

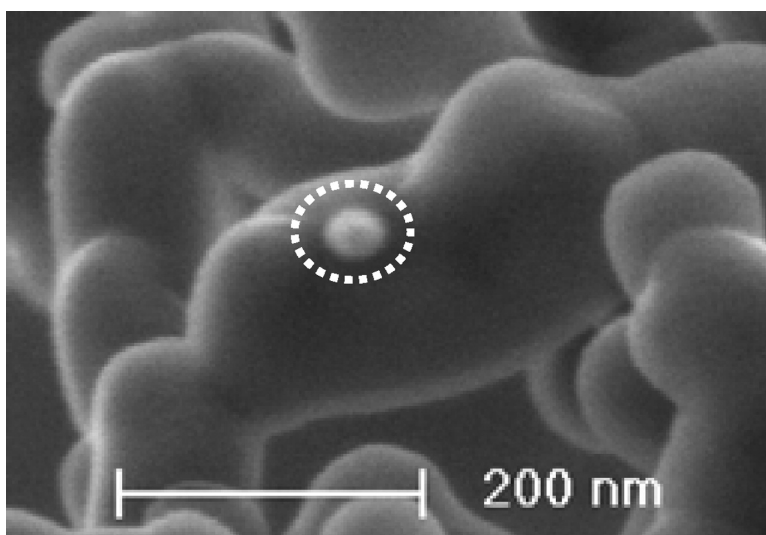
Communication

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## Entrapment of an Organometallic Complex within a Metal: A Concept for Heterogeneous Catalysis

Itzik Yosef, Raed Abu-Reziq, and David Avnir\*

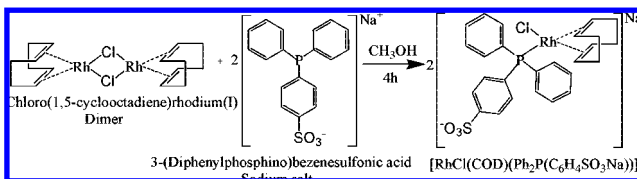
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We have recently introduced a new family of materials, metal–organic composites, in which organic molecules, small or polymeric, are entrapped within metals.<sup>1–7</sup> Besides the basic motivation, namely that these composites have been unknown,<sup>8</sup> the practical motivation is based on the potential ability to tailor metals with any of the properties of the vast library of organic molecules, on the potential to affect the properties of the organic dopant by virtue of immersing it in a sea of electrons, on the potential of creating materials that are “in-between” metal and, say, plastics, and on the potential of the emergence of new properties which are not found in either of the components. Proof-of-concept for these expectations is now rapidly being accumulated. For instance, one can induce unorthodox properties such as having silver which acts as an acid<sup>4</sup> or having right-handed and left-handed enantiomers of chiral gold and silver.<sup>6</sup> Two principal methods were developed for the synthesis of these composites, both of which are based on the reduction of the metal cation in the presence of the molecule to be entrapped. In one method, the process is homogeneous, in that all components, including the reducing agent, are soluble. In the second method, employed in this report, the metal cation is reduced by a heterogeneous dispersion of a sacrificial reducing metal.<sup>1</sup> For instance, solutions of silver and copper salts were treated with metallic zinc powder, and gold salt solution was treated with copper powder in the presence of the dopants, either the polymer Nafion or the dye thionin, thus creating various Nafion@metals and thionin@metals. An important property of these composites, of relevance to this report, is that they are porous and that the dopant is accessible for reaction by substrates diffusing into the composite.<sup>2</sup> Yet despite being accessible, the dopant does not leach out (even in solvents it is normally soluble in), or leaches out to a negligible extent.<sup>1,2</sup>

