_{Pd} as the applied palladium concentration and $\tau_{1/2}$ as the half-life of the substrate.

$$A_{Pd} = k_1 / (\ln 2 \cdot c_{Pd}) = 1 / (\tau_{1/2} \cdot c_{Pd}) \qquad (1)$$
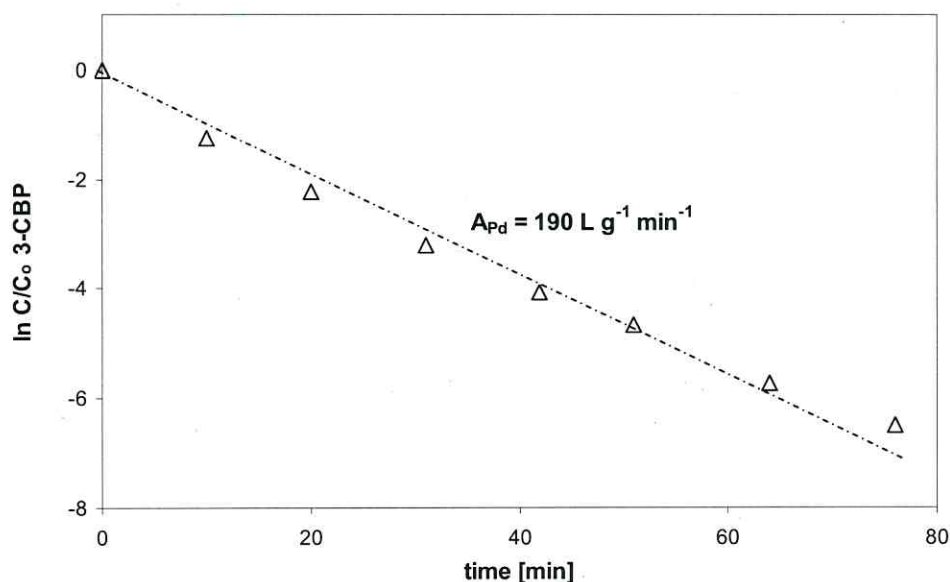
Figure 1. Hydrodechlorination kinetics of 3-CBP with Pd/Al$_2$O$_3$ in water (pH 8.3, $c_{0,3\text{-CBP}}$ = 2.5 mg L^{-1}, c_{cat} = 125 mg L^{-1}). The calculated catalyst activity (A_{Pd}) is taken as the reference activity of the catalyst for dechlorination without interfering effects of co-solvent or surfactants.

The data shown in Figure 1 deliver a specific catalyst activity of about 190 L g^{-1} min^{-1}. 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/Al$_2$O$_3$ (cf. Table 1). Apparently, the transition states in the HDC reaction at the palladium 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. [3] can also be applied to the present catalyst (size fraction 25-63 μm, A_{Pd} = 200 L g^{-1} 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 ($\bar{c}_{pore,i}$ / $\bar{c}_{bulk,i}$) 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 palladium for various classes of catalyst poisons, including many sulfur 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 ($c_{SDBS} = 200$ mg $L^{-1} <$ CMC $\approx 900 \pm 500$ 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.

Table 1:   Catalyst activities for the hydrodechlorination of different palladium catalysts in various reaction media.

Catalyst	Reaction medium	Specific catalyst activity A_{Pd} [L g^{-1} min^{-1}]		
		3-CBP	MCB	TCE
log K_{OW}		4.40	2.84	2.26
Pd/Al$_2$O$_3$ (0.5 wt% Pd)	Water[a]	190 ± 20[b]	150 ± 15	200 ± 20
	SDBS (CMC = 900 ± 500 mg L^{-1})			
	c_{total} = 200 mg L^{-1}	160		
	950 mg L^{-1}	65		
	1500 mg L^{-1}	55		
	CTMAOH (CMC ≈ 450 mg L^{-1})			
	c_{total} = 450 mg L^{-1}	80		
	Tween 80 (CMC ≈ 15 mg L^{-1})			
	c_{total} = 5 mg L^{-1}	220		
	15 mg L^{-1}	220		
	25 mg L^{-1}	220		
	Triton X-100 (CMC ≈ 150 mg L^{-1})			
	c_{total} = 150 mg L^{-1}	230		
	20 vol% methanol	155		
	Soil extract (c_{DOC} = 20 mg L^{-1})	15		
	50 μM NaHSO$_3$[c]		< 0.1	< 0.1
PDMS/Pd/Al$_2$O$_3$ (0.35 wt% Pd)	Water[a]		50 ± 5	80 ± 10
	50 μM NaHSO$_3$		20	45
	Soil extract, 1h		35	
	Soil extract, 24 h		10	
Pd/PDMS (5.6 wt% Pd)	Water[a]		2.5 ± 0.3	
	Soil extract, 24 h		2.3 ± 0.3	

[a] Deionized water + 5 mM NaHCO$_3$ (pH 8.3).
[b] Mean deviation of three single values from the mean value.
[c] S:Pd = 10 moles per mole.
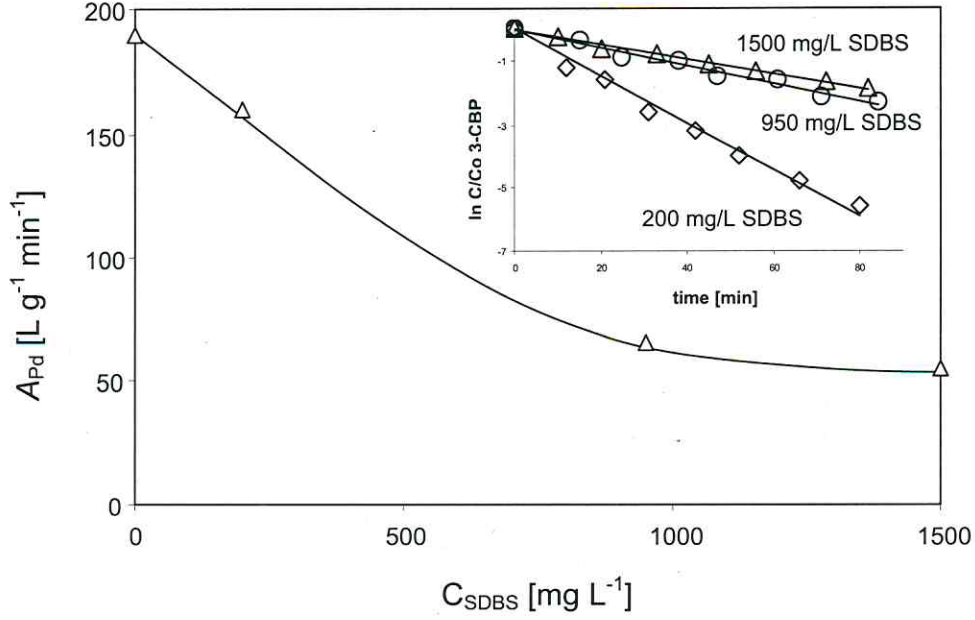
Figure 2. Catalyst activity (A_{Pd}) of Pd/Al$_2$O$_3$ for the HDC of 3-CBP in the presence of SDBS at various concentrations (pH 8.3, $c_{0,3-CBP}$ = 2.5 mg L^{-1}, c_{cat} = 125 mg L^{-1}). The insert shows the original kinetic data for three HDC runs in the presence of SDBS.

