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# Multiple One-Pot Reaction Steps using Organically Doped Metallic Hybrid Catalyst

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The recently developed family of molecularly doped metals (molecule@metal) has opened the possibility of an interesting, useful concept in catalysis: Entrapment of an organic catalyst within a catalytic metal leads to a hybrid material capable of multiple catalytic steps in one pot. In this report we show the feasibility of this idea by effecting catalytic dehydration, catalytic disproportion, and catalytic hydrogenation, all by using Nafion@Pd. Palladium, in this case, serves not only as a metallic heterogenization matrix-by itself a new heterogenization methodology (see below)-but it also serves in its classical role as a versatile catalyst. Examples of the successful use of this methodology for metal heterogenization of homogeneous catalysts include the acid-catalyzed pinacol-pinacolone rearrangement with Nafion entrapped in silver (Nafion@Ag); the dehydration of 2-phenylethanol to styrene with the same catalyst;<sup>[1]</sup> the  $H_3[P(Mo_3O_{10})_4]@Aq$ - or  $H_3[P(W_3O_{10})_4]@Aq$ -catalyzed Friedel-Crafts (FC) adamantylation of toluene and anisole,<sup>[2]</sup> the partially enantioselective hydrogenation of isophorone and acetophenone catalyzed by (-)-cinchonidine@Pd, (+)-cinchonine@Pd, (-)-quinine@Pd, or (+)-quinidine@Pd, $^{[3]}$  the biocatalyzed hydrolysis of *p*-nitrophenyl phosphate with acid phosphatase@Au or acid phosphatase@Ag;<sup>[4]</sup> and the hydrogenation of styrene or diphenylacetylene with the silver-entrapped catalytic organometallic complex [RhCl(cod){Ph<sub>2</sub>P(C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Na)}] (cod = 1,5-cyclooctadiene).<sup>[5]</sup> Enhanced stabilities, improved reaction conversion rates, altered reaction product ratios, and the obtainment of new products were all observed in these studies. For instance, in the FC reaction, alkylation of toluene with either 1-bromoadamantane or the less-reactive 1-chloroadamantane proceeded to >99% yield with  $H_3[P(Mo_3O_{10})_4]@Aq$ in comparison to only 2-3% yield with  $H_3[P(Mo_3O_{10})_4]$  in solution.<sup>[2a]</sup>

The formation of catalysts@metals has been made possible by methodology that enables the doping of metals with organic molecules,<sup>[3,6]</sup> inorganic molecules,<sup>[2a,5]</sup> polymers,<sup>[1,7]</sup> and proteins.<sup>[4]</sup> In addition to the Ag, Au, and Pd mentioned above, successful entrapments have also been carried out with Cu,<sup>[6h,8]</sup> Fe,<sup>[9]</sup> and several alloys (Ag–Au, Cu–Pt, and Cu–Pd).<sup>[6d,10]</sup> Except for the doping of Fe, which involved zero-valent Fe(CO)<sub>5</sub> as the precursor, the general approach utilizes carefully selected re-

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duction conditions of the metal cation in the presence of the molecule to be entrapped (see the Experimental Section for details). The resulting material is composed of tight aggregates of metal crystallites, which hold the dopant in the 3D matrix, on one hand not allowing the dopant to leach out even in its own solvent, and on the other hand allowing free diffusion of the substrate and product molecules in and out. We emphasize that 3D entrapment and 2D adsorption are very different processes, and in all of the reported applications (including also bioapplications, altering physical properties of the metal, and more), the unique performance was observed only for the entrapped 3D case.

As indicated above, the ability to entrap within a metal opens yet another very interesting possibility, namely, the obtainment of heterogeneous catalysts in which both the dopant and the entrapping heterogenizing metal are catalytic. Such materials may thus show multiple catalytic activities, for which two catalysts and two separation steps are usually needed. Here we report the successful demonstration of this concept. Specifically, the dual activity of the composite Nafion@Pd (Nafion entrapped within palladium, Figure 1), and the fact



Figure 1. Typical HRSEM images of Nafion@Pd (scale bar: 500 nm).

that only the hybrid catalyst, but not its separate components, could pull three dual reaction schemes to completion is reported. The selection of these two catalysts was based on their wide use: acid catalysis for the former and mainly hydrogenation for the latter. It is relevant to recall that the use of Pd and Nafion in the same context has been reported, for example, in simple mixing, as in the case of Nafion and Pd/C,<sup>[11]</sup> as Nafion films placed on Pd-modified electrodes by sputtering,<sup>[12]</sup> electrodeposition,<sup>[13]</sup> or electroless deposition;<sup>[14]</sup> and as the use of Pd nanoparticles immobilized in Nafion membranes for fuel cell applications.<sup>[15]</sup> Pd doped with Nafion as developed here has not been studied. Reactions performed in one step in one pot with a hybrid material showing dual catalytic activity have been demonstrated for (Schemes 1 and 2) the dehydration/disproportion of 1,2,3,4-tetrahydro-1-naphthol directly to naphthalene and tetralin, the dehydration/hydrogenation of 1,2,3,4-



Scheme 1. Multiple catalyzed reactions that 1,2,3,4-tetrahydro-1-naphthol undergoes with Nafion@Pd without (top) and with hydrogen (bottom).



