

## Homogeneous Catalysis by Solid Catalysts: The Undervalued Role of Dissolved (Leached) Active Species in Catalytic Reactions in Solid-Liquid Interphases

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The lecture summarizes investigations on the nature and the role of potentially active species of supported metal (oxide) catalysts in catalytic reactions in liquid phases. Particular focus is on carbon-carbon coupling reactions of Heck and Suzuki type by supported palladium (oxide) nanoparticles and complexes. However, also other reactions like copper catalyzed hydrogenations were studied. From an extensive series of experiments over a decade, it can be concluded that the active palladium species are generated *in situ*. Pd is dissolved from the solid catalyst surface under reaction conditions forming very active unsaturated palladium species. Pd is partially or completely re-deposited onto the support at the end of the reaction when the substrates were used up. The Pd dissolution-re-deposition processes correlate with the reaction rate and are influenced strongly by the reaction conditions (Fig. 1). The power of such kinetic experiments will be demonstrated.

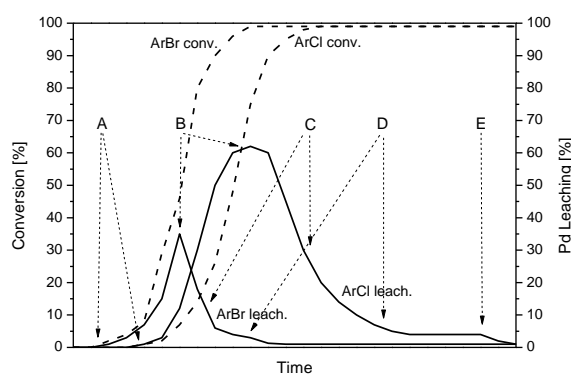


Fig.1: Substrate conversion and concentration of homogeneously dissolved palladium as function of reaction time.

Pd leaching is a prerequisite for the highly efficient catalysis and depends on a variety of parameters (temperature, solvent, base, substrates, and additives). Different leaching mechanisms are proposed within different temperature regimes and for different reactions. Density Functional Theory (DFT) calculations provide a more detailed insight into possible steps and the energetics of dissolution of Pd species from the surface, e.g. initiated by oxidative addition of bromobenzene to corner atoms. Different oxidation states (Pd oxygen clusters) and the solvent influence have been explored as well. In addition, reactions in fact catalyzed by the solid surface were found. Thus, dehalogenation reactions obviously involve metallic palladium surfaces, as also hydrogenations of carbonyl compounds.