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Catalysis in supercritical CO_2 using dendrimer-encapsulated palladium nanoparticles†

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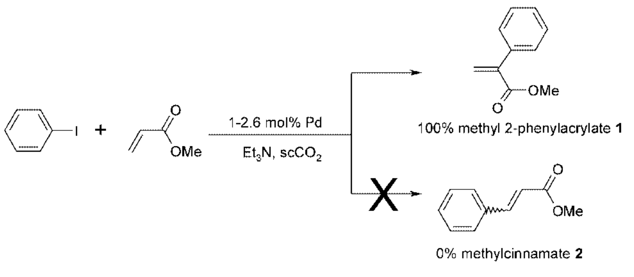
Dendrimer-encapsulated nanoparticles are shown to be versatile catalysts for both the hydrogenation of styrene and Heck heterocoupling of iodobenzene and methacrylate in supercritical CO_2 ($scCO_2$).

Here we present the first examples of catalysis in pure liquid or supercritical CO_2 ($scCO_2$) using soluble metal nanoparticles. The catalysts are composites consisting of functionalized poly(propylene imine) (PPI) dendrimers and Pd(0) nanoparticles. The perfluoropolyether-functionalized dendritic host is responsible for solubilizing the 1–2 nm diameter catalytic Pd(0) nanoparticles in $scCO_2$. The versatility of these dendrimer-encapsulated catalysts (DECs)[1] is illustrated by performing two very different chemical reactions. First, in the presence of hydrogen, the catalyst is effective for the hydrogenation of olefins, such as the reduction of styrene to ethylbenzene. Second, iodobenzene can be coupled with methylacrylate, which is a benchmark reaction for the synthetically useful Heck coupling,[2] to yield exclusively methyl 2-phenylacrylate **1** (Scheme 1). The selectivity for **1** is remarkable when compared with standard palladium complexes[2] or colloidal nanoparticles[3–6] used for Heck couplings in organic solvents, which result in only *cis*- and/or *trans*-cinnamate **2** (Scheme 1). When used in hydrocarbon/fluorocarbon solvents the same Pd-based DECs yield only *trans*-formylcinnamate.[7]

The use of liquid or $scCO_2$ as an alternative to hydrocarbon solvents is attractive because CO_2 is both inexpensive and environmentally benign.[8] Additionally, by changing the density, and thus the 'solvent power' of $scCO_2$, the reaction rates, product distribution,[9] and yields can be tuned,[10–12] and therefore there is intense interest in catalysts and chemical processes that are compatible with this 'green solvent'.[13] There are two approaches for the utilization of liquid and $scCO_2$ as a solvent for both hydrogenation[14–19] and Heck[20–22] reactions. One of these involves the use of CO_2-soluble coordination complexes, and the other utilizes Pd metal on a solid substrate such as carbon.



Scheme 1

The DECs used for both the hydrogenation and Heck chemistry described here consisted of Pd(0) nanoparticles sequestered within fifth-generation poly(propylene imine) (PPI) dendrimers having perfluoro-2,5,8,11-tetramethyl-3,6,9,12-tetraoxapentadecanoyl perfluoropolyether chains covalently attached to their periphery.[23] The general method used to prepare these materials has previously been reported and the specific procedures used in this work are provided in the ESI†.[1,7] Importantly, the dark-brown DECs (dry) could be easily solublized in liquid- and $scCO_2$ (dull-orange solution), and there were no obvious signs of aggregation or precipitation. Note that we and others have recently prepared and characterized Ag[24,25] and CdS[26] nanoparticles in $H_2O/scCO_2$ microemulsions as well as in pure CO_2 solvent[27] utilizing perfluorinated surfactants as either the sole emulsifier or as a co-surfactant.

Although synthetically trivial, the hydrogenation of styrene to ethylbenzene is a convenient example for demonstrating the catalytic activity of DECs.[11] With the novel catalyst (1–2.6 mol% Pd), the progress of styrene reduction was followed by capillary gas chromatography (GC) and shown to be complete in under 4 h (Fig. 1). Evidence of catalyst decomposition, such as Pd(0) precipitation, was not apparent at the end of the reaction. The ethylbenzene could be recovered after depressurization of the reaction vessel and was confirmed by NMR spectroscopy to be the only product.

To demonstrate the versatility of $scCO_2$-soluble DECs, the same catalyst was shown to be active for a Heck-type coupling reaction. In the presence of triethylamine (TEA) and the DEC (1–2.6 mol% Pd), methylacrylate (MA) reacted with iodobenzene (PhI) at 75 °C and 5000 psi, forming methyl 2-phenylacrylate **1**. The progress of the reaction was followed by GC using *n*-decane as an internal reference (Fig. 2). The DECs stopped producing **1** after about 24 h when 57% of the iodobenzene was consumed. This corresponds to a turnover number (TON) of *ca.* 22 (TON = mol of substrate/mol of Pd).

