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Palladium-loaded cucurbit[7]uril-modified iron oxide nanoparticles for C-C cross-coupling reactions

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Abstract: Cucurbit[7]uril modified iron oxide nanoparticles (CB[7]NPs) were loaded with palladium to form nano-catalysts (Pd@CB[7]NPs) that, with microwave heating, catalysed Suzuki-Miyaura, Sonogashira, and Mizoroki-Heck cross coupling reactions. All reactions were run in environmentally benign 1/1 ethanol/water solvent under convenient aerobic conditions. In a preliminary screening, all conversions and yields were uniformly high with turn over frequencies (TOF) ranging from 64 to 7360 h^{-1}. The nano-catalysts could be recovered with a magnet and reused several times (6 times for Suzuki Miayura reaction) without loss of activity.

More than 90% of multi-step industrial chemical processes involve catalysis in at least one step.[1] Development of new, catalysts that make these processes less costly, environmentally benign, and more energy efficient is a primary goal of chemical research. In industry, heterogeneous catalysis tends to be favored over homogeneous catalysis because heterogeneous catalysts are easier to recycle.[2] In the last two decades, nanomaterial-based catalysts with high surface-to-volume ratio and highly active surface atoms have been developed and shown to be comparable in activity and selectivity to homogeneous catalysts.[3] Effective systems in which the nanomaterial core (as opposed to surface) contains catalytically active components have also been reported.[4] Among the various nanomaterials used as solid supports, magnetic iron oxide nanoparticles (NPs) have emerged as a particularly convenient option[5] because they allow for simple magnetic recovery that avoids filtration and centrifugation.[6] Such an approach is cost-effective for cross coupling reactions that rely on expensive metal catalysts such as palladium, platinum, or ruthenium. Another benefit of using nanoparticles, especially those composed of iron oxide, as a catalyst support is synergism. It has been found that interaction between palladium and Brønsted basic sites on the surface of iron oxide nanoparticles can enhance catalytic activity in Heck and Suzuki reactions,[7] whereas acidic support materials have been found to diminish the catalytic activity of the metal.[7-8] Phosphine, salen, and N-heterocyclic carbene ligands have been used to attach palladium to particles for the catalysis of Suzuki-Miyaura, Mizoroki-Heck, and Sonogashira cross-coupling reactions.[9] Recently we proposed an alternative strategy for palladium attachment that relies on a proline-based ligand and allows for the preparation of an efficient, recyclable Pd-supported nano-catalyst for the Suzuki-Miyaura reaction in water and other aerobic media.[10] Cucurbituril (CB[n]) macrocycles have also been shown to function as palladium chelating ligands. Equipped with guest recognition properties and the ability to bind cations to their carbonyl-lined rims, CB[n] macrocycles,[11] and especially the water-soluble CB[7],[12] have recently been used to construct nanomaterial-based supramolecular assemblies that catalyze organometallic reactions.[13] For example, nanocapsules coated with polymerized CB[6][14] have been used as stabilizers of Pd-based nanoparticles that catalyze the Suzuki-Miyaura reaction[15] (though the capsules and catalyst were not magnetically recycled). Recently, we reported the synthesis of CB[7]-coated magnetic iron-oxide nanoparticles (CB[7]NPs) for biomedical applications.[16] Here, we describe adsorbing Pd(II) to CB[7]NPs to form recyclable nanoparticles (Pd@CB[7]NPs) that catalyze Suzuki-Miyaura, Sonogashira and Mizoroki-Heck reactions. We hypothesized that CB[7] cavity would favor the reaction between organic species in aqueous media, acting as a nano-reactor at the surface of the particles.

The surface of the NPs was modified with CB[7] by mixing bare iron-oxide NPs with an excess of CB[7] in water at pH = 2 and 50 °C under microwave irradiation for one hour.[16] Palladium was adsorbed onto the surface of CB[7]NPs by the addition of palladium acetate, $Pd(AcO)_2$, to CB[7]NPs in $MeOH/H_2O$ solvent (Scheme 1).[10]

