Dechlorination of chlorohydrocarbons in groundwater by electrochemical and catalytic reactions

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The high concentration of chloroorganic compounds (COCs) at the Bitterfeld test site requires a fast and complete method suitable for dechlorination of a wide range of dif-ferent COC classes. We chose the reductive dechlorination pathway in order to avoid unpredictable toxic intermediate products, which would have to be considered if an oxidative dechlorination method had been chosen.

In recent years, the traditional pump & treat technology received a strong competitor with the new concept of *in situ* groundwater remediation using reactive iron barriers. The so-called 'rusty walls', which were first developed by GILLHAM and co-workers in 1989 [1] for clean-up of chlorohydrocarbon-contaminated sites, have proved to be a suitable technique.

Metallic iron is able to reduce most aliphatic chlorohydrocarbons to the chlorine-free substances (Equation 1), although with different dechlorination rates.

$$R\text{-}Cl + Fe^0 + H_2O \rightarrow R\text{-}H + Fe^{2+} + OH^- + Cl^- \qquad (1)$$

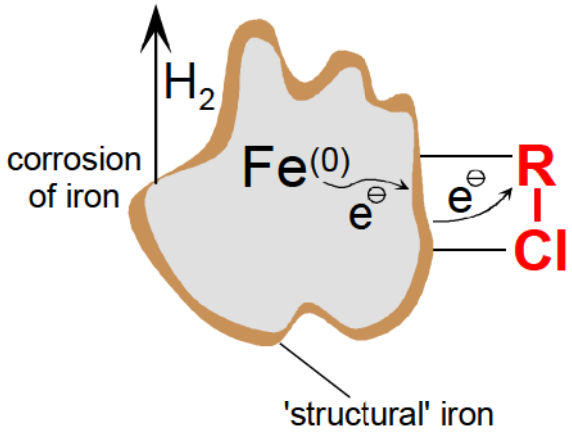

Figure 1 Direct electron transfer as reduction mechanism.

For example, the half-lives for the dechlorination of PCE and TCE are markedly below 1 hour. For other compounds, such as cis-dichloroethylene or vinylchloride, a much longer time period is needed for reduction. Unfortunately, iron fails completely as a reducing agent for compounds such as methylenechloride and the whole class of chlorinated aromatics [1]. Looking at the reduction mechanism using iron barriers,

that is the direct electron transfer from the iron or the so-called structural iron(II)-cation on the iron surface (Figure 1), then it is not immediately apparent why chloroaromatics are not reduced. The reduction potentials for the two-electron-transfer, resulting in chlorine-free hydrocarbons and chloride, are about + 500 mV. The standard redox potential of the iron electrode is about - 440 mV [5]. This means that the free reaction enthalpy for the hydrodechlorination with iron is in the range of about 200 kJ/mol for each dechlorination step. This is actually a very high thermodynamic driving force, whereby the aromatic compounds are no exception. If one assumes that the reduction is a sequence of two single-electron-transfers forming the radical anion in the first step, then the unexpected behavior of the aromatic hydrocarbons can be explained, especially that of monochlorobenzene. The first step of the reduction during a direct electron transfer (e.g. from metallic iron) is therefore kinetically hindered, even though all thermodynamic prerequisites for a successful reduction are fulfilled. Since the thermodynamical conditions for the reduction of chlorobenzene are favourable in principle, a change of the reaction mechanism should lead to success.

We are now using hydrogen as the reducing agent, which is for example always produced by iron-corrosion as shown in the illustration (Figure 2).

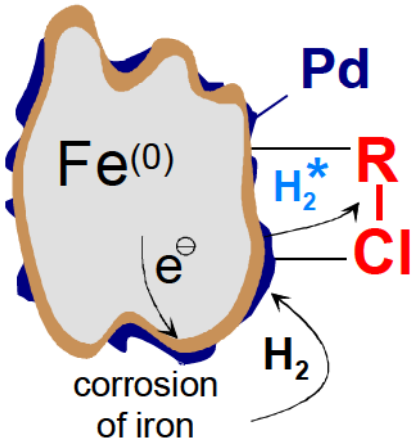

Figure 2 Catalytic hydrodechlorination as reduction mechanism.