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:

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

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 ($X_{freely\ dissolved}$) 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_{Pd} = 55 vs. 65 L g^{-1} min^{-1}). Apparently, sorption of the substrate on the palladium 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. Figure 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/Al$_2$O$_3$. At a total surfactant concentration close to its CMC a catalyst activity A_{Pd} = 80 L g^{-1} 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 (S^{4+} or N^{3-}) plays a decisive role. The positive message is that the palladium 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 (Figure 3). Compared with the reference solution (clean water at pH 8.3) Tween 80 generates a slight but relatively 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. Triton X-100 is another commercially available non-ionic surfactant, but with a 10-fold 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 L g^{-1} 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/Al$_2$O$_3$. 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 (pH_{pzc} ≈ 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.
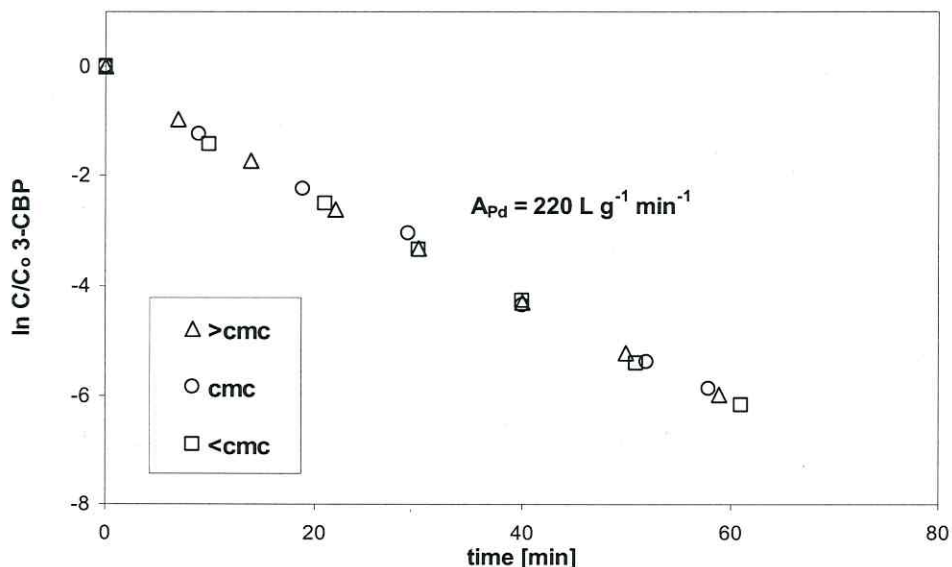
Figure 3.   Effect of the non-ionic surfactant Tween 80 on the HDC of 3-CBP with Pd/Al_2O_3. Variation of $c_{Tween80}$ from 5 mg L^{-1} (< CMC) via 15 mg L^{-1} (≈ CMC) to 25 mg L^{-1} (> CMC). (pH 8.3, $c_{0,3-CBP}$ = 2.5 mg L^{-1}, c_{cat} = 125 mg L^{-1})

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_{Pd} = 155 L g^{-1} 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]:

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

where $\gamma_{i,mixture}$ and $\gamma_{i,water}$ are the activity coefficients of the solute i, $\sigma_{i,solvent}$ is commonly referred to as the co-solvency power of the solvent, and $f_{solvent}$ is its volume fraction ($0 < f_{solvent} < 1$) in the aqueous mixture. With $\sigma_{3\text{-}CBP,methanol} \approx 3.0$ and $f_{methanol} = 0.2$ it follows $\gamma_{i,mixture} / \gamma_{i,water} \approx 4$. 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 and Al-Abed [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/Al_2O_3 catalyst is fed with external hydrogen, the second reason can be ruled out. Apparently, substrate sorption equilibria at the palladium sites do not play a decisive role for the overall reaction rates. Moreover, the solvation power of the applied solvent mixture ($H_2O : MeOH = 80 : 20$) is sufficient for fast chloride desorption. Thus, no chloride poisoning of the catalyst was observed [38].

Wee and Cunningham studied the palladium-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 Ref. [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 Ref. [39] (catalyst: 1 wt% Pd on $\gamma\text{-}Al_2O_3$) are similar to that measured in our study ($A_{Pd} = 200\text{-}300$ L g^{-1} min^{-1} vs. 155-190 L g^{-1} min^{-1}).

*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 $c_{DOC} \approx 20$ mg L^{-1} which corresponds to a DOM concentration of $c_{DOM} \approx 40$ mg L^{-1}. The HDC of 3-CBP was conducted in this supernatant without any dilution or pretreatment. The resulting initial catalyst activity of $A_{Pd} = 15$ L g^{-1} 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 ≥ 24 h.

The palladized-ZVI reagent applied by Fang and Al-Abed [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].

Protection of palladium catalysts by polymer coatings

In order to protect the sensitive palladium 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 ($D_{MCB} \approx 10^{-6}$ cm^2 s^{-1}) which is only a factor of about 10 lower than for liquid water. Figure 4 shows a schematic presentation of a porous catalyst carrier which is filled and coated with a non-porous polymer material. The non-ionic reactants RCl, RH and H$_2$ have unlimited access to the palladium 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 palladium 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.
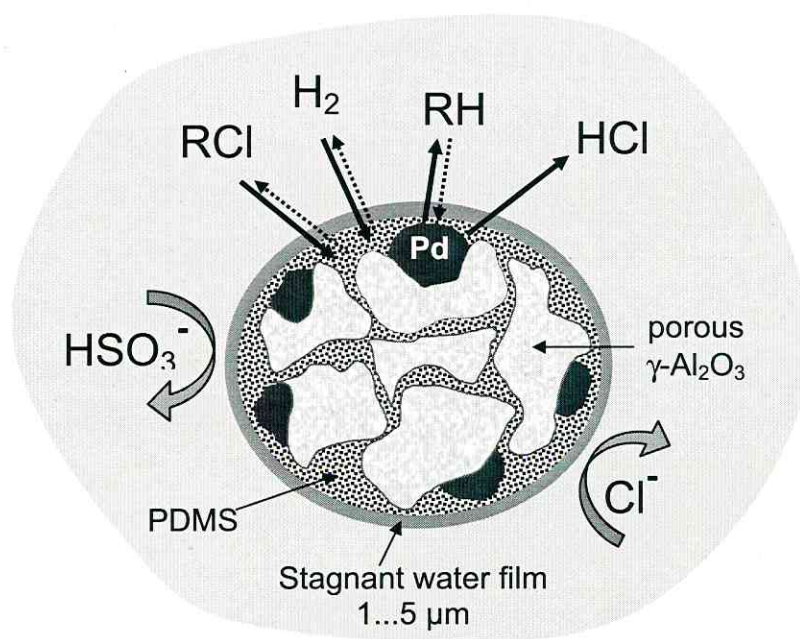
Figure 4.   Schematic presentation of the hydrodechlorination sub-steps at a porous Pd/Al$_2$O$_3$ catalyst which is impregnated with about 30 wt% of a non-porous silicone polymer (PDMS).

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 NaHCO$_3$ at pH $\approx$ 8.3, $c_{0,MCB} = c_{0,TCE} = 20$ mg L^{-1}, $c_{cat} = 125$ mg L^{-1}) and compared with that of the virgin catalyst. The activities for the HDC of MCB were $A_{Pd} = 150$ and 50 L g^{-1} min^{-1} and for the HDC of TCE $A_{Pd} = 200$ and 80 L g^{-1} min^{-1}, respectively. Obviously, the coating caused a loss of activity by a factor of about 3 as also found in Ref. [6]. Next, the protection efficacy of the silicone coating was tested by applying the ionic catalyst poison bisulfite. 50 μM NaHSO$_3$ was added to a catalyst suspension without silicone layer containing 5 μM unprotected palladium (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 ($A_{Pd} < 0.1$ L g^{-1} min^{-1}). The unprotected catalyst was completely deactivated.

It is not obvious from this experiment whether sulfite itself or its reduction product sulfide is the active catalyst poison. Sulfide is well-known as a strong palladium catalyst poison. In order to distinguish between the two possibilities, the catalyst was treated with bisulfite 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 sulfite, and tested for its HDC activity. The catalyst was also completely deactivated in this case. This experiment shows unambiguously that sulfite and/or bisulfite are the active catalyst poisons in our experiments. The distinction between sulfite and sulfide might be important because sulfide has different penetration properties: due to its protonation equilibria ($pK_{A1} \approx 13$, $pK_{A2} = 7.05$) sulfide is present as H$_2$S under neutral conditions. H$_2$S is able to penetrate non-porous silicone polymer coatings even faster than H$_2$ [44].