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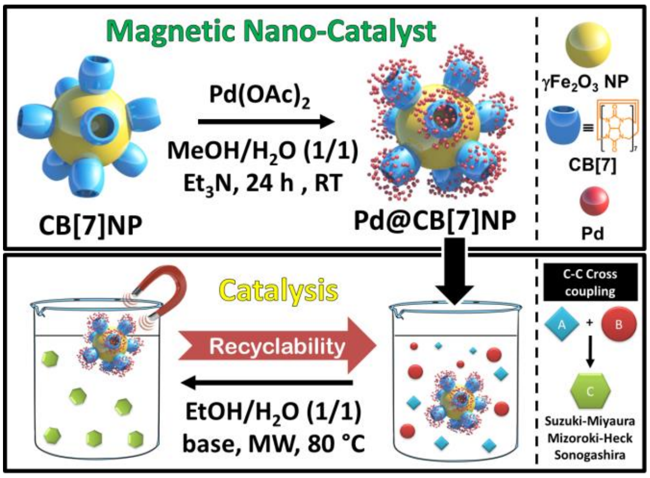


Scheme 1. Schematic representation of the loading of Pd(II) onto CB[7]NPs (top) and the catalytic activity of the metal-loaded particles, Pd@CB[7]NPs, (bottom).

Averages of 450 (± 50) Pd(II) ions per NP and 16 (± 2) Pd(II) ions per macrocycle were deduced by electron dispersive X-ray (EDX) analysis (Figure S7). The palladium was strongly bound: neither several water washes of the particles nor heating of the particles to 50 °C in water/ethanol for several hours significantly diminished the amount Pd(II) adsorbed.

The FTIR spectrum of CB[7]NPs features the characteristic 600 cm^{-1} Fe–O absorption band of iron oxide, as well as separated C=O bands of CB[7] at 1733 cm^{-1} and 1636 cm^{-1} that correspond to uncomplexed and particle-bound carbonyls, respectively (Figure S9). The FTIR spectrum of CB[7]NPs treated with Pd(II) (Figure S9) shows that the chemical constitution of CB[7]NPs is preserved in the presence of Pd, as evidenced by the characteristic Fe–O band and CB[7] absorptions at 1731 and 1632 cm^{-1}, and the fact that no new peaks are present.

X-ray photoelectron spectroscopy (XPS) was used to analyse the elemental composition of the surface of the Pd@CB[7]NPs (Figure S10). Figure S10 displays the Fe 2p XPS spectra characteristic of CB[7]NPs (Figure S10A) and Pd@CB[7]NPs (Figure S10B). In these, the $2P_{3/2}$ and $2P_{1/2}$ peaks are centered at 710.8 and 724.5 eV, respectively. The Fe $2p_{3/2}$ peaks are associated with satellite peaks. The satellite of the Fe $2p_{3/2}$ peak of Fe_2O_3 is located approximately 8 eV to the right.[17] The high resolution XPS spectrum presented in Figure S11 shows intense peaks that correspond to $3d_{5/2}$ (337.4 eV) and Pd $3d_{3/2}$ (342.7 eV) absorptions of Pd(II).[10] Dissolved Pd(II) ions are known to bind to the electron-rich oxygens of the carbonyl-lined portals of surface-attached CB[7].**[18]** Less intense $3d_{5/2}$ and $3d_{3/2}$ absorptions at 335.1 eV and 340.9 eV, respectively, reflect the presence of a small amount of Pd(0).[19] The 1s peak of nitrogen does not appear in the spectrum of Pd@CB[7]NPs (Figures S10C and S10D). This signal suppression might be a consequence of Pd ions and neutral atoms being located inside and around the macrocycles on the surface of the NPs. On the other hand, the 1s peak of carbonyl oxygen is more intense in the spectrum of Pd@CB[7]NPs than in the spectrum of CB[7]NPs (compare Figures S10E and S10F). This result is likely due to the presence of acetate counter ions on the surface of the Pd@CB[7]NPs.

