Solid-Supported Heterogenized Palladium Nanoparticles: Propitious Vehicles for Sonogashira Cross-Coupling Reaction

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Abstract **Key words** Sonogashira, heterogeneous catalysis, supported nanoparticles, aryl acetylenes, palladium

Sonogashira reaction is an important C–C cross-coupling reaction employed for the synthesis of biologically active aryl or vinyl acetylenes using terminal acetylenes and aryl or vinyl halides, in the presence of Pd/Cu salt or Pd metal catalysts.[1,2] Aryl and vinyl acetylenes are structural moieties in polymers, natural products, agrochemicals, and pharmaceuticals. Their constant demand stimulates the upgrading of their synthetic methodologies and the design of newer catalysts.[3]

Currently, the worldwide demand for palladium surpasses the supply, leading to the excessive cost of the catalysts.[4] Therefore, sustainable use and recycling of Pd is vital. Nanocatalysis is a green and benign approach, which is desirable for sustainability and economic viability.[5] These catalytic systems are cheap, ligand-free, and are generally stable to air and moisture.[5] Nanoparticles (NPs) with controlled compositions, uniform and low particle sizes, high number of surface atoms, large surface area, shape selectivity, zeta potential values, and superior surface chemistry exhibit tailorable catalytic properties and selectivity.[6] Selection of a suitable solid support for nanocatalysts is critical as it not only controls the shape, size, and distribution of NPs on its surface but also eases a cooperative and efficient pathway to achieve the target product through strong metal-support interaction (SMSI), high surface area, a substantial number of participating active sites, increased stability, decreased leaching and agglomeration of metal nanoparticles and increased recyclability.[7,8] Solid-supported heterogenized Pd nanoparticles are now being explored as useful

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catalysts for Sonogashira, Heck, Suzuki–Miyaura, and several other C–C cross-coupling reactions.[9–11] The recent reports on the synthesis of heterogenized Pd nanoparticles with controlled shapes, sizes, detailed structures, and choice of a plethora of nanostructured solid supports has led to meaningful progression in the field.[8–11] This spotlight article lists some examples of solid supports used for tailoring Pd nanoparticles (Figure 1, Table 1) and their catalytic application in Sonogashira cross-coupling reaction (Table 1).

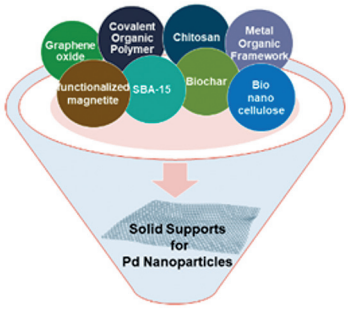
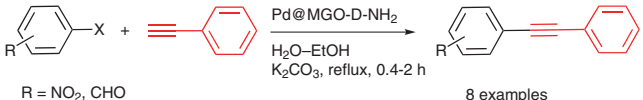
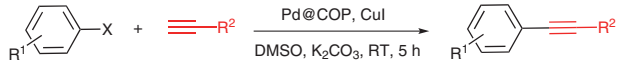
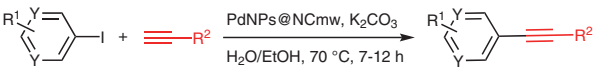
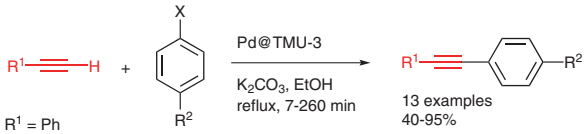
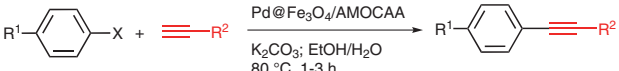
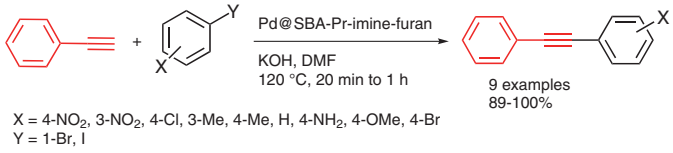
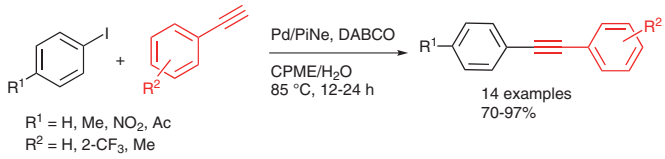
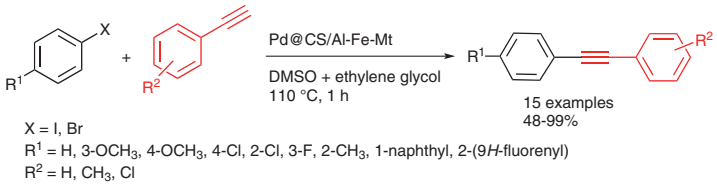