Applying the same deactivation procedure to the silicone-coated catalyst (1 h exposure to 50 μM bisulfite under hydrogen purging) resulted in only a slight deactivation. TCE and MCB were completely dechlorinated with $A_{Pd} = 45$ and 20 L g^{-1} min^{-1}, respectively, which corresponds to about 50% of the initial catalyst activity. The dechlorination followed first-

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order kinetics in both cases. Obviously, a large fraction of the palladium sites were protected against sulfite. 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 bisulfite which is the dominating species under slightly acidic conditions ($pK_{A1} = 1.8$, $pK_{A2} = 7.0$).

Applying the soil extract as reaction medium, the catalyst activity of the silicone-coated palladium catalyst decreased from $A_{Pd} = 50$ to 35 and 10 L g^{-1} 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 palladium catalyst has been described in Refs. [6, 33]. It contains 5.6 wt% of palladium clusters ($d_{cluster} \approx 5$ nm) embedded in a PDMS membrane in a triple-layered arrangement (thickness ≈ 330 µm) [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 ($A_{Pd} \approx 2.5$ L g^{-1} min^{-1}) is significantly lower than that of the alumina-supported catalyst. One reason for the lower apparent palladium 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 palladium sites are steadily protected against particulate and dissolved constituents of a soil extract.

Conclusions

Results obtained in this study show that Pd/Al$_2$O$_3$ 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 palladium catalyst.

The stability of the catalyst was significantly improved by coating with silicone polymers. This modified Pd/Al_2O_3 catalyst was partly protected against ionic poisons such as bisulfite and NOM. Despite the significantly altered chemical environment around the palladium 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 ($A_{Pd} \approx 80$ to 2.3 L g^{-1} min^{-1}) with those of unprotected Pd/Al_2O_3 catalysts in long-term operation under field conditions ($A_{Pd} \approx 0.05$ L g^{-1} 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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6 Summary

Chlorinated organic compounds (COCs) are environmentally relevant chemicals because they are commonly found as pollutants in environmental media, such as in surface water, groundwater, soils and sediments. The presence of COCs in the environment and their antagonistic impact on wildlife and human health necessitates a remedial action of contaminated areas. Hydrodechlorination is a promising treatment technique whereby chlorinated pollutants are transformed, in most cases, to less or non-harmful substances. This employs palladium-based catalysts, for example palladium on γ-alumina support (Pd/Al_2O_3), to catalyze the reductive dechlorination of COCs to non-chlorinated hydrocarbon products. In aqueous phase, Pd/Al_2O_3 catalytically reduced a wide range of chlorinated pollutants at high reaction rates under ambient conditions. Hence, this encourages the application of palladium catalysts for pollution abatement, such as in groundwater remediation and wastewater treatment. The successful full-scale application of palladium is, however, oftentimes hindered by the deactivation of the catalyst caused by dissolved water constituents. In particular, poisoning of the noble metal induced by reduced sulphur compounds (e.g. sulfides) is a critical problem.

In this thesis, the protection and regeneration of palladium catalysts are principally dealt with to allow a stable catalytic performance under environmental conditions. In addition, the further applicability of palladium as hydrodechlorination catalyst in complex wastewater effluents is introduced. In the first approach (as presented in the first manuscript), protective measures in the form of oxidative water pretreatment were carried out. Potassium permanganate was applied to oxidize and remove sulfides before they have the chance to come into contact with palladium and to induce the poisoning of the catalyst. Experimental results showed that permanganate was efficient in oxidizing not only the inorganic sulfides and sulfite but also organosulfides like dimethyldisulfide and mercaptans. Thus, the complete removal of catalyst poisons had led to the successful hydrodechlorination of the test substance

chlorobenzene in the pretreated water. However, the dechlorination reaction was initially inhibited as a consequence of the residual permanganate which was not consumed during the pretreatment procedure. The inhibitory effect of permanganate can be explained by a competition between permanganate and chlorobenzene for activated hydrogen provided at the palladium surface. The hydrophobically protected catalysts (e.g. Pd/PDMS, Pd/zeolite) appeared to be more stable against permanganate than the naked catalyst Pd/Al$_2$O$_3$. Permanganate at a concentration level of ≥ 0.08 mM temporarily inhibits the reductive dechlorination on Pd/Al$_2$O$_3$ while a 10-fold concentration of the oxidant did not cause any inhibitory effect on the membrane-coated catalyst Pd/PDMS. This may be attributed to the impermeability of the non-porous PDMS film for the permanganate ion. The inhibitory effect of permanganate can be avoided by quenching with hydrazine or by adjusting the concentration to a threshold level (e.g. 0.08 mM for catalyst Pd/Al$_2$O$_3$) whereby the desired hydrodechlorination is not inhibited. This further allows a steady presence of permanganate in the reaction medium which can act as biocide. As biocide, permanganate can prevent undesired microbial activity so that *in situ* production of sulfides in the H$_2$-fed reactors is prevented. This is the technical implication of such an approach which harness the potential of palladium catalysts for treating chlorinated pollutants in real waters.

Nonetheless, in the event of catalyst poisoning it is of great advantage if a simple but efficient regenerative measure is available in restoring the catalyst performance. Hence, the second approach (as presented in the second manuscript) describes the liquid phase regeneration of sulfide-deactivated catalysts using permanganate. At first, the inherent stability of the tested catalyst Pd/Al$_2$O$_3$ in clean water and its deactivation behaviour in the presence of sulfides were elaborately investigated. Experimental results showed that parameters such as number of reaction cycles, catalyst ageing and the pH value of the reaction medium do not significantly affect the stability and the activity of the palladium catalyst for hydrodechlorination. This is an important technical application when Pd/Al$_2$O$_3$ is to be

applied for long-term operation. The addition of sulfides into the catalyst suspension resulted in the partial or complete deactivation of Pd/Al$_2$O$_3$. Further pH studies showed that the catalyst seemed to be more resistant to sulfide poisoning under low pH conditions (e.g. pH 3). But the exposure of the catalyst to higher doses of sulfide (e.g. 14 mM, S : Pd$_{surface}$ = 12 atoms per atom) resulted in the fast and complete deactivation of the catalyst regardless of the pH condition of the bulk phase. The liquid phase regeneration of sulfide-fouled Pd/Al$_2$O$_3$ with permanganate ensured the recovery of the catalyst performance. Moreover, the efficacy of permanganate as oxidative regenerant showed strong pH dependence. Regeneration under neutral to basic conditions showed a complete but relatively slow recovery of the catalytic activity of Pd/Al$_2$O$_3$. But when regeneration was conducted at low pH values (i.e. pH 3) the fouled catalyst was completely re-activated in a short period of time ranging from 10-30 min. The effective regeneration of the fouled catalyst under acidic conditions may be accounted to the higher redox potential of permanganate (MnO$_4^-$ + 8 H$^+$ + 5 e$^-$ $\rightarrow$ Mn^{2+} + 4 H$_2$O with E$^\circ$ = 1.51 V). Additionally, the positive surface charge of the carrier alumina at low pH value may facilitate the access of permanganate anion to the palladium sites. This simple and efficient regenerative treatment contributes significantly to the recycling of sulfide-deactivated catalyst which is an important aspect in industrial and environmental catalysis.

