

Spectroscopic evidence for the substantial catalyst deactivation under “ligand-free” Suzuki-Miyaura reaction with aryl chlorides

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Operando kinetic study combining kinetic control of the reaction proceeding with simultaneous spectroscopic monitoring of the concentration of a catalyst form during a catalytic reaction is the extremely helpful tool for the elucidation of the role of this form in catalysis. We applied this approach to investigate catalyst transformations in thoroughly studied Suzuki-Miyaura reaction where the most challenging aryl chlorides were used as substrates under so-called “ligand-free” conditions, i.e., when no phosphines, amines, carbenes, or any other strong organic ligands were added. The combination of gas chromatography for the kinetic control of the reaction product accumulation and UV/Vis-spectroscopy for the measurements of the concentration of Pd compounds having the absorbance in this region was applied. Using Pd(acac)₂ as the catalyst precursor (absorption maximum at 328 nm) in the reaction with 1,4-dichlorobenzene or chlorobenzene it was demonstrated that the precursor concentration predictably decreased during the reaction, and no additional well-defined maximum was observed. However, smooth increase of absorbance at 350-400 nm allowed proposing formation in the reaction mixture of Pd nanoparticles (PdNPs) with no significant amounts of Pd (II) molecular complexes. The formation of Pd black was observed only when the reaction stopped. Using the method of least squares and proposing that all Pd loaded presents in two spectroscopically fixed forms, i.e., Pd(acac)₂ and PdNPs, the set of molar extinction coefficients for proposed PdNP was found. Analyzing the literature data [1], PdNPs with 5 nm diameter were most probably formed under the reaction conditions, and their amount in the reaction solution passed through a maximum during the reaction. By the analysis of the dependencies plotted in various coordination systems including the rate of product formation and concentrations of the reaction product and Pd species (precursor and PdNPs) it was demonstrated that under Suzuki-Miyaura reaction PdNPs are inactive catalyst form. At the same time, the concentration of Pd molecular complexes responsible for catalytic activity was negligible in comparison with total amount of Pd loaded and was not observed spectroscopically.

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[1] B.G. Ershov., N.L. Sukhov, D.A. Troitsky, *Zh. Fiz. Khim.* **1994**, *68*, pp. 820-824.