Cross-Linked "Poisonous" Polymer Support for Tuning Chemoselectivity

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Catalyst poisons can be deliberately added in various reactions for tuning chemoselectivity. The poisons can be adsorbed on the catalyst surface, which modulates the adsorption/desorption behaviors of reactants/intermediates. However, the poisons are readily decomposed or leached out during reactions. This means that catalyst poisons should be continuously supplied to the reaction feeds for maintaining selectivity.
In the present work, we supported Pd catalysts on a thermochemically stable crosslinked organic polymer. The resultant catalyst was tested in partial hydrogenation of alkynes to alkenes, which is an important model reaction for fundamental investigation of chemoselectivity and also a key transformation in fine chemical synthesis. Various structural characterization results showed that the sulfide groups in the polymer matrix fully ligated (or poisoned) the entire surface of Pd catalyst. The sulfide groups capping the Pd surface behaved like a 'molecular gate' that enabled exceptionally discriminative adsorption of alkynes over alkenes.