Hydrogen is collected and activated by a noble metal catalyst (preferentially Pd), and therefore usable for splitting-off the C-Cl bonds. The reaction is a hydrogenolysis resulting in a fast and complete dechlorination of a broad spectrum of COCs (Equation 2). In contrast to iron, which is stoichiometrically consumed during reduction, the noble metal catalyst is not released into the aquifer.

$$R\text{-}Cl + H_2 \xrightarrow{\text{Pd catalyst}} R\text{-}H + HCl \qquad (2)$$

In water, Pd and Rh catalysts have the highest dechlorination activity. However, Pd causes a pure hydrodechlorination, whereas Rh effects a subsequent hydrogenation to the corresponding naphthenes.

Because the end products of the reaction (the dechlorinated hydrocarbons) are left to be dealt with by the microbiology of the aquifer, their biological degradability is naturally of considerable importance. In the case of the dechlorination products of chlorobenzenes, benzene the more human-toxic, but it is much better biodegradable than cyclohexane. Because of the latter and the lower costs compared with Rh, Pd has been chosen as the preferred catalyst. The Pd catalyst is not dependent upon iron as a carrier: it only requires the availability of hydrogen. Hydrogen can in principle be made available by three methods: from an external source, from iron corrosion (as shown), or electrochemically.

Exactly this principle (in-situ generation of hydrogen and use of a Pd catalyst) was recently described by an American research group [4]. The authors used an electrolytic cell with graphite electrodes to generate hydrogen. The TCE-contaminated water is enriched with hydrogen and the dechlorination occurred at a commercially available Pd/Al_2O_3 catalyst. The system permits relatively high flow rates. The results of McNab & Ruiz show that catalytic dechlorination on a large scale is successful in principle, but they also show that the system has a severely limited life. The catalytic activity is halved after only about 50 hours of operation. Although the catalyst may be regenerated by washing, nevertheless this makes the system unsuitable for *in situ* application. The potential of the catalytic dechlorination technique for in situ groundwater treatment depends mainly on the long-term stability of the catalytic system.

While preparing our field tests evaluating the suitability of the Pd-catalyzed hydrodechlorination for the Bitterfeld groundwater contamination, we carried out extensive laboratory experiments and found commercially available Pd systems (Pd on various oxidic carriers and activated carbon) to be very active hydrodechlorination catalysts. We have also evaluated the lifetime of Pd systems adding various potential catalyst poisons and came to the expected conclusions: when applying active but sensitive catalytic systems, one must always reckon with the problem of deactivation. After adding traces of sulfide ions to the test solution, the Pd-system completely loses its catalytic activity within seconds.

Under aquifer conditions, deactivation occurs mainly due to mechanisms such as poisoning by heavy metal or sulphur compounds. However, suspended matter or biofilms clog the catalytic surface.

Nonetheless, in the SAFIRA pre-study in Bitterfeld we wanted to use a very similar reactor concept: a commercially available Pd catalyst and electrochemical generation of hydrogen by in-situ water electrolysis.

We wanted to learn a bit more about the catalytic dechlorination under groundwater condition and we wanted to overcome the problems, which McNab and Ruiz reported about.

In contrast to [4], we used a separated electrolytic cell, where the anode and cathode compartments are passed subsequently. Because of the high chloride content in the Bitterfeld groundwater, hypochlorite (chlorine) is produced at the anode, which acts as an disinfectant, until it is completely reduced along the cathode. Figure 3 shows the construction scheme of the electro-catalytic reactor (a combined electrolytic cell / fixed-bed catalytic dechlorination reactor).