Scheme 2. Catalyzed reactions that 1-phenyl-2-propanol undergoes with Nafion@Pd and hydrogen.

tetrahydro-1-naphthol directly to tetralin, and the dehydration/ hydrogenation of 1-phenyl-2-propanol directly to 1-propylbenzene.

An important characteristic of the material that enables its action as a catalyst is its porosity, which is due to its aggregated nature (Figure 1 and Figure S1, Supporting Information), and the resulting accessibility of the entrapped sulfonic acid groups to incoming substrate molecules. The aggregated nature that gives rise to the interstitial porosity is revealed by the very low density of the composite, 1.5 g cm<sup>-3</sup> (compared to the true density of Pd, 12.02  $g cm^{-3}$ ), by the shape of the nitrogen adsorption-desorption isotherms and their small hysteresis opening (Figure S1, Supporting Information), by the nitrogen BET surface area of approximately 7  $m^2g^{-1}$ , by the Barrett– Joyner-Halenda (BJH) average pore diameters of 19 nm for adsorption and 17 nm for desorption, and by the fact that these last values are close: all are very typical of aggregated mesoporosity. The accessibility of the acidic protons of Nafion was demonstrated by a cation-exchange experiment. If Nafion@Pd is placed in 0.01 M salt solutions, either sodium chloride or magnesium sulfate, a drop in pH is observed (Table 1). The drop in pH occurs very quickly and remains unchanged for at least 24 h. Note that the drop in pH indicates that the final concentration of the protons released into the solution by MgSO<sub>4</sub> is twice that released into the solution by NaCl. This

Table 1. The of Nafion@Pc	<b>able 1.</b> The cation-exchange pH drop of salt solutions in the presence of Nafion@Pd.				
Salt solution	Initial pH	pH after 2 h	pH after 24 h		
(0.1 м)	(H <sup>+</sup> concentration)	(H <sup>+</sup> concentration)	(H <sup>+</sup> concentration)		
MgSO₄	6.5 (3.2×10 <sup>-7</sup> )	4.9 (1.3×10 <sup>-5</sup> )	4.8 (1.6×10 <sup>-5</sup> )		
NaCl	6.5 (3.2×10 <sup>-7</sup> )	5.1 (7.9×10 <sup>-6</sup> )	5.1 (7.9×10 <sup>-6</sup> )		

can be attributed to the fact that the charge of the magnesium ions replacing the protons is twice that of the sodium ions. In addition, the ionic radius of  $Mg^{2+}$  is smaller than that of  $Na^+$ , and therefore,  $Mg^{2+}$  is more likely to access pores containing sulfonate end groups. Further material properties of the hybrid catalyst are given below.

The direct conversion of 1,2,3,4-tetrahydro-1-naphthol into tetralin and naphthalene (Scheme 1, top) by Nafion@Pd (80 °C, 2 h) proceeds through catalyzed dehydration to afford 1,2-di-hydronaphthalene, which then undergoes catalyzed disproportion. Figure 2 follows the kinetics of this reaction: It is seen



**Figure 2.** Reaction profiles of the dehydrogenation and disproportion reactions of 1,2,3,4-tetrahydro-1-naphthol catalyzed by Nafion@Pd.

that when the substrate concentration drops to zero, the percentage of 1,2- dihydronaphthalene present reaches a maximum. The disproportion continues until naphthalene and tetralin reach a similar ratio with no (NMR-)traceable 1,2-dihydronaphthalene.<sup>[16]</sup> The GC separation between naphthalene and 1,2-dihydronaphthalene was possible only with coupling to a mass spectrometer.

Significantly, the dehydration did not occur at all if only Nafion (or palladium) was used. The disproportion reaction pulled the dehydration-rehydration equilibrium, which also leads to 1,2,3,4-tetrahydro-2-naphthol as an intermediate (Scheme 1), and lies heavily towards the alcohol side, to completion of the double-bond formation. As recyclability of heterogeneous catalysts is one of their important properties, this was tested four consecutive times; the result is encouraging, as the yield did not drop below 95%.

