A cross-linked reverse micelle-encapsulated palladium catalyst†

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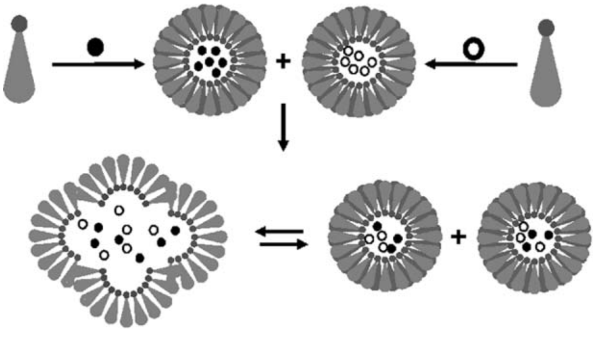
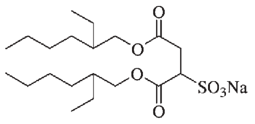
Cross-linked reverse micelle-palladium catalysts are effective and stable cross-coupling catalysts; cross-linking is crucial for stability.

Reverse micelles (RMs) are important components of catalysts, cosmetics, foods, and paints.[1] In general, RMs transfer polar substances into nonpolar environments,[2] but they can also be used to template the formation of nanoparticles.[3] RMs—stable water droplets surrounded by an amphiphile monolayer—are formed by adding water to an amphiphile dissolved in a nonpolar solution. With diameters ranging from 5–100 nm, RMs form isotropic solutions.[4] RM solutions, unlike normal micelle solutions, contain very low concentrations of monomeric amphiphile, prompting one to speculate that RM solutions are not dynamic.[4] Despite low monomer concentrations, RMs undergo dynamic budding and fusing, mixing both amphiphiles and cores (Scheme 1). Rates of core mixing were measured to be as high as 10^7 s^{-1} at room temperature.[4]

This rapid mixing can be deleterious to many RM applications, especially catalyst site isolation. Even though RM-based catalysts show enhanced surface area, permeability, selectivity, and activity,[5] budding and fusing can lead to catalyst aggregation, reducing catalyst lifetime. For example, Wai *et al.* reported a highly active Pd-nanoparticle hydrogenation catalyst prepared by reducing sodium tetrachloropalladate trapped in sodium bis(2-ethylhexyl) sulfosuccinate (**AOT**)/n-hexane/water micro-emulsions.[6] These particles efficiently catalyzed hydrogenations but underwent nanoparticle aggregation and precipitation after only 15 min.



Scheme 1 Reverse micelle dynamics.



AOT

Wai's catalysts are particularly attractive because they are soluble and phosphine-free. Phosphines are widely used ligands for palladium but are expensive and can often contribute to side reactions.[7] It should be noted, however, that Wai's approach complements many other phosphine-free approaches including heterogeneous particles,[8] coacervates,[9] sol-gels,[10] block co-polymer matrices,[11] organic zeolites,[12] microcapsules,[13,14] inorganic supports,[15] and dendrimers.[16–18] Herein, we demonstrate that phosphine-free Pd-nanoparticles trapped within cross-linked reverse micelles (xRMs) show excellent stability and high catalytic activity relative to a soluble catalyst.[19] This new general approach creates the same microenvironment as that created by traditional RMs, but it prevents budding and fusing, thus preventing catalyst aggregation and precipitation.

xRMs (15 nm–30 nm) were prepared using methods previously reported[20] and were impregnated with palladium by mixing xRMs with $Pd(OAc)_2$ (Scheme 2). The $Pd(OAc)_2$-containing xRMs were then incubated in toluene/ethanol for 8 h and washed with absolute ethanol, yielding Pd-xRMs (**2**). The Pd content of our Pd-xRMs was 2.5% (determined *via* inductively coupled plasma atomic absorption spectroscopy), corresponding to a 1 : 8 ratio of Pd atoms to carboxylate groups. We speculate that the carboxylate head groups ligate the Pd-nanoparticles. During preparation, the Pd(II) is converted to Pd(0) as indicated by the lack of the acetate-Pd(II) charge-transfer band at 394 nm.[21] Once prepared, Pd-xRMs can be concentrated to an air-stable (over many months), brown, free-flowing solid that readily dissolves in a variety of nonpolar organic solvents. Pd-xRMs precipitate on addition of polar solvents such as acetonitrile and DMF, allowing collection and recycling. Recovered catalyst shows similar activity relative to the fresh catalyst. After subsequent reuses, however, the activity declines. We are in the process of understanding this maturation.

