**PTR-TOF-MS as novel tool for online monitoring of nanoparticle catalyzed dehalogenation reactions of persistent organic pollutants**

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Persistent organic pollutants (POPs) such as hexachlorobenzene (HCB) are known to be persistent, bioaccumulative, and toxic. Due to insignificant physicochemical elimination and slow microbial degradation, they can persist in environmental media for many decades. However, under reductive conditions we successfully demonstrated the dehalogenation of several POPs in the presence of zerovalent palladium [Pd(0)] nanoparticles as catalysts. Novel Pd(0) nanocatalysts, synthesized by controlled coalescence (D90: 63 nm), have shown a rapid dechlorination of HCB to benzene. HCB at environmental relevant water concentrations was fully dehalogenated within minutes. The high HCB dechlorination rate of APd,HCB = 420 L g-1 min-1 (CHCB = 3 *µ*g L-1) complicates elucidation of dehalogenation processes and reaction kinetics with high temporal resolution by conventional off-line analysis such as GC-MS.

Proton Transfer Reaction Time-of-Flight Mass Spectrometry (PTR-ToF-MS) is a state-of-the-art technique for on-line and real-time monitoring of volatile organic compounds (VOCs) without sample preparation, solvent extraction and clean-up steps. With its high mass resolving power of > 4000 M/ΔM, reaching a limit of detection below 5 pptV and sensitivity of more than 120 cps/ppbV for *e.g.* benzene, it is very promising for environmental analysis.

For the present experimental setup, *nano*Pd(0)-catalyzed dehalogenation of HCB and its potential dehalogenation intermediates was tested in separate experiments. The compounds were dissolved in ultra-pure water in airtight flasks and continuously purged with N2/H2 (98%/2%). After equilibrium of the parent compounds, the hydrogen-activated aqueous Pd(0) nanoparticle suspensions were injected. The headspace of the samples was continuously analyzed by PTR-ToF-MS using H3O+ or O2+ as primary reactant at a time resolution of 10 s. Exemplarily, the dehalogenation of a saturated HCB solution (CHCB ≈ 6 µg L-1) in the presence of 192 µg L-1 Pd(0) nanocatalysts resulted in the immediate formation of 28 ppbV benzene, but depending on nanocatalyst types and concentrations, different dehalogenation products and altered dehalogenation rates were observed.

To assess the stability of the nanocatalysts and to estimate their durability under environmental conditions, the approach was extended to experiments using different nanoparticle fractions, synthesis routes (including laser ablation and microbially synthesized “bioPalladium”), controlled catalyst poisoning by reduced sulfur compounds, and oxidative catalyst inactivation. Further successful tests with “old” and emerging persistent organic pollutants demonstrate the high potential of Pd(0) nanocatalysts for clean-up of drinking water, aquifers and specific municipal and industrial effluents, as well as the suitability of PTR-ToF-MS to assess relevant transformation and detoxification reactions.