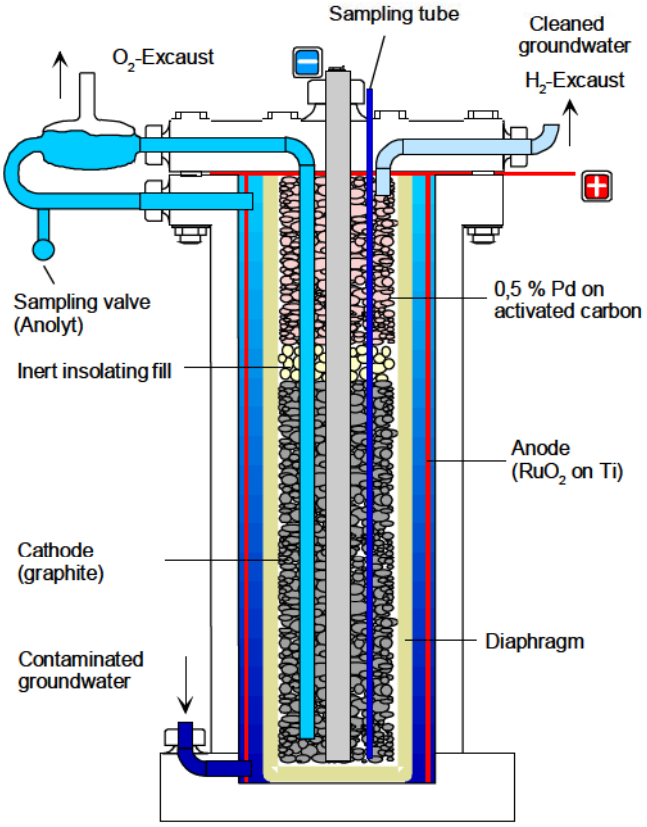

Figure 3 Scheme of the electro-catalytic reactor.

The reactor (described in detail by [2]) has been designed as a 20-liter flow-through type electrolytic cell, where the groundwater passes anode and cathode compartments in succession. The compartments are divided by a porous polyethylene diaphragm. The groundwater flows first through the anode compartment vertically from the bottom to the top of the reactor. The cathode is designed as a three-dimensional graphite electrode to which iron filings were mixed in order to ensure binding of sulfide ions which may possibly be carried in the groundwater or produced in anaerobic zones. The water electrolysis occurring after applying the voltage releases oxygen (and small concentrations of hypochlorite) into the anode compartment. The anolyte is then spontaneously degassed just before entering the cathode compartment, where dissolved oxidation products from the anodic process are reduced at the three-dimensional cathode. At the cathode, hydrogen is produced and dechlorination of aliphatic COCs may already occur. The groundwater enriched with hydrogen then passes the catalyst bed, where all remaining COCs can be reduced. Catalyst bed

and cathode are separated by a fill of inert and electrically insulating glass spheres. The operation of the reactor under field conditions is divided into different periods. Only the first three operation periods (180 days) will be discussed here: The electrocatalytic reactor was put into operation with a groundwater flow of 1.28 L/h and a current of 1 A (cell voltage 5 V). This corresponds to a mean residence time in the catalyst bed of about 75 min. ($\rho_{catalyst}$ = 330 g/L, $\varepsilon \approx 0.75$) or a catalyst load of 0.6 v/vh. Figure 4 shows the concentrations of benzene and chlorobenzene at the reactor outlet and the input of chlorobenzene as a function of time. Up to the operation day 50, only insignificant amounts of chlorobenzene and benzene are detected in the water leaving the reactor (removal > 99.5%). This alone is no proof of chemical reactions, because both compounds can be sorbed by the catalyst carrier.