The TEM image of CB[7]NPs in Figure S12A shows almost spherical nanoparticles with sizes ranging from 8 to 12 nm. Upon adsorption of Pd(II) to the particles, size and morphology remain unaffected, but dark regions on the surface of the particles appear by TEM. We performed elemental mapping on both CB[7]NP and Pd@CB[7]NP samples to determine the nature of these dark regions. We found that CB[7]NPs are composed of iron and oxygen and, as expected, show no trace of Pd (Figure S12). The clear outline around the clustered CB[7]NPs that are visible in STEM images (Figure S12B) indicate the presence of CB[7] macrocycles on the surface of the particles. Elemental mapping of Pd@CB[7]NPs (Figure S15) indicates the iron and oxygen composition and also provides clear evidence for the presence of Pd(0). Pd(0) particles are also clearly visible as bright spots in STEM-HADF images (Figure S13), owing to the high molecular weight of Pd. We examined lattice planes in order to identify the oxidation state of the palladium detected. High resolution images of CB[7]NPs (Figures S12 C and D) exhibit the interplanar spacing (2.54 Å) that matches with the d-spacing value of (2 2 0) plane of maghemite. Images of Pd@CB[7]NPs (Figures S15C and D) exhibit two different plane spacings of 2.2 Å and 2.5 Å which are characteristic of the (1 1 1) and (2 2 0) planes of Pd(0) and γ-Fe_2O_3, respectively. The spacings were analyzed using IFFT on the highlighted areas. The minimal, scattered presence of Pd(0) apparent in the images is consistent with the XPS analysis.

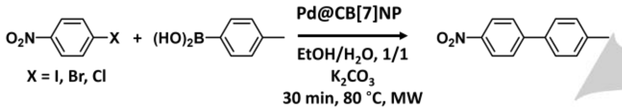
The crystalline structure of the cores of CB[7]NPs and Pd@CB[7]NPs were confirmed (Figure S16) by powder X-ray diffraction (PXRD). The reflections in the XRD patterns can be easily indexed with the inverse spinel structure of maghemite (ICDD PDF039-1346). The similarity of the data for the two sample types indicates that the core structure of NPs is unaffected by Pd(II) treatment. Extra peaks in the pattern associated with the Pd@CB[7]NP sample correspond to Pd^0 (ICDD 98-004-1517) and indicate, as did XPS and TEM analyses, the presence of palladium nanoparticles in small quantity (Figure S17).

After establishing the presence of Pd(II) on the CB[7]NPs, the magnetic properties of Pd@CB[7]NPs were determined in the solid state using a magnetic reader.[20] Strong superparamagnetic signals (4.9×10^8 M.U.)[20] predicted strong attraction to a magnet and convenient catalyst recycling, a significant practical advantage.

The obtained Pd@CB[7]NPs were stable for 30 minutes in a 1/1 ethanol/water mixture but subsequently precipitated. Because of this relative lack of stability in solution, Pd@CB[7]NPs were evaluated as catalysts in vigorously stirred water/ethanol solvent mixtures. From a practical standpoint, this aggregation was an advantage that facilitated catalyst recovery and recycling.

The ability of Pd@CB[7]NPs to act as nano-catalyst for C-C cross-coupling was evaluated in Suzuki-Miyaura, Sonogashira, and Mizoroki-Heck reactions under microwave irradiation. Also, although inert atmosphere is a usual requirement for these reactions,[21] we were able to run them successfully under aerobic conditions, which represents another major practical advantage.

Suzuki-Miyaura couplings of 4-tolylboronic acid (0.22 mM) and 4-iodonitrobenzene (0.20 mM) were attempted in vigorously stirred 1/1 water/ethanol solvent that was maintained at 80 °C under microwave irradiation for 30 minutes (Scheme 2). We first performed control experiments without palladium and without CB[7]NPs (Table 1, entry 1), as well as with only CB[7]NPs that lacked surface-adsorbed palladium (Table 1, entry 2). In both cases, no product was detected, which confirmed that the reaction does not occur to any appreciable extent without catalyst and that CB[7]NPs alone do not catalyze the reaction. In contrast, near quantitative yields of product were isolated when Pd@CB[7]NPs were used (Table 1, entries 2-6).

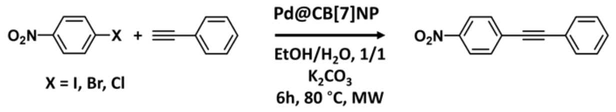


Scheme 2. Suzuki-Miyaura C-C cross-coupling catalysed by Pd@CB[7]NPs.

We then reduced the amount of palladium (0.025 mol % Pd) which resulted in 100% conversion, 92% isolated yield, turn over number (TON) of 3680 and turn over frequency (TOF) of 7360 h^{-1}. It is worth noting that 0.025 mol % represents only 250 ppm of Pd and, in these reactions, required the addition of only 125 µg of Pd@CB[7]NPs, an extremely small amount of heterogeneous catalyst. Furthermore, no side-products from dehalogenation or homocoupling were detected by ^1H NMR analysis in any of the crude reaction mixtures.