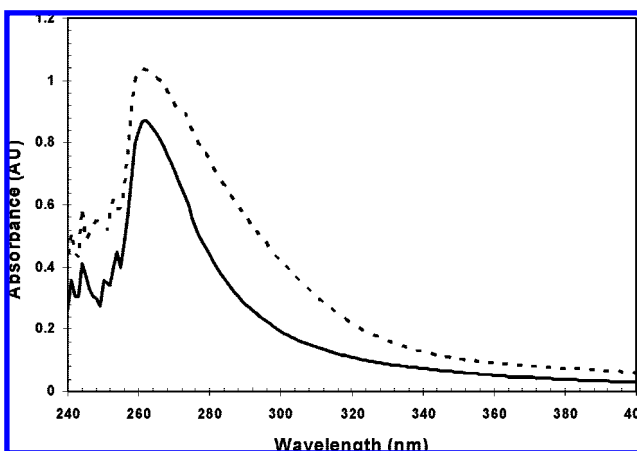
The proven ability to entrap an organic molecule within a metal while retaining its accessibility opens up interesting questions: First, traditionally, heterogenization of a homogeneous catalyst has been done on two major types of supports: inorganic oxides<sup>9–12</sup> and organic polymers;<sup>13</sup> can metals be used for that purpose? And second, will a metal as a heterogenizing environment affect the activity of the homogeneous catalyst? We report here a feasibility study which has provided positive answers to these two questions, thus opening, we believe, a new direction in heterogeneous catalysis. Specifically, we have synthesized (Scheme 1) and entrapped a COD–rhodium(I) complex ( $\text{RhCl}(\text{COD})(\text{Ph}_2\text{P}(\text{C}_6\text{H}_4\text{SO}_3\text{Na}))$ ) in silver ( $[\text{Rh}]@\text{Ag}$ ) and tested its ability to catalyze the hydrogenation of styrene and diphenylacetylene. With these reactions we have shown that a metal can act as a heterogeneous carrier of a homogeneous complex, the entrapped complex is stabilized by the metallic matrix, and the nature of the products is affected by the entrapment. We have also shown that adsorption of  $[\text{Rh}]$  on Ag and entrapment are entirely different processes and only by entrapment could these observations have been made. For completion of these introductory notes it is relevant to recall the reports

**Scheme 1.** Synthesis of the Rh(I) Catalyst

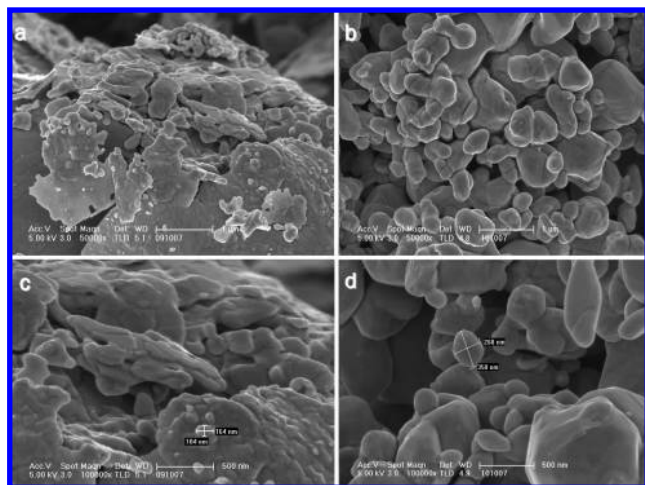


on styrene hydrogenation with silica entrapped  $\text{RhCl}(\text{PPh}_3)_3$ ,<sup>14</sup> on diphenylacetylene hydrogenation with a Rh complex incorporated in a siloxane network,<sup>15</sup> on the coentrapment of a Rh complex with Pd in a silica sol–gel matrix, and the anchoring of a Rh complex to a silica surface containing dispersed Pd.<sup>16</sup>

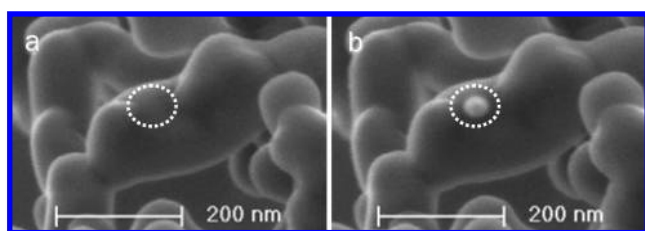
Entrapment was carried out according to (redox balanced):  $[\text{Rh}](\text{aq}) + 2\text{AgNO}_3(\text{aq}) + \text{Zn}(\text{s}) \rightarrow [\text{Rh}]@(\text{2Ag})(\text{s}) + \text{Zn}(\text{NO}_3)_2(\text{aq})$ . In order to ascertain that the entrapped Rh–complex ( $[\text{Rh}]$ ) remained intact, its extraction from  $[\text{Rh}]@\text{Ag}$  was needed. It was found that water, in which  $[\text{Rh}]$  is soluble and which was therefore used as a solvent for the preparation of the doped metal, could not extract the entrapped complex. This is one of several indications that the entrapment process is a completely different process compared to adsorption, and we shall see more indications for this below. DMSO was found to be a good solvent for the purpose of extraction. As seen in Figure 1, spectral analysis of the DMSO-extracted catalyst proves that the complex was kept intact during the entrapment process. Of course, this does not exclude the possibility that, in its entrapped form, the complex is a precatalyst to the actually active species. Nitrogen adsorption–desorption isotherms reveal that the composite is mesoporous with an average pore size of 13 nm and a consequent low surface area of 1.5 m<sup>2</sup>/g. Still, these values are larger than those obtained for pure Ag synthesized under similar conditions: 5 nm and 0.3 m<sup>2</sup>/g. The organometallic complex seems



**Figure 1.** Spectra of the rhodium(I) catalyst in DMSO before entrapment (dotted line) and after extraction from  $[\text{Rh}]@\text{Ag}$  (smooth line).