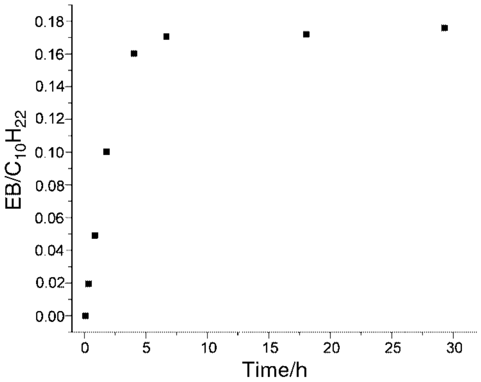


Fig. 1 Gas chromatographic data showing the appearance of ethylbenzene (EB) from the DEC catalyzed reduction of styrene in a supercritical H_2/CO_2 mixture with *n*-decane ($C_{10}H_{22}$) as an internal standard.

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† Electronic supplementary information (ESI) available: DEC synthesis and specific reaction conditions used for the hydrogenation and Heck reactions. See http://www.rsc.org/suppdata/cc/b1/b106594g/

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Although this TON does not approach values obtained in other solvent systems,[28] it is comparable to previous reports of Heck catalysis in $scCO_2$ using both soluble complexes and heterogeneous catalysts.[20–22]

Importantly, even after 52 h the $scCO_2$ Heck reaction solution did not show evidence of Pd(0) precipitates or other catalyst decomposition products. The DECs and product were recovered by slowly venting the CO_2 followed by washing the depressurized reaction vessel with 1,1,2-trichlorotrifluoroethane (CFC-113). ^1H NMR analysis of the extract revealed a mixture of the *n*-decane internal GC reference, the starting materials (PhI and MA), and methyl 2-phenylacrylate **1**, but no evidence of byproducts or other impurities[29,30]

Prior to drying and loading into the CO_2 reactor, the CFC-113 DEC solution is dark-brown. However, the recovered CFC-113 solution was dull-orange in color, reminiscent of the color of the Pd(II)-containing PPI dendrimers [from which the Pd(0)-containing DECs were prepared].[1] This color change suggests that the Pd is oxidized from Pd(0) to Pd(II) during the course of the Heck reaction. Indeed, upon treatment of the recovered Pd(II)-containing DEC solution with an excess of $NaBH_4$, the solution turned dark-brown, UV-VIS spectroscopy indicated the formation of intradendrimer nanoparticles, and the solution remained precipitate free. We also noted that the Pd-containing DEC can be subjected to the reaction conditions described above, but in the absence of substrate, and then recovered without signs of Pd(0) oxidation. These findings provide a reasonable hypothesis for the cause of reaction termination and the low TON.

It is widely accepted that the last step in the catalytic Heck cycle involves the reductive elimination of the halide from the Pd metal and neutralization of the resulting acid.[31,32] Moreover, the use of excess tertiary amine has led to rate enhancements for a Heck-type coupling reaction resulting from both the neutralization effect of the base and weak ligand–complex stabilization.[33] We propose that at the start of the reaction in $scCO_2$, the inherently more basic[34] and proximal tertiary amines of the dendrimer neutralize the eliminated acid more effectively than the slightly less basic TEA. However, an equilibrium develops in which the interior tertiary amine hydrogen iodide salt disproportionates back to the free amine and acid, resulting in Pd(0) oxidation and halting the catalytic cycle. In fact, past studies have shown that stronger bases lead to increased rates and completion of Heck reactions because dissociation to the free base and acid is not a concern.[32,35]

To summarize, we have described the first example of catalytically active nanoparticles solublized in environmentally benign $scCO_2$. This versatile catalyst is able to reduce styrene exclusively to ethylbenzene and to catalyze the carbon–carbon bond forming Heck reaction. Although the conditions have not been optimized, it is clear that DECs can select for particular products (*e.g.*, methyl 2-phenylacrylate for the Heck reaction). The high selectivity is due in part to the steric environment the dendrimer template imposes on the reaction intermediates, but primarily results from the $scCO_2$ solvent in view of our recent finding that the same DEC in an organic/fluorocarbon solvent system yields exclusively the *trans*-coupled isomer.[7]

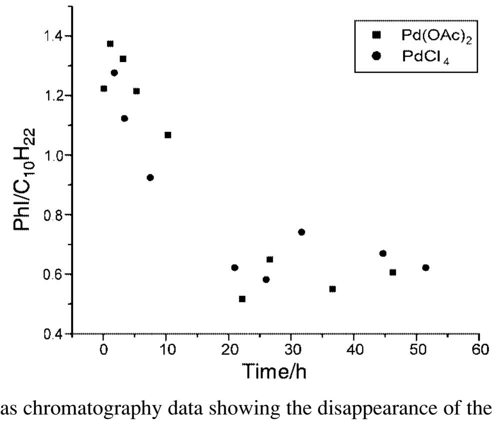

Fig. 2 Gas chromatography data showing the disappearance of the limiting reagent (PhI) for the Heck reaction as a function of time. The two sets of data correspond to independently run reactions using DECs prepared from different molecular sources of palladium, $Pd(OAc)_2$ and K_2PdCl_4.

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