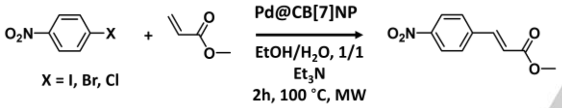
In order to evaluate the effectiveness of our catalyst for coupling other halogenated benzenes, we tested 4-bromo and 4-chloronitrobenzene. Conversion with the former (97%, TOF = 1920 h^{-1}) was similar to that obtained with 4-iodobenzene, whereas conversion with the latter was low (20%, TOF = 400 h^{-1}), though it was expected to be so due to the lower reactivity of chlorine. In terms of TOF, our results compare favorably to those obtained in Suzuki-Miyaura reactions involving previously reported Pd-based catalysts (see S.I.). To test the recyclability of the Pd@CB[7]NPs, we ran reactions with 0.1 mol % Pd (0.5 mg Pd@CB[7]NPs). We were able to recover the catalyst from these reactions with a small magnet, and the recovered catalyst could be used up to six more times with no decrease in conversion (Table 1, entry 7) representing a cumulative TON of 5760. On the seventh cycle, conversion dropped rather abruptly to 65% (Table 1, entry 8). This decrease may have been due to deactivation of the palladium that was caused by partial discharge of the palladium salt from the macrocycles or formation of palladium oxide. Another control reaction was run in the presence of 0.1 mol % palladium in the form Pd@CB[7]NPs. However, after the usual 30 minutes of heating at 80 °C, the catalyst particles and product were removed from the reaction medium and fresh aryl iodide and boronic acid were added. When this partially reconstituted mixture was subjected to the same reaction conditions, conversion was less than 5%, indicating that during the initial reaction the nanoparticles had leaked a small amount of palladium during the initial reaction and/or that less than 100% of the Pd@CB[7]NPs had been recovered by the magnet. Finally, we also evaluated the catalytic efficiency of a mixture of free (unrecoverable) $Pd(OAc)_2$ and CB[7]. With these reagents, conversion was only 60%. No Pd NPs were formed during this reaction, which leads us to conclude that, beyond allowing for easy recovery, immobilization of Pd onto magnetic CB[7]NPs increases palladium's catalytic activity under the given conditions, a result that may be linked to the synergetic effect already described in the literature.[7]

To test the effectiveness of the Pd@CB[7]NPs in other typical, palladium-catalyzed reactions, we ran Sonogashira and Mizoroki-Heck cross couplings. Prior to catalyst evaluation, we performed the same type of control experiments as described above for the Suzuki-Miyaura reaction. None of these controls yielded product. We found that, with Pd@CB[7]NPs, Sonogashira reactions could be carried out without the usual addition of copper and phosphine ligands.[21] We also found that, like the Suzuki-Miyaura reactions, both Sonogashira and Mizoroki-Heck reactions could be performed under aerobic conditions. A representative Sonogashira reaction (Scheme 2) involved the condensation of phenylacetylene (0.22 mM) and 4-iodonitrobenzene (0.20 mM) using K_2CO_3 as a base in a 1/1 water/ethanol solvent mixture heated to 80°C by MW irradiation for 6 h. Only a small amount of the nano-catalyst (1.25 mg, 0.25 mol%) was necessary to achieve 100% conversion of the starting materials and 94% isolated yield (TON = 384, TOF = 64 h^{-1}) of the cross-coupled product. No side-products were detected (see NMR analysis in the SI). In general, conversions and yields with MW heating were similar to those obtained when the reaction was heated in an oil bath. Decreasing the reaction time or the amount of nano-catalyst resulted in incomplete conversion. Total conversion was reached for up to three consecutive cycles (cumulative TON = 1152) before the Pd@CB[7]NPs began to lose activity and yields decreased (see SI). This decrease is consistent with the longer reaction time that was required. The greater exposure to aerobic atmosphere and the prolonged heating during the 6 h cycles of Sonogashira reaction decreased the catalyst's activity more per cycle than during the shorter 30 minute Suzuki-Miyaura reaction cycles. When replacing iodonitrobenzene by bromo or chloro substrates, we observed the same trend as we saw with the Suzuki-Miyaura reaction: good conversion with 4-bromonitrobenzene (82%) and lower conversion with 4-chloronitrobenzene (20%).