Furthermore, the possible applicability of palladium as hydrodechlorination catalyst for polychlorinated biphenyls extracted into the co-solvent or surfactant-based solution is introduced in the third manuscript. Results from batch experimental studies showed that Pd/Al$_2$O$_3$ can catalyze the reductive dechlorination of the test substance 3-chlorobiphenyl at appreciable reaction rates, almost similar to that obtained in the hydrodechlorination of simpler substrates like chlorinated ethenes and benzene. However, the presence of co-solvent or surfactant in the reaction medium slightly influenced the overall rate of hydrodechlorination depending on the type and concentration of the additives. The non-ionic surfactants like Tween 80 and Triton X-100 promotes a slight enhancement of the catalyst

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activity. On the contrary, charged surfactants like CTMAOH and SDBS seemed to exhibit slight antagonistic effects. These effects may become notable when the surfactant (e.g. SDBS) is applieded at higher concentrations. It should be noted that surfactants above their critical micelle concentration may affect the solubility of the substrate. Additionally, surfactant monomers or aggregates may attach to the solid catalyst forming hydrophobic layers around the palladium clusters. This may consequently affect the sorption and partitioning processes of the substrate and may increase or decrease the concentration of the substance available for dechlorination. Since the general effect of surfactants on the catalyzed reaction is minimal and less pronounced, sorption of the substrate on the palladium sites may not be the major rate-determining step. In addition, the presence of co-solvents (i.e. 20 vol% methanol) in the solution matrix did not significantly affect the catalyst activity of Pd/Al_2O_3. Co-solvents can enhance the solubility of the hydrophobic substrate and can cause a shift in the substrate adsorption equilibrium. Since the catalyst activity obtained in water-methanol mixtures is slightly lower than that obtained in pure water, it shows again that substrate sorption equilibria at the palladium sites do not play a decisive role for the overall reaction rates. It should be noted that the presence of 20 vol% methanol in the reaction medium also decreased the chemical activity of 3-chlorobiphenyl by a factor of about 4 compared with pure water, but interestingly, this change in chemical activity is not reflected in the obtained hydrodechlorination rates in water-methanol mixtures. However, the catalyst activity of Pd/Al_2O_3 was markedly decreased when hydrodechlorination of the test substrate was conducted in soil slurry supernatant. This may be caused by the presence of natural organic matter (NOM) which may competitively adsorb at the catalyst surface blocking the reactive sites. Nevertheless, the coating of the catalyst with a silicone polymer (i.e. with SE30) had protected the catalyst not only from NOM present in soil slurry supernatant but also from catalyst poisons like bisulfite.

In conclusion, the high catalytic activity of palladium catalysts can be exploited for the treatment of chlorinated organic pollutants found in environmental media such as groundwater and also for the treatment of wastewater effluents obtained from soil washing. The coating of the catalyst with a hydrophobic membrane can protect the palladium active sites from ionic solutes and improve its stability. The total protection of the catalyst against sulfide-induced poisoning can be achieved by conducting oxidative water pretreatment. As an alternative approach, sulfide-fouled catalysts can be efficiently re-activated by liquid phase oxidative regeneration with permanganate. In general, these protective and regenerative measures against sulfide poisoning are of high practical significance in terms of realizing the potential of palladium catalysts for pollution abatement.

Zusammenfassung

Chlorkohlenwasserstoffe (CKW) sind umweltrelevante Chemikalien, weil sie häufig als Schadstoffe in Oberflächengewässern, im Grundwasser, im Boden und in Sedimenten zu finden sind. Die schädliche Wirkung von CKW auf die Umwelt und die menschliche Gesundheit erfordert in vielen Fällen eine aktive Sanierung kontaminierter Areale. Die Hydrodechlorierung ist eine viel versprechende Reaktionsklasse, durch die CKW mit nur sehr wenigen Ausnahmen in ungefährliche oder weniger gefährliche Substanzen umgewandelt werden. Dazu werden Palladium-basierte Katalysatoren, zum Beispiel Pd auf Aluminiumoxidträgern eingesetzt. In wässrigen Lösungen reduziert der Katalysator Pd/Al$_2$O$_3$ mit molekularem Wasserstoff eine Vielzahl von CKW mit hoher Reaktionsgeschwindigkeit bei Umgebungsbedingungen. Darum sollten sich Palladium-basierte Katalysatoren prinzipiell zum Reinigen von Grundwasser und für die selektive Behandlung von Abwässern eignen. Jedoch wird ein erfolgreicher Einsatz von Palladium-basierten Sanierungsmaßnahmen oft durch die Desaktivierung des Katalysators durch andere Wasserbestandteile als CKW behindert. Insbesondere die Empfindlichkeit des Edelmetalls gegen Vergiftung durch reduzierte Schwefelverbindungen (z. B. Sulfide) ist ein Problem.

Die vorliegende Arbeit befasst sich hauptsächlich mit dem Problem der sulfidinduzierten Desaktivierung von Palladiumkatalysatoren. Es wurden Schutzmaßnahmen und regenerative Maßnahmen vorgestellt, die eine stabile Katalyseleistung unter realen Bedingungen erlauben können. Im ersten Ansatz (wie im ersten Manuskript dargestellt) wurde die „oxidative Vorbehandlung" als Schutzmaßnahme untersucht. Hierbei wurden reduzierte Schwefelverbindungen entfernt, bevor sie in Kontakt mit Palladium kommen und zu einer Vergiftung des Katalysators führen konnten. Die oxidative Vorbehandlung des Wassers wurde mit Kaliumpermanganat als selektivem Oxidationsmittel für die Schwefelverbindungen durchgeführt. Die Ergebnisse des Batchexperiments zeigen, dass Permanganat eine große Anzahl von potentiellen Katalysatorgiften einschließlich

anorganischer Sulfide und Sulfite, aber auch Mercaptane und Dimethyldisulfid schnell und vollständig entfernt. Reduzierter Schwefel wird dabei zu Sulfat oxidiert. Die anschließende Hydrodechlorierung der CKW kann danach erfolgreich durchgeführt werden. Jedoch wird die Dechlorierung durch einen Überschuss an Permanganat in der Wasserphase zeitweise gehemmt. Überschüssiges Permanganat konnte mit Hydrazin gequencht werden, welches dann auch gleichzeitig als zusätzlicher Wasserstoffspender für die Hydrodechlorierung diente. Permangant kann aber auch unter einem Schwellenwert von 0,08 mM gehalten werden, unter dem die Hydrodechlorierung nicht mehr inhibiert wird. Das Vorhandensein von Permanganat in der Wasserphase hat noch einen zusätzlichen Vorteil, nämlich seine Wirkung als Biozid. Permanganat kann unerwünschte mikrobielle Aktivität im Reaktionsmedium unterbinden, so dass im Reaktor die *In-situ*-Produktion von Sulfiden und das Biofouling des Katalysators verhindert werden. Diese präventiven Maßnahmen gegen die Sulfidvergiftung mit Hilfe der oxidativen Wasservorbehandlung erlauben den Einsatz von Palladium zur Behandlung von chlorierten Schadstoffen unter Realbedingungen.

Dennoch ist es von großem Vorteil, eine einfache und effiziente regenerative Maßnahme zur Wiederherstellung der Katalysatorleistung verfügbar zu haben. Diese ist dann im Fall der Katalysatorvergiftung hilfreich. Darum befasste sich der zweite Ansatz (wie im zweiten Manuskript dargestellt) mit der Regeneration des Sulfid-desaktivierten Katalysators mit Permanganat in der Wasserphase. Untersuchungen über die Stabilität des getesteten Katalysators Pd/Al$_2$O$_3$ in sauberem Wasser und des Desaktivierungsverhaltens in Gegenwart von Sulfiden zeigten, dass Parameter, wie die Anzahl der durchlaufenen Reaktionszyklen, die Katalysatoralterung und der pH-Wert des Reaktionsmediums, keine signifikanten Auswirkungen auf die Aktivität des Palladiums hatten. Der Zusatz von Sulfiden, selbst in Spuren, in die Katalysatorsuspension führte zu einer schnellen und vollständigen Desaktivierung von Pd/Al$_2$O$_3$. Jedoch zeigten Untersuchungen zum Einfluss des pH-Wertes, dass der Katalysator im sauren Milieu resistenter gegen die Sulfidvergiftung war. Offenbar

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sind die ionischen Spezies HS⁻ und S^{2-} noch stärker inhibierend wirksam als die nichtionische Spezies H_2S (pK_{S1} = 7,05). Wurde der Katalysator aber hohen Konzentrationen an Sulfid ausgesetzt, führte dies immer zu einer vollständigen Desaktivierung, unabhängig vom pH-Wert der Bulkphase. Die Regeneration des Sulfid-vergifteten Pd/Al_2O_3 in wässriger Suspension führte zu einer erfolgreichen Wiederherstellung der Katalysatorleistung. Die Wirksamkeit von Permanganat als oxidatives Regenerationsmittel für vergiftete Katalysatoren war darüber hinaus stark vom pH-Wert abhängig. Eine Regeneration unter basischen bis neutralen Bedingungen zeigte eine vollständige, aber langsame Wiederherstellung der katalytischen Aktivität von Pd/Al_2O_3. Wurde die Regeneration bei einem niedrigen pH-Wert durchgeführt, war der Katalysator innerhalb eines kurzen Zeitraums von 10 bis 30 Min. reaktiviert. Dieses wichtige Ergebnis zeigt eine effiziente Methode auf, Sulfid-vergiftete Katalysatoren unter Umgebungsbedingungen zu regenerieren.

