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Groundwater remediation methods based on noble metal catalysts – results from the pilot unit *Treatment Train*

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Abstract

Water phase as well as gas phase catalysis using noble metals is a promising technology for water treatment. However, catalytic reactions are in general hampered by catalyst deactivation due to complex water chemistry, especially the presence of reduced sulfur species. In a mobile pilot scale treatment unit (*Treatment Train*) techniques were developed to, (i) optimize reaction rates and, (ii) to increase the stability of the catalysts against deactivation. Examples are presented for both, water phase catalysis and gas phase catalysis. Approaches for the water phase rely on tailored support materials for catalyst protection while in the gas phase pretreatment of the poisonous compounds is favored.

Key words

Water treatment, catalytic hydrodechlorination, chlorinated solvents, catalyst deactivation

Introduction

Destructive catalytic processes hold an enormous potential in water treatment as they exhibit a broad reactivity with potentially very fast reaction rates. Especially palladium (Pd)-based catalysts were found to rapidly hydrodechlorinate many halogenated organic compounds with dissolved hydrogen as the reductant, even under unfavorable ambient conditions. The catalytic process can either be performed in the water phase directly, or, after stripping of volatile target compounds, in the gas phase. Numerous laboratory studies have shown this potential [1], however, the scarcity of published data that demonstrate the longevity of such catalysts under real conditions may have hindered the implementation of the technology.

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The main handicap is that in groundwater Pd-catalysts can suffer rapid deactivation, e.g. by sulfur poisoning and interference with biological processes. Likewise, in the gas phase volatile sulfur species, e.g. hydrogen sulfide or carbon disulfide, can poison noble metal catalysts or cause massive corrosion due to the formation of sulfuric acid.

In the SAFIRA and TASK projects of the Helmholtz Centre for Environmental Research (UFZ) a mobile and modular treatment unit was constructed to (i) develop innovative remediation technologies for contaminated waters and to (ii) demonstrate their applicability under real treatment conditions. The modular design of the unit allows to incorporate various treatment technologies that can be bundled as needed resulting in adaptive 'treatment trains'. With this, *Treatment Train* can be adjusted to varying boundary conditions at specific sites (Fig. 1).



Fig. 1: View into one of two *Treatment Train* containers and placement of the units at a field site for plot testing.

Treatment Train is currently used to especially optimize water phase and gas phase catalytic processes and to advance these technologies from pilot scale to practical use.

Experimental Approaches

Water phase: For water phase catalysis, the protection of the active Pd sites is the key step long term catalyst stability. Especially ionic sulfur species cause rapid catalyst deactivation. However, catalysts can be protected by hydrophobic support materials that exclude ionic species from the reactive sites but give access for hydrophobic target compounds. This concept was followed in using a hydrophobic zeolite Y as the Pd support [2], by coating a standard Pd/Al₂O₃ with silicone [3], or alternatively by embedding the Pd

in a hydrophobic polymer membrane (Fig. 2). With this, high and sustained dehalogenation rates could be archived at a field site with groundwater contaminated with trichloroethylene (TCE) [4].

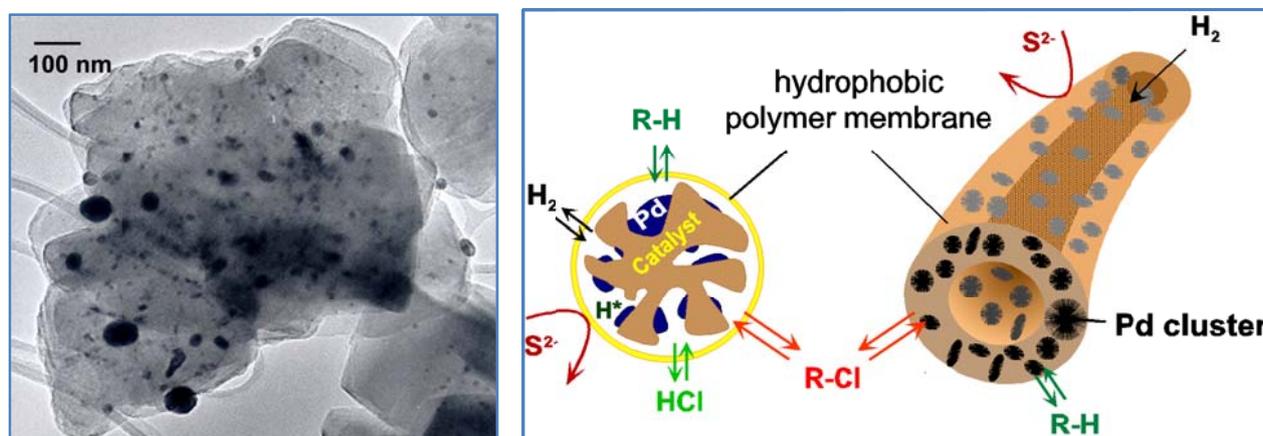


Fig. 2: A hydrophobic zeolite Y wet impregnated with Pd (left) and Pd embedded in a hydrophobic polymer membrane (right) to protect catalysts from sulfur poisoning in the water phase.

Gas phase: In the presence of hydrophobic sulfides in the water phase, e.g. carbon disulfide (CS_2), hydrophobic support materials will not function as a catalyst protection. Therefore a method was developed at a test site close to Leipzig to deal with the presence of CS_2 in the water phase. For this, target compounds (i.e. chlorinated solvents) are stripped out of the water phase to achieve catalytic destruction in the gas phase. However, also the sulfur species will be stripped out and have to be removed from the gas stream before catalytic processing. Metallic copper (Cu^0) was found to selectively oxidise CS_2 to copper sulfate under mild reaction conditions ($\sim 150^\circ\text{C}$) following the following reaction: $\text{CS}_2 + 2 \text{Cu} + 5 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{CuSO}_4$. As this is not a catalytic process, offline regeneration of the copper contact is required. This can easily be achieved by washing the copper sulfate from the copper contact with water. With this sustained catalytic activity of the downstream processing of the chlorinated target compounds could be achieved.

Conclusion

Examples of tailored Pd-based catalytic treatment systems that have been tested in pilot units for groundwater treatment. The results give clear evidence that Pd catalysts can be operated over extended periods of time with high efficiencies for the direct reductive

destruction of chlorinated contaminants in groundwater, as well as in the gas phase if some essential conditions are met. Some precautions to prevent catalyst deactivation are discussed.

References

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