**Figure 2.** High resolution SEM images of [Rh]@Ag, ((a): bar = 1  $\mu$ , (c): bar = 500 nm), and, for comparison, [Rh] adsorbed on silver ((b): bar = 1  $\mu$ , (d): bar = 500 nm).



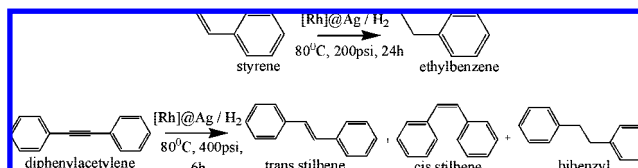
**Figure 3.** High resolution SEM images for [Rh]@Ag sample - the oozing out of the organic dopant due to the high energy of the electron beam (see circled area): (a) First taken, and (b) after a few seconds.

to interfere with the growth process of the silver crystals (as indeed observed in the SEM images; see below). It should be noted that the surface area value was obtained by using the BET equation, the compliance to which was excellent; such compliance is usually associated with high surface homogeneity of the adsorbing material. High-resolution SEM further underlines the differences between the doped silver and the pure one: HR-SEM images of [Rh]@Ag are shown in Figure 2 and contrasted with [Rh] adsorbed on silver. Smaller crystalline particles can be seen in the doped silver (around 150 nm compared to  $\sim$ 360 nm for the [Rh] adsorbed on silver). This demonstrates again that entrapment and adsorption are different processes: Silver on which [Rh] was adsorbed is affected to a much lesser extent and resembles the pure silver (Figure 1S, Supporting Information). Another visible distinction is that [Rh]@Ag is more sheetlike while in the adsorbed case the particles are more spherical. Higher resolution is provided in Figure 3, where a very interesting observation and proof of the composite nature of the material is shown: the organic dopant is seen oozing out of the composite due to the high energy electron beam focused on the sample.

Adsorption measurements of hydrogen on [Rh]@Ag did not reveal any chemisorption, in agreement with the known fact that hydrogen is not soluble in silver;<sup>17</sup> typically, at 820 mmHg and 77 K, only 0.03 wt % of H<sub>2</sub> was adsorbed (see Supporting Information for details and Figure 2S there). This indicates that the observed effects of the entrapment are not due to synergism between the entrapped complex and the metal but that the metal is acting here mainly as a protecting matrix which provides a confined environment around the [Rh] molecules.

The [Rh]@Ag-catalyzed hydrogenation of styrene (Scheme 2) was carried out in 1,2-dichloroethane under 200 psi of H<sub>2</sub> at 80 °C and stopped after 24 h at 85% conversion. GC analyses showed

### Scheme 2. Catalytic Hydrogenation Reactions



**Table 1.** Hydrogenation<sup>a</sup> of Styrene to Ethylbenzene

catalyst	conversion (%) <sup>b</sup>		
	1st cycle	2nd cycle	3rd cycle
[Rh]@Ag	85	65	45
pure [Rh] <sup>c</sup>	50	—	—
adsorbed [Rh]	7	0	0
pure Ag	0	0	0

<sup>a</sup> Reaction conditions: 24 h, 80 °C, 200 psi. <sup>b</sup> Conversion determined by GC. <sup>c</sup> Cannot be recycled.

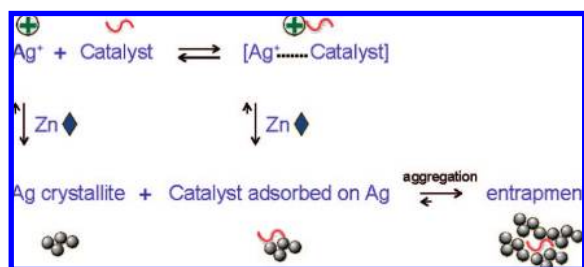
**Table 2.** Hydrogenation<sup>a</sup> of Diphenylacetylene

Catalyst	Conversion (%) <sup>b</sup>								
	1 <sup>st</sup> cycle			2 <sup>nd</sup> cycle			3 <sup>rd</sup> cycle		
	<i>cis</i> -stilbene	<i>trans</i> -stilbene	bibenzyl	<i>cis</i> -stilbene	<i>trans</i> -stilbene	bibenzyl	<i>cis</i> -stilbene	<i>trans</i> -stilbene	bibenzyl
[Rh]@Ag	44	8	7	32	5	2	20	3	0
Pure [Rh] <sup>d</sup>	0	8	32 <sup>c</sup>						
Adsorbed [Rh]	12.5	4.5	trace	0	0	0	0	0	0
Pure Ag	0	0	0	0	0	0	0	0	0