To demonstrate that cross-linking provides greater stability relative to uncross-linked RMs, we prepared RM catalysts using **4**, the hydrogenated version of **1** (Scheme 3). As expected, organic solutions of **4** were able to dissolve water, indicating RM formation. The RMs were treated with $Pd(OAc)_2$ followed by incubation and reduction with hydrogen. The RM solution became black. In contrast to Pd-xRMs, the palladium began to precipitate almost immediately upon addition of an aryl iodide, an acrylate, and a base. Despite their instability, the Pd-RMs provided yields similar to those of the Pd-xRMs. Collection and recycling, however, were not possible. In addition, the Pd-RMs

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† Electronic supplementary information (ESI) available: experimental details, characterization of new compounds. See http://www.rsc.org/suppdata/cc/b4/b416892e/

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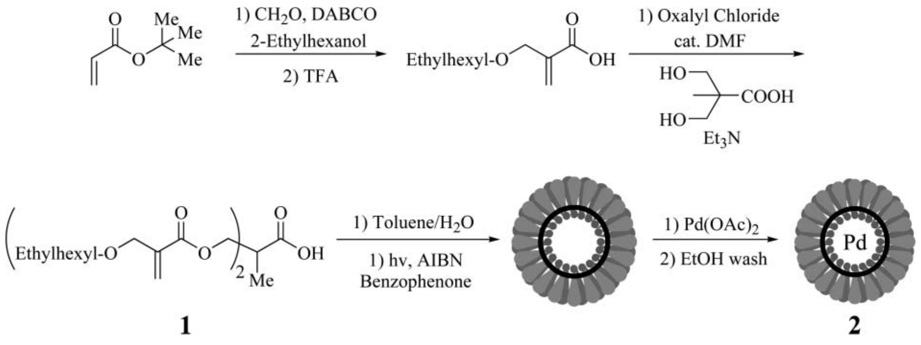
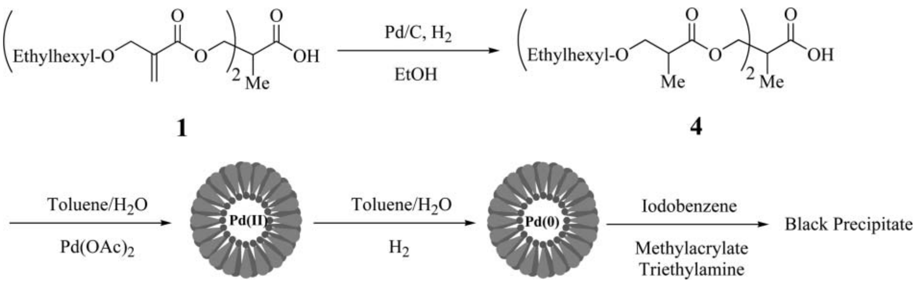


Scheme 2 Preparation of Pd-xRMs.

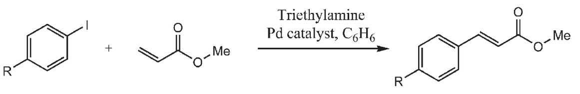


Scheme 3 Preparation of Pd-RMs.

would not yield reliable rate data because of catalyst precipitation. Regardless, experiments with **4** illustrate that RMs yielded less stable Pd catalysts relative to Pd-xRMs.[6] *We suggest, in the case of Pd-RMs, that metal aggregation and precipitation result from rapid budding and fusing*. Because Pd-xRMs cannot bud and fuse, they protect the entrapped catalysts from aggregating.