In a second reaction scheme (Scheme 1, bottom), when1,2dihydronaphthalene was subjected to Nafion@Pd, this time under hydrogen pressure (690 kPa, 80 °C, 24 h), full conversion to fully hydrogenated tetralin was achieved. This shows, firstly, that catalytic hydrogenation is by far faster than disproportion, and secondly, that here too, the Pd-catalyzed step pulls the more difficult Nafion-catalyzed step to completion. Palladium alone did not show any reaction when used under the same conditions. As catalysts are expected to effect similar reactions of various substrates, we next tested the dehydration/hydrogenation of another substrate, 1-phenyl-2-propanol. Indeed, it

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was fully converted under similar conditions into 1-phenylpropane (via 1-phenyl-2-propene, Scheme 2). As with the previous observation, treatment of 1-phenyl-2-propanol with Nafion only did not yield detectable levels of (1-propenyl)benzene. If the reaction is performed under  $H_2$  pressure, the minute quantity of (1-propenyl)benzene that is in equilibrium with the starting material is consumed by the much faster hydrogenation reaction, which pulls the reaction to completion. It is important to note that full conversion of this reaction required the addition of molecular sieves to hinder the hydration back reaction.

We conclude with some additional comments on Nafion@Pd: In search for the proper conditions for the successful entrapment of the catalytic polymer, it was found that slowing down the reduction rate of Pd<sup>II</sup> was needed; otherwise, separate phases formed. Successful slowing down was achieved by replacing water-soluble Pd complexes (such as K<sub>2</sub>PdCl<sub>4</sub>, which was a first, natural choice), with sparingly soluble PdCl<sub>2</sub>. That Nafion does exist in the composite was proven by the detection of fluorine ( $\approx$ 2.4%) by energy-dispersive X-ray spectroscopy (EDAX) measurements (Figure S2, Supporting Information) and by SEM elemental mapping (Figure 3). Residual Zn is



Figure 3. Elemental mapping of Nafion@Pd performed on the micrograph depicted (scale bar: 600 nm).

seen in Figure S2, probably too buried to be washed away, in the form of zinc oxide (in passing, we note that alloying of metals with Zn is known to improve their catalytic activity<sup>[17]</sup>). Oxygen ( $\approx$ 6.5%) originates from Nafion, and probably from some PdO and ZnO, although backscattered electrons and XRD measurements did not show these oxides. Mapping the elements (Figure 3) revealed the homogeneous nature of the composite, at least on the scale of the diameter of the ray of electrons, which was approximately 1 µm area-wise and depthwise. XRD measurements (Figure 4) were performed on the composite to compare its crystallinity to that of pure elemental palladium powder produced by using the same reduction process. Comparison of the two samples revealed that the matrix crystalline structures are essentially identical, except that the



Figure 4. XRD spectra of pure Pd powder (top) and Nafion@Pd (bottom).

average palladium crystallite size (calculated from the Scherrer equation) was found to be somewhat larger in Nafion@Pd, that is, 9.6 nm compared to pure Pd at 7.8 nm. This may be attributed to growth inhibition of the metal nanocrystals by the coating polymer chains.

In conclusion, we displayed here a heterogeneous hybrid catalyst capable of performing two catalytic steps in one pot. The two steps can be carried out only with the dual catalyst, as the first reaction must be pulled to completion by the second step. The new concept of a catalyst entrapped within a metal framework that is itself a catalyst was demonstrated, which opens the possibility to form many new catalysts that are of this composite nature.

### **Experimental Section**

#### Preparation of the dual Nafion@Pd catalyst

Nafion-H (0.6 g), EtOH (100 mL), and H<sub>2</sub>O (100 mL) were placed in a flat-bottomed flask.  $PdCl_2$  (1.6 g, 0.96 g free palladium) was added to the stirred solution (Nafion to palladium ratio was 3 % w/ w) and then zinc (0.7 g) was added. The slurry turned black almost immediately, which indicated that the reduction had started to progress. The reaction mixture was left for 24 h to enable the completion of the reaction. The product suspension was then filtered under vacuum by using 0.8 µm filter paper. The solid was washed with 0.1 m HCl (30 mL) to dissolve the remaining zinc and with triply distilled water (3×) and dried overnight under vacuum. Microanalysis indicated 1.75 wt% of Nafion in the doped Pd. Before use, each batch was homogenized with a mortar and pestle.

# Dehydration-disproportion of 1,2,3,4-tetrahydro-1-naphthol to naphthalene and tetralin as a typical one-step dual catalytic reaction

1,2,3,4-Tetrahydro-1-naphthol (0.2 mL) was placed in cyclohexane (8.0 mL) along with Nafion@Pd (0.24 g) in a round-bottomed flask. The mixture was brought to boiling and heated at reflux for 2 h. The reaction was followed every 10 min by GC until full conversion was achieved, which occurred after 2 h. All of the components of the reaction were determined by NMR spectroscopy.

Please see the Supporting Information for the other catalytic reactions.

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