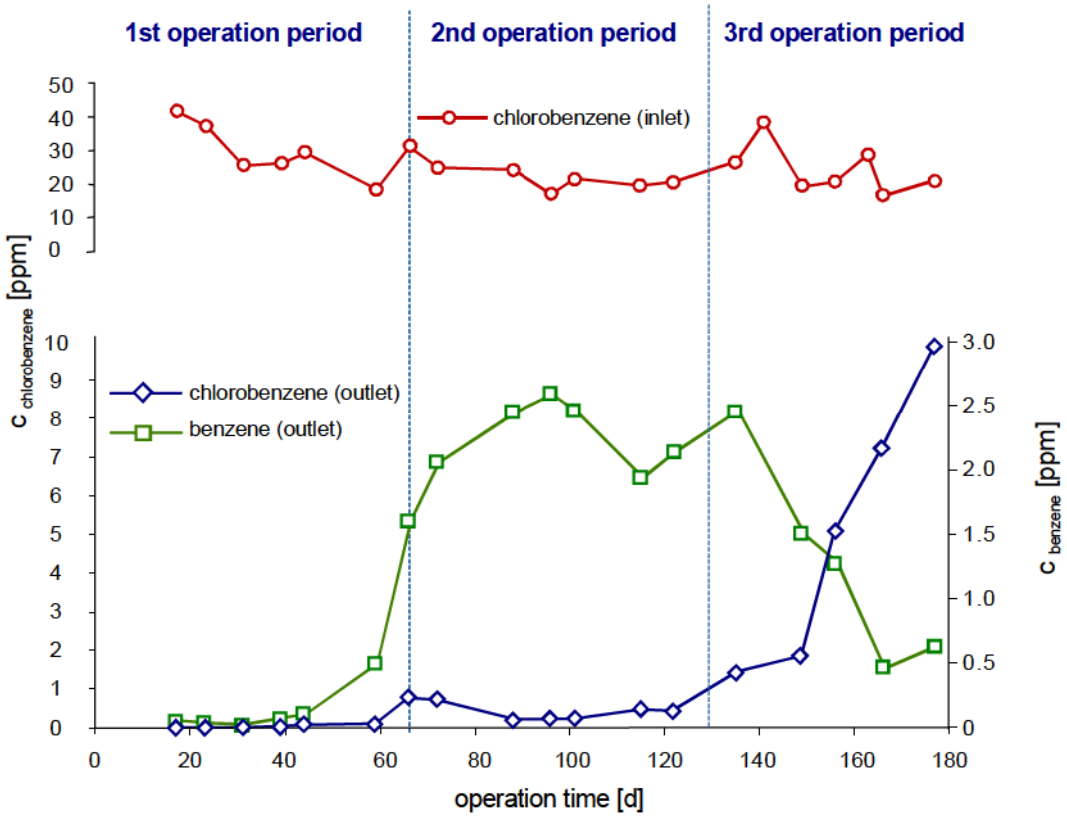

Figure 4 Chlorobenzene and benzene concentrations at the reactor in- and outlet.

Starting from operation day 59, benzene was analyzed in the outlet water as clear evidence of the reduction pathway. An activity test of the catalyst (sampled from various layers of the catalyst bed) at day 64 in the laboratory showed that the catalytic activity was undiminished.

After 6 months of operation the reactor was disassembled, because chlorobenzene started to break through. Activity tests of the catalyst showed the almost total loss of catalytical activity. Inspection of the reactor internals showed that the catalyst was covered with a brownish coating - washing the catalyst with diluted HCl evolved H_2S. The reason for the catalyst poisoning is depicted in Figure 5 and can be found from the analysis of inorganic groundwater constituents:

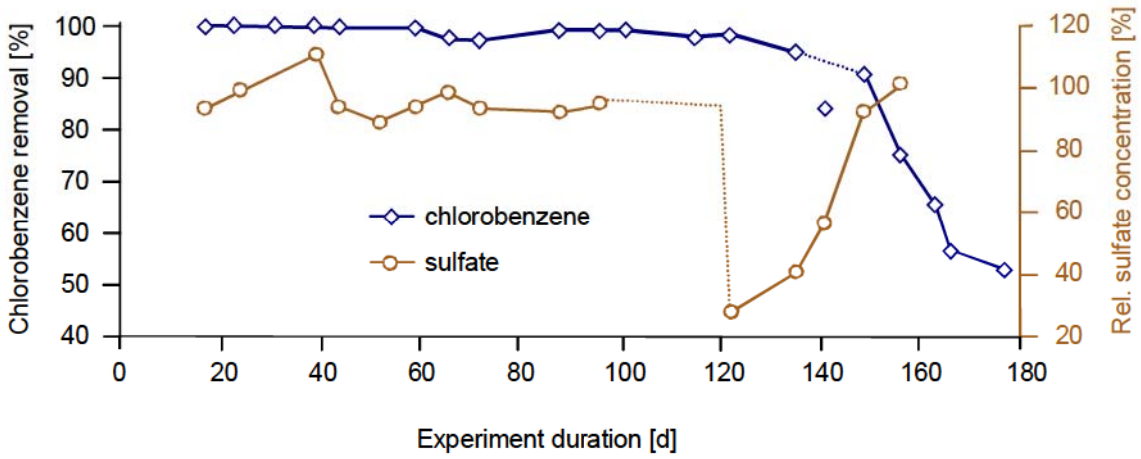

Figure 5 *Removal rate for chlorobenzene compared to the relative sulfate concentration in the reactor efflux.*

At day 121 a drastic decrease in the sulfate concentration from 800 mg/L to 220 mg/L was analyzed, whereas the concentrations of sulfate are equal under normal conditions at reactor in- and outlet. sulfides are known as very effective catalyst poisons produced presumably by microbial sulfate reduction. The reason for the spontaneous sulfate reduction is unclear. It may have been due to the break down of groundwater flow after outlet plugging. Because the water electrolysis (and therefore the gas production) continued during this operational disturbance, this led to an enrichment of the reducing agent hydrogen in the cathode compartment (formation of anaerobic conditions and total withdrawal of inhibiting agents).