Scheme 3. Sonogashira C-C cross-coupling catalyzed by Pd@CB[7]NPs.

As a representative Mizoroki-Heck reaction, we condensed methyl methacrylate (0.88 mM) with 4-iodonitrobenzene (0.20 mM) for 2 h at 100 °C under MW irradiation (Scheme 3). Again, low catalyst loading (0.25 mol % Pd) was used. The reaction was performed in 1/1 water/ethanol under aerobic conditions but with NEt_3, rather than K_2CO_3, as base to avoid saponification of the ester or transesterification with ethanol. Under these conditions, conversion, yield, TON and TOF were 95%, 90%, 360 and 180 h^{-1}, respectively. Replacing iodine substitutents with bromine or chlorine affected the results more dramatically than in the case of Suzuki-Miyaura or Sonogashira reactions. Conversion with 4-bromonitrobenzene decreased to 40%, and no product was observed with 4-chloronitrobenzene under these conditions.



Scheme 4. Mizoroki-Heck C-C cross-coupling catalyzed by Pd@CB[7]NPs.

Conclusions

In summary, an initial screening demonstrated that Pd@CB[7]NPs are effective nano-catalysts for Suzuki-Miyaura, Sonogashira, and Mizoroki-Heck reactions under conditions that are convenient and green. Under an air atmosphere and in an environmentally benign 1/1 ethanol/water solvent mixture, conversions were high, especially in Suzuki-Miyaura and Sonogashira reactions involving iodo and bromo electrophiles. As anticipated, yields were lower when chlorinated substrates were used.[22] Further investigations will be conducted to improve yields with these more challenging substrates. None of the reactions required the addition of ligands such as phosphines, and the Sonogashira reaction did not require copper. The Sonogashira and Mizoroki-Heck reactions could be run at lower temperatures, with lower catalyst loadings, and for shorter reaction times than those required when Pd-based catalysts are used in organic solvents.[6b, 9a, 23] Palladium concentration in the ppm range was effective for the Suzuki-Miyaura reaction, representing, to our knowledge, the lowest effective catalyst loading yet achieved with a CB[7]/Pd nano-catalyst assembly: 20 to 200 times less palladium than used in similar, previously reported work.[15a] Also, in terms of TOF, the results were generally high compared to those reported in the literature for similar reactions run in aqueous media (see S.I.). Unlike dissolved $Pd(OAc)_2$, Pd@CB[7]NPs were recyclable and could be used several times without losing activity, in particular, in the Suzuki-Miyaura and Sonogashira reactions. These initial results demonstrate that Pd@CB[7]NPs are an efficient, economical, and environmentally benign catalyst system with potential for application in the pharmaceutical industry and the broader chemical industry.

Entry	X	Conditions	Pd Quantity mol %	Conversion %[a] (isolated yield)
1	I	No catalyst	0	traces
2	I	CB[7]NPs	0	traces
3	I	Pd@CB[7]NPs	1	100 (98)
4	I	Pd@CB[7]NPs	0.25	100 (95)
5	I	Pd@CB[7]NPs	0.10	100 (96)
6	I	Pd@CB[7]NPs	0.025	100 (92)
7	I	Pd@CB[7]NPs 6th cycle	0.10	100
8	I	Pd@CB[7]NPs 7th cycle	0.10	65
9	Br	Pd@CB[7]NPs	0.10	97
10	Cl	Pd@CB[7]NPs	0.10	20

Table 1. Evaluation of Suzuki-Miyaura reaction conditions. [a] Conversion was measured by ^{1}H NMR spectroscopy.

Acknowledgements

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Conflicts of interest

There are no conflicts to declare.

Keywords: Magnetic nano-catalyst • Suzuki-Miyaura, Mizoroki-Heck, and Sonogashira cross-coupling reactions • Cucurbit[7]uril • Palladium

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COMMUNICATION

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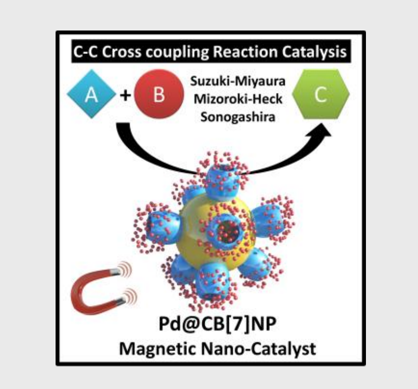

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