Figure 1 Some solid supports for Pd nanoparticles

Table 1 Examples of Sonogashira Reaction Catalyzed by Solid-Supported Heterogenized Pd Nanoparticles

(A) Pd@MGO-D-NH_2[11] – solid support: graphene oxide – higher yields – fast reaction – simple operation – easy catalyst separation 4 times	 R = NO_2, CHO X = Cl, Br, I 8 examples 85-95%
(B) Pd@COP[12] – solid support: covalent organic polymer – excellent yield – fast reaction – electron-deficient aryl halides preferred – mild conditions 8 times	 26 examples 54-97% R^1 = H, 4-NO_2, 4-CN, 4-NH_2, 4-NHAc, 4-NHBz, 2-F, 4-CHO, 4-Ac X = Cl, Br, I R^2 = Ph, C_4H_9, C_3H_6OH, CH_2Br, C_3H_6CN
(C) PdNPs@NCmw[13] – solid support: nanocellulose – renewable source – short reaction time – size-controlled spherical NPs – wide substrate scope, including heteroaryl halides 3 times	 8 examples 70-98% Y = C, N R^1 = COMe, CH_3, NO_2 R^2 = Ph, C_4H_9, C_6H_{11}, *p*-CH_3-C_6H_5
(D) Pd@TMU-3[14] – solid support: metal-organic framework – facile preparation – excellent yields – high efficiency – high purity – fast reaction – easy transfer 5 times	 13 examples 40-95% R^1 = Ph R^2 = NO_2, Me, OMe, H X = Cl, Br, I
(E) Pd@Fe_3O_4/AMOCAA[15] – solid support: functionalized magnetite – excellent yield – fast reaction – easy recovery 7 times	 12 examples 79-96% R^1 = H, 4-Me, 4-OMe, 1-naphthyl, 4-NO_2 X = I, Br, Cl R^2 = Ph, CH_2OH

(F) Pd@SBA-Pr-imine-furan[16] – solid support: mesoporous organosilicate (SBA) – excellent yield – fast reaction – stable catalyst 7 times	
(G) Pd/PiNe[17] – solid support: biochar – circular economy – continuous-flow protocol – high catalyst stability – good yield – low E-factor 5 times	
(H) Pd@CS/Al-Fe-Mt[18] – solid support: chitosan – well-encaged Pd NPs – thermally stable – high selectivity – high TON, TOF – high yields with ArI and ArBr 18 times	

The data reviewed in this spotlight has revealed that nanomaterial-supported Pd NPs have unveiled several opportunities for the accomplishment of economical, greener, and sustainable Sonogashira cross-coupling transformations by preventing oxidation, agglomeration, and promoting recycling of NPs. The future of supported Pd NPs will depend on how well the scientific community can address challenges like low cost, simple procedures for synthesis, leaching, falling-off of activity, regio- and chemoselectivity in asymmetric transformations, utilization of biowaste materials for support. The key to all pertinent issues probably lies in the design of superior heterogeneous support systems using diverse material design philosophies.

Conflict of Interest

The authors declare no conflict of interest.

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