16d Investigation of Transition Metal Leaching from Supported Pd Catalysts during the Heck Reaction

Surbhi Jain, Yaying Ji, and Robert J. Davis

The Pd-catalyzed Heck reaction is a very important C-C bond forming reaction in organic synthesis because of its wide use in the manufacture of fine chemicals, intermediates for pharmaceuticals, agrochemicals, and fragrances. Homogeneous catalysts used in this reaction generally suffer from the problem of catalyst recovery. For industrial applications, it is preferable to use a solid catalyst that can be used without the loss of the active phase. Although a variety of solid catalysts such as Pd supported on carbon, silica, polymers and molecular sieves have been widely studied in the Heck reaction, the leaching of Pd is reported to occur under some reaction conditions.

In this work, several silica-supported Pd materials, including amorphous silica (Pd-SiO2), mercapto-functionalized amorphous silica (Pd-SH-SiO2) and mercapto-functionalized mesoporous silica (Pd-SH-SBA-15), along with a zeolite-supported Pd (Pd-Y) sample have been prepared with the traditional wet impregnation and ion exchange techniques and used to catalyze the Heck reaction of iodobenzene with n-butyl acrylate in the presence of triethyl amine as base and DMF as solvent. A detailed investigation of Pd leaching has been carried out with the use of batch and continuous reactor experiments. Hot filtration tests at 10-20% iodobenzene conversion, poly(4-vinylpyridine) (PVPy) poisoning tests and elemental analysis were performed to probe the nature of the catalytically active species in the reaction medium.

Results from hot filtration tests and Pd trapping experiments suggest that the active catalytic species was associated with the leached or soluble Pd in the reaction solution. In addition, high catalytic activity was obtained from the collected effluents of the continuous reaction with Pd-SiO2 and Pd-SH-SiO2 catalysts indicating that soluble Pd is the active species in the fixed bed reactor. Apparently, functionalization of silica with sulfur did not prevent leaching of Pd into the reaction medium. In every case, the supported Pd catalyst appeared to act as a reservoir for the active catalytic species in solution.

The leaching pathway appears to be correlated with the state of Pd on the support. In the case of an unreduced Pd-Y catalyst, the base was required to leach Pd and the addition of iodobenzene to the base accelerated Pd leaching. The base was apparently needed to reduce cationic species located in the zeolite supercages. In all the other catalysts with metallic Pd residing on the support, no leaching was observed from the treatment with the base alone. However, treatment with iodobenzene caused significant leaching of the reduced metal. These results can be rationalized by the generally accepted Heck reaction mechanism in which the oxidative addition of an aryl halide to reduced Pd is a key step.