Weitere experimentelle Untersuchungen wurden durchgeführt, um das hohe Potenzial von Palladium für die Hydrodechlorierung von CKW auf eine komplexere Wassermatrix zu erweitern. Hier wurden als Beispiel Abwässer aus Bodenwäschen betrachtet. Die Abwässer sind sekundäre Abfallströme, die beim Waschen oder der Extraktion von Böden mit Lösungsvermittlern wie Co-Solventien oder tensidbasierten Lösungen entstehen. Dies erleichtert die Extraktion von stark hydrophoben chlorierten Schadstoffen, wie z. B. polychlorierten Biphenylen (PCB), aus der Bodenmatrix. Wie in Batch-Versuchen gezeigt wurde, kann Pd/Al_2O_3 PCB mit beachtlichen Reaktionsraten reduktiv dechlorieren, ähnlich den für einfachere Substrate, wie chlorierte Ethene und Benzol, gefundenen. Darüber hinaus wurde die Reaktionsrate der Hydrodechlorierung durch die Gegenwart von Co-Solventien oder Tensiden nicht signifikant beeinflusst, wobei aber Tendenzen erkennbar waren. Nichtionische Tenside wie Tween 80 und Triton X-100 erhöhten die katalytische Aktivität für die Dechlorierung leicht. Dodecylbenzolsulfonat (SDBS) als anionisches Tensid zeigte einen schwach hemmenden Effekt, wobei dieser für hohe Konzentrationen oberhalb der kritischen

Mizellkonzentration (CMC) stärker ausgeprägt war. Außerdem wurde die Katalysatoraktivität von Pd/Al$_2$O$_3$ durch das Vorhandensein von Methanol als Co-Solvenz bis zu einer Konzentration von 20 Vol.-% in der Lösungsmatrix kaum beeinflusst. Der Katalysator zeigte aber eine viel geringere Aktivität, wenn die Hydrodechlorierung im wässrigen Überstand einer Bodenextraktion durchgeführt wurde. Dies kann durch z.T. kolloidal gelöstes natürliches organisches Material (NOM, DOM) verursacht sein, welches an der Katalysatoroberfläche adsorbiert wird und damit die reaktiven Palladium-Zentren für die Dechlorierung blockiert. Die Beschichtung des Katalysators mit dem Silikonpolymer SE-30 schützte den Katalysator nicht nur vor NOM, sondern auch vor Katalysatorgiften wie dem Bisulfit.

Als Fazit kann gesagt werden, dass die hohe katalytische Aktivität von Palladium-Katalysatoren zur Behandlung von chlorierten organischen Schadstoffen in natürlichen Wässern (z. B. Grundwasser) und Abwässern (z. B. von Bodenwäschen/-extraktionen) eingesetzt werden kann. Die Beschichtung des Katalysators mit einer hydrophoben Membran schützt die aktiven Zentren des Palladiums vor ionischen gelösten Stoffen und verbessert seine Stabilität unter Realbedingungen. Durch präventive Maßnahmen gegen die Sulfid-induzierte Vergiftung, wie die oxidative Wasservorbehandlung, kann ein vollständiger Schutz des Katalysators erreicht werden. Ein ergänzender Ansatz ist die oxidative Regeneration des vergifteten Katalysators mit Permanganat. Diese regenerativen und schützenden Maßnahmen sind von hoher Signifikanz für die Anwendbarkeit Palladium-basierter Katalysatoren zur Beseitigung chlorierter Wasserschadstoffe in der Umwelt.

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Acknowledgements

Curriculum Vitae

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4th UFZ-PhD Conference
Leipzig, 23 May 2008
Water Remediation with Pd Catalyst: the Ups and Downs

1st BuildMoNa Workshop
Leipzig, 16-17 October 2008
Palladium Catalysts for Environmental Applications

The 2nd WSEAS/IASME International Conference on Waste Management, Water Pollution, Air Pollution and Indoor Air Climate
Corfu, Greece, 26-28 October 2008
Protection and Regeneration of Pd Catalyst for Dechlorination of Contaminants in Groundwater

ICESE 2008: International Conference on Environmental Sciences and Engineering

Venice, Italy, 29-31 Ocotber 2008

Pd-catalyzed Hydrodechlorination for Water Remediation: Catalyst Deactivation and Regeneration

Leipzig, March 2010

Application, Protection and Regeneration of Palladium as Hydrodechlorination

Catalyst for Chlorinated Organic Pollutants

Der Fakultät für Chemie und Mineralogie der Universität Leipzig

eingereicht von

M. Sc. Dalia Angeles-Wedler

im März 2010

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Introduction

Chlorinated organic compounds are man-made chemicals which are indispensable to the society for their industrial and commercial uses. They are largely produced and their unwanted release to the environment is caused by improper disposal, accidents and spillages. Many chlorinated compounds are recalcitrant, that is, they are hardly susceptible to chemical or microbial degradation and so they persist and accumulate in the environment. Furthermore, chlorinated hydrocarbon compounds are known to be toxic to wildlife and they are considered as potential human carcinogens. To counteract these adverse impacts, efficient remediation technologies are highly needed to clean and restore contaminated environmental media. Palladium-based catalysts (e.g. Pd/Al_2O_3) are known to efficiently catalyze the transformation of chlorinated organic compounds to non-chlorinated hydrocarbon products which are less harmful and readily biodegradable. In liquid phase, palladium catalyst together with molecular hydrogen or hydrogen donor catalytically reduces a wide range of chlorinated organic compounds ($R\text{-}X + H_2 \xrightarrow{Pd} R\text{-}H + HX$). The reaction proceeds at high reaction rates under ambient conditions. Thus, this makes palladium-catalyzed hydrodechlorination a promising technique for groundwater remediation and for treatment of wastewater. However, the inherent presence of catalyst poisons (e.g. sulfides) in real water bodies induces a fast and

complete deactivation of the catalyst. This limits and hinders the full environmental application of palladium as hydrodechlorination catalyst for chlorinated organic pollutants.

Practical significance of the study

This thesis work principally addresses the problem of sulfide-induced poisoning of palladium and offers alternative approaches to realizing the high catalytic performance of palladium for pollution abatement. Therefore, this thesis develops a strategy (Manuscript 1) by which sulfide-induced poisoning of palladium is prevented. The approach is presented as oxidative water pretreatment which employs potassium permanganate as preoxidant for sulfur species like hydrogen sulfide, sulfite and organosulfur compounds like mercaptans and dimethyldisulfide. These sulfur compounds are endogenously produced in nature and considered as strong catalyst poisons under natural water conditions. Therefore, the successful removal of catalyst poisons by water pretreatment can allow the effective hydrodechlorination of the target pollutants on the palladium catalyst. In addition, this study also proffers the idea that permanganate can be utilized at the same time as biocide to thwart microbial activity in the reaction bulk phase. It is known that microbial activity in H_2-fed systems is responsible for the production of sulfide inside the reactor. Thus, the steady presence of permanganate (maintained at a certain threshold level) in the bulk phase can hinder the *in situ* production of sulfides and prevent the biofouling of the catalyst bed. This promotes, consequently, a long catalyst life and maintains the high catalytic performance of palladium for the transformations of the chlorinated contaminants.