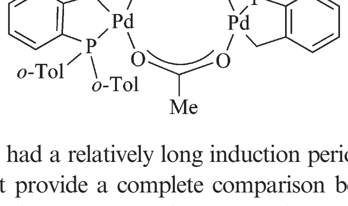
Catalytic activity was demonstrated using the Heck reaction.[22] Rate and turnover numbers (TON)/turnover frequency (TOF) data were used to compare and contrast Pd-xRMs and Herrmann's catalyst, **5** (a soluble control catalyst).[23] As shown in Table 1, Pd-xRMs and **5** catalyzed the Heck reaction of methyl acrylate with iodobenzene, iodoanisole, and 4-iodobenzotrifluoride. For Pd-xRMs, electron-rich arenes had rates that were an order of magnitude slower than the electron-poor arenes, implying that the rate-determining step was the oxidative addition of the iodoarene to the metal.[22] Alternatively, **5** showed similar rates for each substrate, indicating that oxidative addition was not the rate-determining step. For the electron-rich iodoarenes, the rate catalyzed by **5** was approximately 10 times faster than that with Pd-xRMs, even though the rates were comparable for electron-poor iodoarenes. In all cases, conversions were typically high at low catalyst loading, 0.1–0.45 mol% (100 °C). We observed *trans*-cinnamate ester formation exclusively in all cases. Unlike Herrmann's catalyst, Pd-xRMs do not show high activity with aryl bromides and chlorides.

Table 1 Comparison of palladium-cross-linked reverse micelles (xRMs) to Herrmann's catalyst



	Catalyst	Loading (mol%)	R	k_{rel} 60 °C	% Yield 60 °C[a]	% Yield 100 °C[c]
1	Pd-xRM	0.45	H	1	22	97
2	Pd-xRM	0.45	OMe	1.4	45	> 95
3	Pd-xRM	0.45	CF_3	15	> 99	> 99
4	**5**	0.45	H	8.4	63	> 95
5	**5**	0.45	OMe	12.6	97	> 99
6	**5**	0.45	CF_3	10.8	> 99	> 99
7	Pd-xRM[b]	0.45	H	1	68	> 95
8	Pd-xRM	0.1	H	N/A	88	> 99
9	**5**[b]	0.45	H	2	96	> 99

[a] Yields obtained *via* GC after 21 hours. See supporting information for experimental procedures. [b] These experiments were performed in neat iodobenzene. [c] Yields obtained using ^{1}H–NMR after 1 hour. Greater than 95% and 99% reflect whether ^{13}C satellites could be discerned.



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Catalyst **5** had a relatively long induction period, thus rate data alone do not provide a complete comparison between Pd-xRMs and **5**. As such, we measured TON and TOF for each catalyst (Table 1).[24] As can be seen in Table 2, both catalysts had similar activities and stabilities (first two entries). The stability of the Pd-xRMs was pushed further by measuring the TON and TOF at 0.1% loading. The xRM catalyst surprisingly showed an increase in activity at this loading.

Table 2 Comparison of turnover number (TON) and turnover frequency (TOF) values

Catalyst	Mol%	°C	% Conv.	TON[a]	TOF (h^{-1})[b]
Pd-xRM	0.45	60	68	149	7
5	0.45	60	99	213	11
Pd-xRM	0.1	60	88	861	43

[a] TON units (mol product/mol catalyst). [b] TOF units ((mol pdt/mol cat)/hour).

In conclusion, we have demonstrated that Pd-xRMs are robust catalysts with a number of desirable characteristics. xRM catalysts are much more stable than uncross-linked RMs, indicating that the cross-linked structures provide a unique phosphine-free environment. Pd-xRMs perform Heck couplings with efficiency comparable to that of catalyst **5**. Soluble xRM catalysts are attractive because they eliminate problems associated with heterogeneous catalysts such as mass transport, and are easy to prepare and modify.

As shown in our initial work in this area, the xRM core has the capacity to be modified by using amphiphiles with head groups other than carboxylates. Currently, we are examining the influence that core properties have on catalyst performance and the effect of cross-linking density on size selectivity. In addition, we are investigating metal leaching from the core and catalyst recycling.

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24 The Herrmann induction period is shorter when it has been preincubated with the iodoarene, indicating an iodoarene-based maturation.