The field experiment showed that the electro-catalytic reactor was able to almost completely remove chlorobenzene from groundwater over a time period of several months. The experiment also showed that the catalyst can be dramatically influenced by catalyst poisons and microbiological interference. *Therefore, a way to protect the catalytic system is required!*

Our approach favours membrane-supported Pd catalysts. The basic hypothesis is simple and plausible: the catalyst is embedded in a hydrophobic polymer membrane, which protects it from deactivation (Figure 6). The membrane acts simultaneously as a shield against hydrophilic, ionic catalyst poisons and as an absorber ('concentrator') of hydrophobic chlorohydrocarbons. The membrane enriches the pollutants to be treated and thereby supports the reaction kinetics.

The membrane materials preferred are silicon polymers (e.g. poly(dimethylsiloxane) = PDMS), because of their high diffusion coefficients. For example, the diffusion coefficient of benzene in PDMS is only 3 times lower than that in water. This is important in order to keep the transport resistance through the membrane as low as possible. Using a silicon matrix, one is not dependent upon additional catalyst carriers. Pd may as well be embedded in a highly dispersed form within the PDMS matrix. In

order to keep the transport hindrance of the silicone bulk phase as low as possible, we aimed to use thin polymer coatings. The membrane catalysts were designed (partially in co-operation with Dr. Fritzsch, GKSS Geesthacht) as silicone-coated commercially available supported catalysts, as foil (about 750 µm wall thickness), as 7 µm-coating on polyacrylonitrile fleece and as hollow fibre (wall thickness between 200 µm and 1 mm).

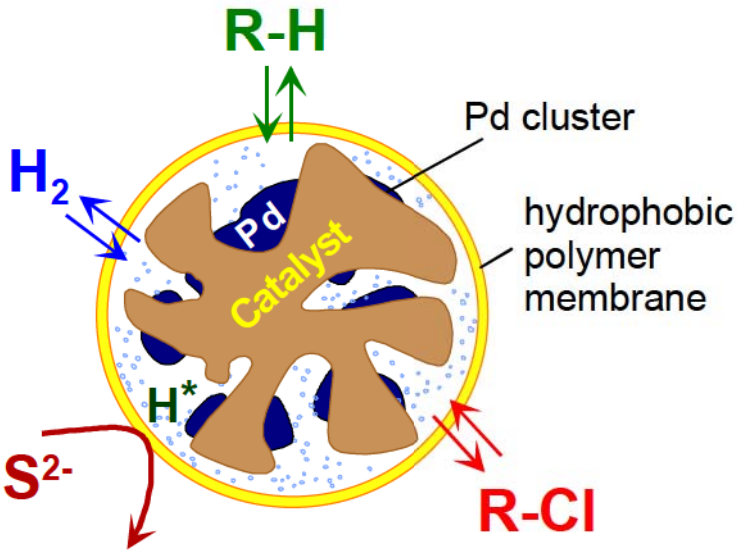

Figure 6 *Scheme of the operating mode of a supported-catalyst particle coated by a hydrophobic polymer membrane.*

The transport of the reaction product HCl out of the system is also important for the long life of the catalyst. We found in all our membrane investigations that HCl left the membrane completely, so that deactivation of Pd due to an excess of chloride did not occur.

We have achieved some very promising results on the laboratory scale with the systems outlined. The Pd/PDMS membranes (foil type) showed no reduction of the catalytic activity in the presence of sulfite ions, where conventional Pd catalysts were completely deactivated. In presence of sulfide ions, a reduction of catalytic activity was eventually observed. However, no complete destruction of the catalyst function occurred. The application of unprotected catalysts under these conditions would be unthinkable. We found that the unprotected Pd/Al_2O_3 catalysts loses its catalytic activity after addition of sulfite ions within seconds. In our experiments, the tube-like form proved to be an even more elegant method of applying membrane-supported Pd catalysts. The preparation of tube-like hollow silicone fibres containing 0.7 to 1.1% Pd led to catalysts which were very suitable for dechlorination applications even in presence of sulfur compounds, as can be seen in Figure 7. Even the addition of sodium sulfide and sulfite in stoichiometrical amounts does not result in deactivation of the Pd catalyst.