The sulfide-induced poisoning of palladium is a difficult problem which is not only encountered in aqueous phase hydrodechlorination but also in palladium-catalyzed gas-phase reactions. A typical regeneration procedure for sulfide-fouled catalysts is a high temperature treatment with hydrogen which is, however, energy inefficient and unsuitable for palladium used in liquid phase hydrodechlorination under ambient conditions. Therefore, this thesis further develops and presents for the first time an efficient regenerative measure for sulfide-fouled palladium catalysts (Manuscript 2). This employs potassium permanganate as an oxidative regenerant in restoring catalyst activity. The oxidative regeneration in aqueous phase is optimized so that a low oxidant demand and a short regeneration time in the span of a few minutes are needed to completely recover the catalyst's performance. Most importantly, the presented regeneration procedure can take place under ambient conditions. This simple and cost-effective regenerative treatment can be a major contribution to industrial and environmental catalysis in terms of recycling the catalyst after losing its high initial activity

due to poisoning induced by sulfur species. In addition, the wider applicability of palladium-based catalysts to hydrodechlorinate polychlorinated biphenyls in wastewater effluents obtained from soil washing is introduced (Manuscript 3). This can serve as an alternative treatment method to detoxify pollutants in such a complex matrix system when conventional treatment techniques proved to be inefficient. Moreover, matrix effects exhibited by co-solvent, surfactants and organic matter on the palladium-catalyzed reaction are singly investigated. This helps to identify if the presence of additives in the reaction medium either enhances or inhibits the desired catalytic reaction. In such a case where a positive influence is displayed, the reaction can be optimized to bring reaction rate enhancement. In the opposite case, the catalyst can then be protected against the deactivating effect of the background matrix.

Summary of results and discussions

1. Oxidation of sulfur compounds to prevent poisoning of palladium catalysts

This part of the thesis deals with a strategy whereby the sulfide-induced poisoning of the palladium catalyst (e.g. Pd/Al_2O_3) is prevented. This is achieved by conducting oxidative water pretreatment whereby sulfide species in the aqueous bulk phase are removed by oxidation. Potassium permanganate was employed as preoxidant and proved to be efficient in selectively oxidizing potential catalyst poisons like the reduced sulfur compounds (RSCs). The complete removal of the catalyst poisons led to the successful dechlorination of the test substance chlorobenzene (MCB) in the permanganate-treated water samples (Figure 1). Also shown in Figure 1 is the initial inhibition of the dechlorination reaction which was a consequence of the residual permanganate which was not consumed during the pretreatment procedure. However, the addition of hydrazine quenches the surplus permanganate instantaneously so that the dechlorination of MCB proceeded immediately, delivering a catalyst activity (A_{Pd}) similar to the initial catalyst activity in clean deionized water, that is, in the range of 150-200 L g^{-1} min^{-1}. Interestingly, the catalyst showed no deactivation behaviour when the concentration of permanganate in the bulk phase is at a concentration level of ≤ 0.07 mM. With a residual oxidant concentration of ≥ 0.08 mM, a significant inhibition of the dechlorination was observed. The inhibitory effect of permanganate on the palladium-catalyzed reaction is only temporary as shown in Figure 2. At extended reaction times the dechlorination reaction re-starts and the catalyst regains its original catalytic performance. Also shown in this graph is the kinetics of permanganate reduction in the reaction mixture. Notably, the reduction of MCB is inhibited while the reduction of permanganate takes place.

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The temporary inhibitory effect of permanganate can be explained by a competition between permanganate and chlorobenzene for activated hydrogen provided at the palladium surface.
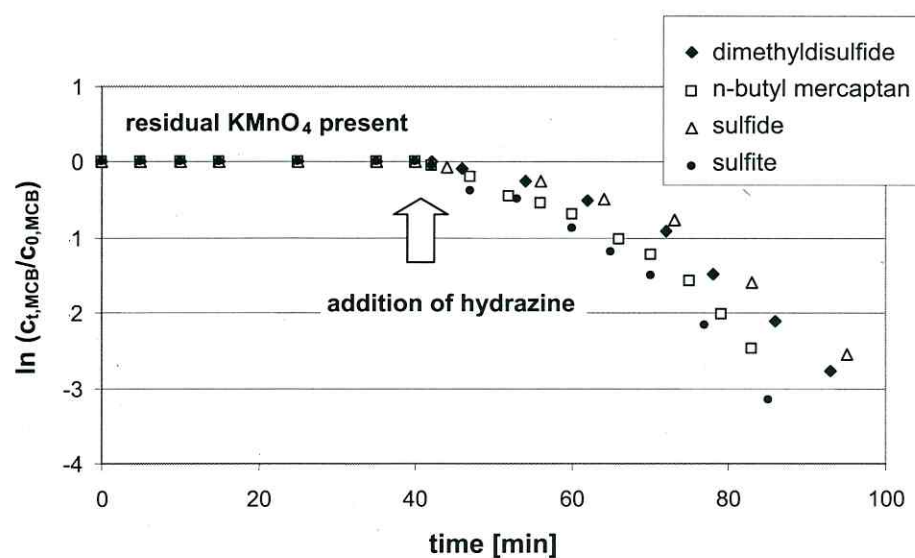
Figure 1: Hydrodechlorination of chlorobenzene over Pd/Al$_2$O$_3$ in permanganate-treated water samples that were contaminated with RSCs, demonstrating the inhibitory effect of excess residual permanganate on the catalyst after RSC oxidation (S : Pd = 8…20 moles per mol, $c_{0,MCB}$ = 20 mg L^{-1}, c_{Pd} = 0.75 mg L^{-1}, $c_{0,RSC}$ = 5 mg L^{-1}, $c_{0,KMnO4}$ = 0.6 to 2.7 mM).
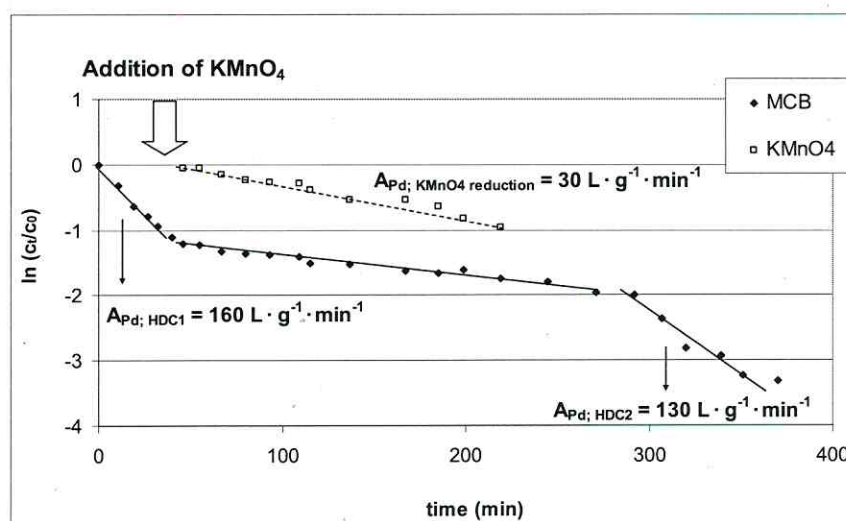
Figure 2: Temporary inhibitory effect of KMnO$_4$ on the Pd/Al$_2$O$_3$-catalyzed hydrodechlorination of chlorobenzene (c_{Pd} = 0.25 mg L^{-1}, $c_{0,MCB}$ = 20 mg L^{-1}, $c_{0,KMnO4}$ = 0.08 mM).

The hydrophobically protected catalysts (e.g. Pd/PDMS and Pd/zeolite) showed higher tolerance to permanganate whereby the presence of a 10-fold concentration of the oxidant in the reaction medium did not inhibit the reductive dechlorination of MCB on the membrane-based catalyst Pd/PDMS. This can be attributed to the impermeability of the non-porous PDMS film for the permanganate ion. However, permanganate still takes place and this can be accounted to the small fraction of palladium still available for the ionic species (e.g. at the outer surface of the PDMS membrane) or that some reducing species (e.g. H*) are sufficiently mobile and long-lived that it reaches the dissolved permanganate (hydrogen spillover).