<sup>a</sup> Reaction conditions: 6 h, 80 °C, 400 psi. <sup>b</sup> Conversion determined by GC. <sup>c</sup> After  $\sim$ 3 h: *cis* – 12%, *trans* – 0%, bibenzyl – 20%. <sup>d</sup> Cannot be recycled.

that ethylbenzene is the only product of the styrene hydrogenation. Table 1 gives the hydrogenation activities of the [Rh]@Ag heterogeneous catalyst, the dissolved homogeneous rhodium complex catalyst, the pure Ag metal, and the rhodium complex catalyst adsorbed on silver. It is seen that the pure Ag is inactive as a catalyst, adsorbed [Rh] on silver is only marginally active, and under homogeneous conditions [Rh] affects a 50% conversion but is destroyed after one cycle. This deterioration is due to reductive formation of metallic rhodium deposit<sup>11a</sup>—a black deposit—which is inactive in this reaction. [Rh]@Ag performs better than all of these blanks: The first cycle conversion is the highest (85%), and the easily separated catalyst can be used again, losing however some of its activity. UV–vis and NMR analyses of the liquid phase that was separated from the reaction mixture showed that no detectable [Rh] catalyst had leached into the liquid phase. On the other hand, DMSO extraction of [Rh]@Ag proves that [Rh] remained intact.

The [Rh]@Ag-catalyzed hydrogenation of diphenylacetylene was carried out under a somewhat higher pressure of 400 psi of H<sub>2</sub> and was stopped after 6 h at 60% conversion. GC and NMR analyses revealed *cis*-stilbene to be the main product with *trans*-stilbene and bibenzyl as the secondary ones (Table 2; the preference for the kinetically dictated *cis* product in heterogeneous catalysis has been proposed to be due to *syn*-addition<sup>18</sup>). No *cis*-stilbene was obtained under homogeneous [Rh] catalysis conditions, bibenzyl being the main product in this case (At shorter times, *cis*-stilbene could be detected as an intermediate, e.g., 12% after  $\sim$ 3 h). The homogeneous reaction proceeds to the final reduction product, but the conversion is lower, due to the gradual deterioration of [Rh]; [Rh]@Ag, in contrast, can be reused. And again, the adsorbed

**Scheme 3.** Suggested Mechanism of Heterogeneous Entrapment

configuration gives much lower conversions and becomes inactive after one cycle, and pure silver is inactive in this reaction. When the reaction time is extended up to full conversion (90 h), *cis*-stilbene remains the main product, with an increase in the percentage of bibenzyl (Table 1S, Supporting Information). Yet another proof that entrapment and adsorption provide different catalytic materials is obtained by the following experiment: [Rh]@Ag and [Rh] adsorbed on Ag were treated with an acidic solution of HCl (0.1 M), and the resulting materials were tested again as heterogeneous catalysts in the dipenylacetylene hydrogenation reaction. The conversion in the reaction catalyzed by [Rh]@Ag was still fairly high—50% after 6 h—compared to residual 4% in the adsorbed case.

What then is the mechanism of entrapment that makes it different from adsorption? Scheme 3 illustrates our proposition: Silver ions are known to form stable complexes with various atoms of groups V and VI,<sup>19</sup> phosphorus in our case. Thus, shortly after mixing, some ion pairing occurs between the silver cation and the negatively charged catalysts, bringing the two into close proximity. As the nanometric seed crystals of Ag form heterogeneously by the Zn particles, the dopant, already present in the vicinity, associates with these seeds through a reversible adsorption process. The adsorption takes place through the negatively charged sulfonate groups of catalyst and the silver.<sup>20</sup> During the residence time of the adsorbed species, fast precipitation of Ag atoms and clusters catches and encapsulates the molecule. This process thus pumps most of the dissolved dopant into the 3D Ag matrix.

Indeed, adsorption and entrapment are also different from the point of view of the dimensionality of the event: While adsorption is a 2D process, entrapment renders the dopant—the Rh complex—being surrounded by a 3D metallic cage. This enhances its stability in two ways: First, through the physical protection of the rigid cage and, second, through the reductive sea of electrons of the metal, which, apparently, protect the Rh cation from being reduced, as is the case for the homogeneous procedure. Still, the gradual decrease in activity in the second and third cycle may point to some in situ conversion into metallic Rh.

## Conclusions

In conclusion, we have shown that a homogeneous catalyst can be heterogenized by entrapment within a metal. The silver matrix

meets the basic requirements of a heterogeneous carrier: Stability to the reaction conditions (temperature and pressure), nonleachability, inertness to the reactants and products, and porosity which is open enough for the transport of the substrates in and out. Since a metal and a dopant can each be catalysts, we believe that a potential for interesting exploration of synergism has been opened.

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**Supporting Information Available:** Experimental details and additional results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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