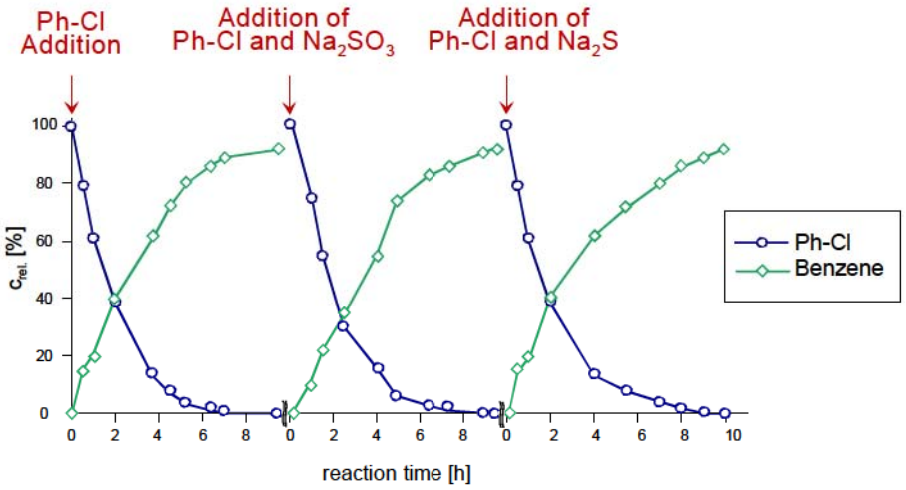

Figure 7 *Chlorobenzene reduction using Pd/silicone catalysts of the hollow-fibre type with and without the addition of catalyst poisons (fibre: 4.2mm x 1.0mm x 500 mm, 0.7% Pd; Pd : S = 1 : 1).*

We have successfully tested this system in the laboratory on various scales, where it proved to be more efficient and robust than all other catalytic systems investigated.

Figure 8 shows the scheme of a membrane reactor based upon which we built our membrane module in Bitterfeld. The tubular form of the catalytic system has the advantage of bringing hydrogen directly to its reaction partner, so that both reactants are present in high concentrations at the reaction site.

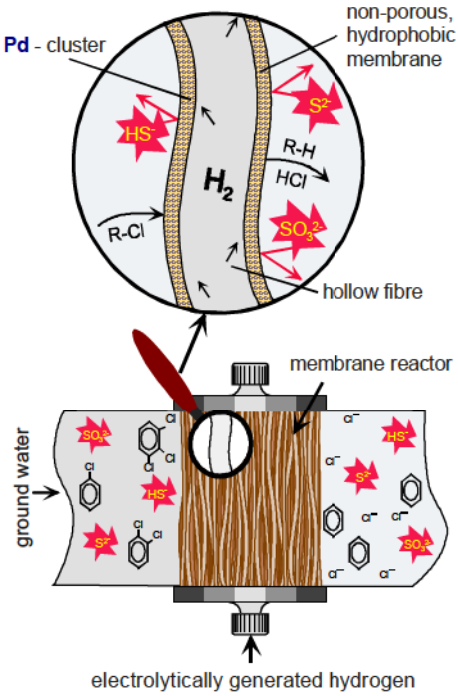

Figure 8 *Scheme of a membrane reactor.*

Our catalytic reactor (Figure 9) is installed at a depth of 19 m as part of a modular construction. The reactor module contains a 60m-Pd/fibre catalyst. The groundwater flows vertically from below through the reactor; pressure and temperature are analogous to the groundwater aquifer. The fibre catalyst is fed with externally-generated hydrogen from the inside of the tube.

Groundwater will be sampled frequently to inspect the performance of this new type of remediation method, where it must prove its worth and long-term stability under real groundwater conditions in the Bitterfeld region.

Figure 9 Membrane module installed in Bitterfeld in the pilot plant.