It should be noted that excess permanganate can additionally act as biocide and thwart microbial activities in H_2-fed systems. But this should be maintained at a concentration level (e.g. ≤ 0.07 mM for the naked catalyst Pd/Al$_2$O$_3$ or 0.8 mM for membrane-based catalyst PDMS) whereby the desired hydrodechlorination reaction is not inhibited.

2. Sulfide-induced deactivation of Pd/Al$_2$O$_3$ and its oxidative regeneration with permanganate

This second part of the thesis investigates in details the inherent stability of the catalyst Pd/Al$_2$O$_3$ in clean water, its deactivation behaviour in the presence of sulfides and its response to a regenerative treatment using aqueous solutions of permanganate. Experimental results showed that parameters such as the number of batch reaction cycles, catalyst ageing and the pH value of the bulk reaction media do not significantly affect the stability and activity of Pd/Al$_2$O$_3$ for reductive dechlorination. However, the presence of sulfides in the reaction medium results in the partial to complete deactivation of the catalyst. Further pH studies showed that the deactivating effect of sulfide on the employed catalyst is more pronounced under neutral to basic conditions (i.e. pH 7-13). However, the exposure of the catalyst to higher sulfide doses (e.g. 14 mM, S : Pd$_{surface}$ = 12 atoms per atom) resulted in the fast and total deactivation of Pd/Al$_2$O$_3$ regardless of the applied pH conditions. The aqueous phase regeneration of the completely deactivated catalyst with potassium permanganate proved to be highly effective under acidic condition. As demonstrated in Figure 3, short regeneration times of 10 min and 30 min completely recovered the catalyst activity. The effective regeneration of the fouled catalyst may be accounted to the higher redox potential of permanganate ($MnO_4^- + 8\ H^+ + 5\ e^- \rightarrow Mn^{2+} + 4\ H_2O$ with E° = 1.51 V) under acidic conditions. Additionally, the positive surface charge of the carrier alumina at low pH value may facilitate the access of permanganate anion to the palladium sites. Remarkably, the hydrodechlorination activity of the newly regenerated Pd/Al$_2$O$_3$ (i.e. A_{Pd} = 466 L g^{-1} min^{-1}) appeared to be even higher than the baseline activity (i.e. A_{Pd} = 120 L g^{-1} min^{-1}) typically

exhibited by the fresh catalyst. The key factors responsible for this accelerating effect are not apparent. They can possibly be accounted to the new catalyst state and composition of the reaction medium resultant of the regenerative treatment.
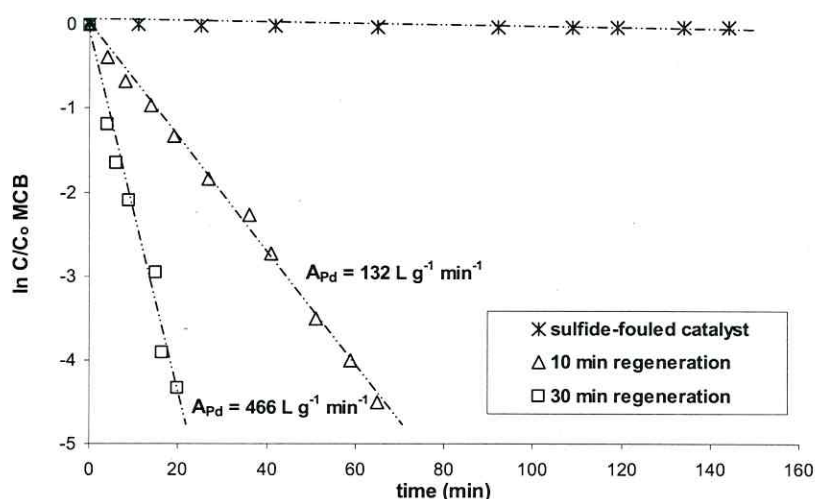

Figure 3.   Recovered catalyst activities (A_{Pd}) after oxidative regeneration of sulfide-fouled Pd/Al$_2$O$_3$ under acidic condition (pH 3). Regeneration was conducted using 0.18 mM KMnO$_4$ for 10 and 30 min (c_{cat} = 150 mg L^{-1}, $c_{0,MCB}$ = 20 mg L^{-1}).

3. Palladium-catalyzed hydrodechlorination of chlorinated aromatics: effects of surfactants, organic matter and catalyst protection by silicone coating

This part of the thesis study introduces the wider applicability of palladium as hydrodechlorination catalyst for polychlorinated biphenyls found in soil washing effluents. These wastewater effluents contain not only the target pollutants but also co-solvents, surfactants and organic matter and, therefore, their effects on the palladium-catalyzed hydrodechlorination were further investigated. Batch hydrodechlorination experiments showed that in clean water, the catalyst Pd/Al$_2$O$_3$ can effectively catalyze the test compound 3-chlorobiphenyl (3-CBP) at reaction rates similar to that obtained in the hydrodechlorination of simpler substrates like chlorinated ethenes and benzenes. The presence of non-ionic surfactants like Tween 80 in the reaction medium afforded a slight but significant increase in catalyst activity of about 15% (i.e. A_{Pd} = 220 L g^{-1} min^{-1}) as shown in Figure 4. This is when compared to the activity obtained in the reference solution without surfactants (i.e. A_{Pd} = 190 L g^{-1} min^{-1}). Additionally, a consistent catalyst activity was maintained even when the surfactant Tween 80 was applied at various concentrations.
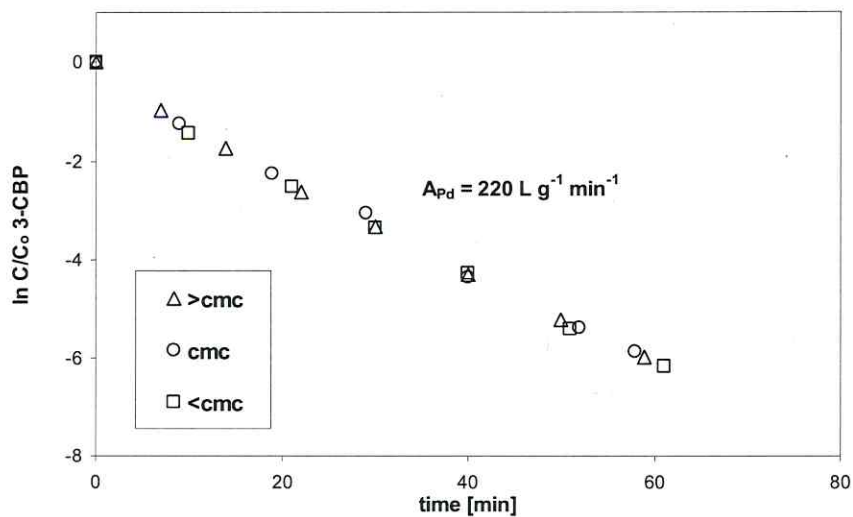
Figure 4. Effect of the non-ionic surfactant Tween 80 on the HDC of 3-CBP with Pd/Al_2O_3. Variation of $c_{Tween80}$ from 5 mg L^{-1} (< CMC) via 15 mg L^{-1} ($\approx$ CMC) to 25 mg L^{-1} (> CMC). (pH 8.3, $c_{0,3-CBP}$ = 2.5 mg L^{-1}, c_{cat} = 125 mg L^{-1})
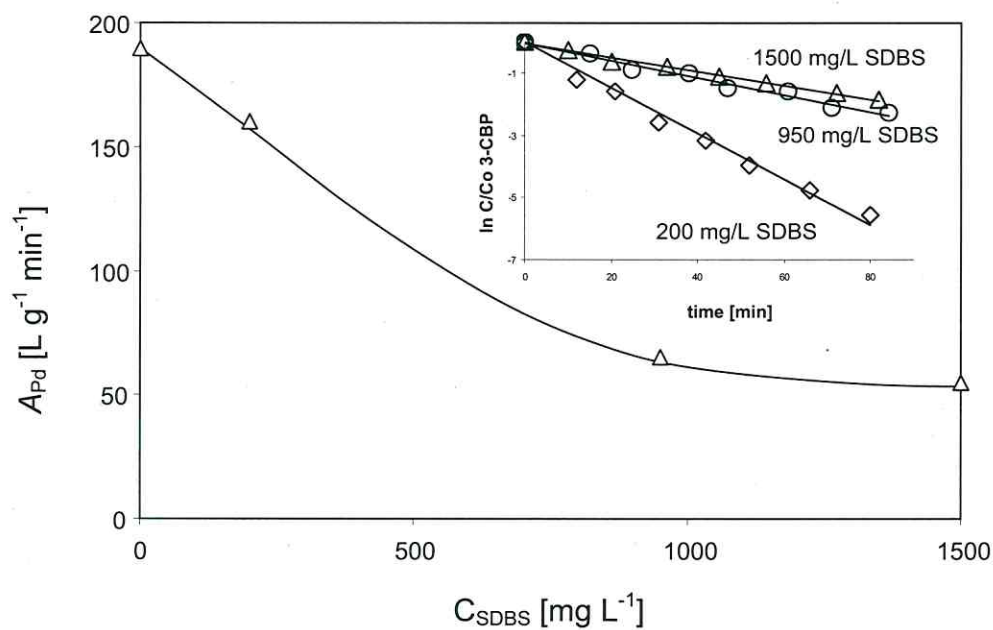
Figure 5. Catalyst activity (A_{Pd}) of Pd/Al_2O_3 for the HDC of 3-CBP in the presence of SDBS at various concentrations (pH 8.3, $c_{0,3-CBP}$ = 2.5 mg L^{-1}, c_{cat} = 125 mg L^{-1}). The insert shows the original kinetic data for three HDC runs in the presence of SDBS.

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In the case of ionic surfactants like CTMAOH and SDBS, they appeared to exhibit slight antagonistic effects on the catalyzed reaction. Figure 5 shows the change in the hydrodechlorination activity of the catalyst Pd/Al_2O_3 in the presence of SDBS surfactant. A pronounced decrease in the catalyst activity was obtained when SDBS was employed at higher concentration. It should be noted that surfactants above their critical micelle concentration may affect the solubility of the substrate. Additionally, surfactant monomers or aggregates may attach to the solid catalyst forming hydrophobic layers around the palladium clusters. This may consequently affect the sorption and partitioning processes of the substrate and may increase or decrease the concentration of the substance available for dechlorination.

Co-solvents, like the surfactants, can also enhance the solubility of the hydrophobic substrate and can cause a shift in the substrate adsorption equilibrium. However, the presence of a co-solvent (i.e. methanol) in the solution matrix up to 20 vol% did not strongly affect the activity of Pd/Al_2O_3. That is, the catalyst activity obtained in water-methanol mixtures is slightly lower than that obtained in pure water. This shows that substrate sorption equilibria at the palladium sites do not play a decisive role for the overall reaction rates.
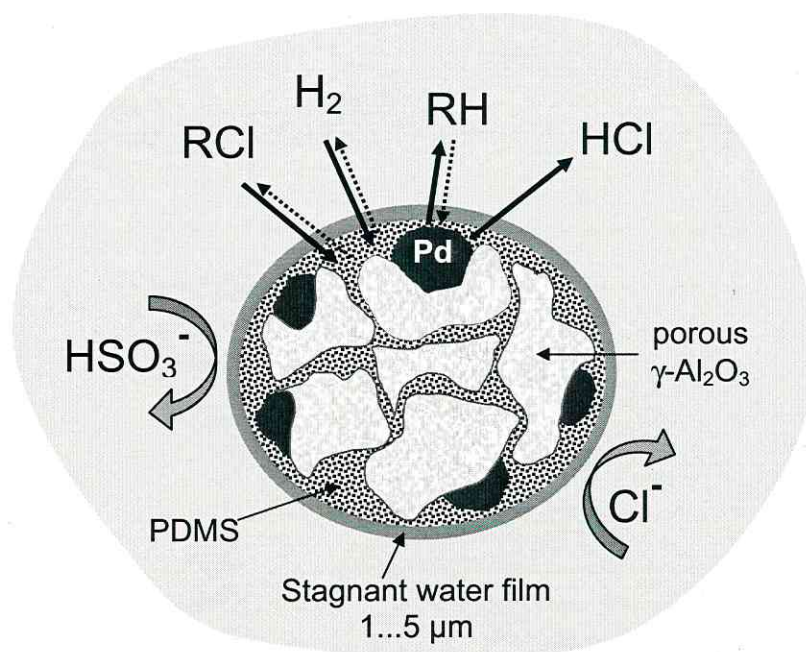
Figure 6.   Schematic presentation of the hydrodechlorination sub-steps at a porous Pd/Al_2O_3 catalyst which is impregnated with about 30 wt% of a non-porous silicone polymer (PDMS).

The hydrodechlorionation of 3-CBP in a soil slurry supernatant (c_{DOM} = 40 mg L^{-1}) afforded a much lower catalyst activity which may results from the competitive adsorption of

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natural organic matter on the catalyst surface. In order to protect the palladium catalyst from the deactivating effect of the background matrix as well as from catalyst poison like bisulfite, the catalyst was coated with a thin non-porous polymer layer (PDMS). Figure 6 illustrates the protection of catalyst by polymer coatings and the hydrodechlorination sub-steps taking place at the impregnated catalyst.

Conclusions

Chlorinated organic compounds are pollutants commonly found in the environment (e.g. in surface water, groundwater, soils and sediments). Hydrodechlorination, catalyzed by palladium, is a promising treatment technique whereby chlorinated organic pollutants are transformed to less or non-harmful substances without leaving spent materials and toxic byproducts. A significant drawback of this method is the sensitivity of palladium to poisoning and deactivation induced by sulfide species and wastewater constituents detrimental to the catalyst (e.g. NOM).

In the first approach, the protection of the catalyst (e.g. Pd/Al_2O_3) from sulfide-induced poisoning was achieved by a combination of oxidative water pretreatment and hydrophobic catalyst protection. By such an approach, sulfides are oxidized and removed before they have the chance to come into contact with the noble metal. The complete removal of sulfides in the water matrix allows the successful dechlorination of the target pollutants. Additionally, the presence of permanganate in the reaction medium does not inhibit the desired reaction when maintained at a certain threshold level (e.g. ≤ 0.07 mM for Pd/Al_2O_3). These experimental results can help to define the design of a flow-through reactor (*ex situ* or *in situ*) in which permanganate can be added prior to the palladium catalyst zone to prevent sulfide-induced deactivation of the noble metal and biofouling of the catalyst bed.

The second approach of the thesis presents a successful regenerative procedure for sulfide-fouled Pd/Al_2O_3. This is conducted in the liquid phase under ambient conditions and employs potassium permanganate. The efficacy of permanganate as oxidative regenerant for the fouled catalyst showed strong pH-dependence. Regeneration under neutral to basic conditions resulted in a complete but relatively slow recovery of the catalyst activity of Pd/Al_2O_3. Under acidic condition (i.e. pH 3), the sulfide-fouled catalyst can be re-activated completely within a short time of 10-30 min. This simple and efficient regenerative treatment is a major contribution in confronting the problem of sulfide-induced poisoning of palladium during industrial and environmental applications. In catalytic processes, it is oftentimes more

economical to regenerate catalysts than to dispose them when a reliable and highly efficient regenerative treatment is available.

Lastly, the further applicability of palladium-catalyzed hydrodechlorination for treating polychlorinated biphenyls in wastewater effluents (e.g. from soil washing) was tested. The effects of additives (e.g. surfactants, co-solvent) on the palladium-catalyzed reaction were, in general, minimal and less pronounced. However, the presence of natural organic matter (NOM) from soil slurry supernatant had deactivated the employed catalyst. Polymer coatings of the catalyst had maintained the catalyst activity for a certain period of time and protected the catalyst from poisons like bisulfite.