Parallel to the field experiments, studies at the laboratory scale were carried out.

It is important to determine how active a new catalyst is compared to conventional catalysts and whether it is economical enough to work with such a system. We determined specific activities for the palladium in different catalysts, which we tested for the reduction of chlorobenzene.

Because the Pd dispersity is not known for all catalyst samples, we calculated the specific activities as reaction volume divided by the Pd-mass and the reaction half time.

The commercially available catalyst Pd on γ-alumina shows the highest activity of the samples compared (more than double the activity of the membrane catalysts). At first sight, the hydrophobically protected systems, such as the zeolite-pellets or our membranes, show a much lower specific activity. It seems we have to pay for a hydrophobic protection from catalyst poisoning with a considerable amount of activity. However, the activity data alone can not sufficiently predict the performance of the catalytic system as a whole. In the last figure, an example of other important factors will be given: Figure 10 shows an example for the influence of the catalyst matrix on the selectivity of the catalytic system. We used the hydrodechlorination of carbontetrachloride as model reaction. In principle, carbontetrachloride can react on two pathways: directly in one step without the release of intermediates, and over a sequential channel, where we can observe intermediates. And indeed, we find both reaction channels simultaneously. Besides, chloroform does not use both reaction pathways, there is no sequential reduction. This can easily be proved by the absence of methylenechloride, which would be stable under the reaction conditions. Unfortunately, the hydrodechlorination of chloroform is slower by one order of magnitude than the direct reduction of carbontetrachloride. Therefore, the formation and reaction of chloroform dictate the reaction rate of the whole process.

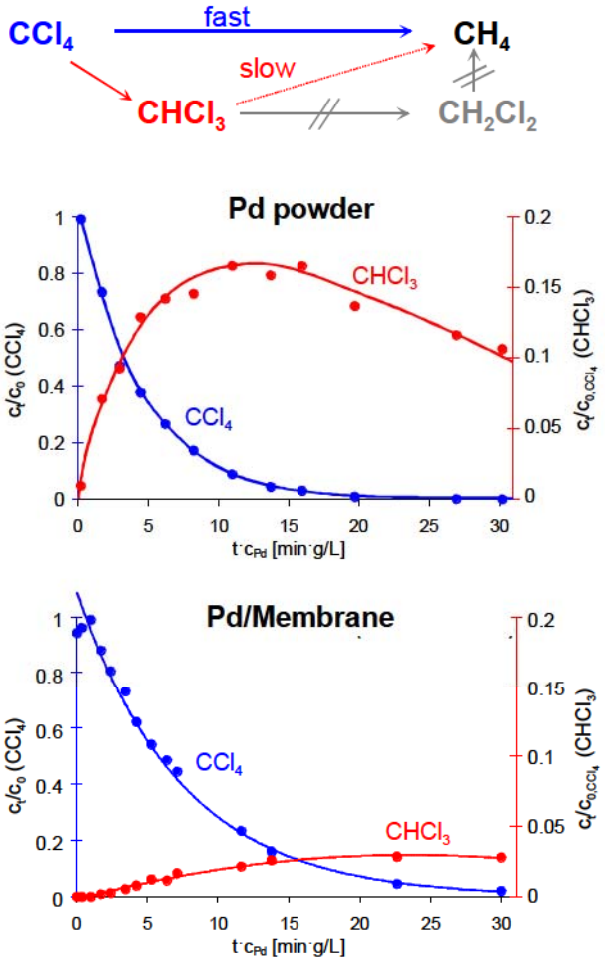

Figure 10 Influence of the catalyst matrix on the dechlorination selectivity

In figure 10 the concentrations of carbontetrachloride (in blue) and chloroform (in red) during the reaction are depicted for two catalyst systems. In the upper part using Pd powder and in the lower part using our Pd/Membrane. The specific activities of both catalysts are very similar for this reaction. However, the selectivity for the unwanted intermediate chloroform is very different. About 20% of carbontetrachloride is transformed to chloroform using Pd without the hydrophobic matrix and only 2% are converted using our new catalytic system. This is a very welcome experimental result, but there is no plausible explanation for it yet.

The comparison of simple activity data can smudge the whole picture of the performance of a catalytic system. Under field condition, we think only the resistance against biofouling will decide over the practical suitability of this new catalyst.

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