Dual Catalytic Activity of Palladium Doped with a Rhodium Complex in a One-pot, Four Step Process

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The extraction of the two competing reactions from the same catalyst—a composite catalytic-complex@catalytic-metal—is reported. A Wilkinson rhodium based catalyst entrapped within metallic palladium catalyst is shown to perform both hydroformylation and hydrogenation with a ratio that depends on H_2 and CO pressures. Here we demonstrate this special reactivity in a one-pot, four step sequence, which include hydroformylations of phenyl acetylenes, reduction of nitrobenzene to aniline, carbonyl-amine condensations forming imines; and imine reductions.

Introduction

Despite the fact that metals have been a key component in catalysis since its birth, methods for affecting their elementary properties and thus also their catalytic activity have been limited, and have included co-chemisorption of molecules, which are not substrate molecules, alloying the metal with another metal,^[1] downsizing to the nanoscale,^[2] affecting the metal particle through their interaction with their support.^[3] Recently we have introduced a novel approach to that challenge: Doping the metal with molecules.^[4] The metals doping methodology, which has been developed in the past decade, gave rise to the ability of merging properties from the very rich library of several tens of millions of organic molecules with the rather limited library of metals, resulting in the formation of new metallic hybrids, denoted molecule@metal, with new or improved properties, practically wherever metals have been used.^[4,5] Needless to say, metal catalysis is one of the areas to potentially gain most from this new materials methodology.^[6] In principle, three directions in catalysis can be identified: First, using the metal as a heterogenization support for

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201500240.

This publication is part of a Special Issue on Palladium Catalysis. To view the complete issue, visit: http://onlinelibrary.wiley.com/doi/10.1002/cctc.v7.14/issuetoc

molecular homogeneous catalysts, including organometallic,^[7] polymeric,^[8] and inorganic catalysts^[9] (we recall that the classical supports for dispersed metals included mainly ceramic and polymeric supports, but never metals); the second direction is to affect the catalytic properties of the metal by doping it,^[10] and the third direction has been the utilization of the catalytic properties of both the metal and the dopant^[11]—progress in the latter direction is the main topic of this report. Some examples for the first direction include enantioselective electrohydrogenations with alkaloid@Ag,^[12] the acid catalyzed pinacolpinacolone rearrangement by Nafion@Ag,^[13] the hydrogenation of styrene with [RhCl(cod){Ph₂P(C₆H₄SO₃Na)}]@Ag,^[7] the Friedel–Crafts adamantylation of aromatics bv $H_3[P(Mo_3O_{10})_4]@Ag$ and $H_3[P(W_3O_{10})_4]@Ag,^{[9]}$ the partial enantioselective hydrogenation of ketones with (-)-cinchonidine@Pd^[14] and the biocatalyzed hydrolysis of *p*-nitrophenyl phosphate with acid phosphatase@Au.[15] An example of the second direction-affecting the catalytic activity of the metal-is the efficient oxidation of methanol to formaldehyde by silver doped with Congo red.^[10a,b] These reports demonstrated the synthesis of products that cannot be obtained by the separate components, as well as improved stabilities and higher conversions. All of these types of reactivity are possible because the 3D metallic cage which forms around the dopant consists of tight aggregates of metal crystallites, and this porous hierarchal nature, allows on one hand diffusion of substrate and product molecules in and out of the catalytic material, yet not allowing the dopant to leach out even in the solvent used for entrapment. The accumulated data with these materials has shown that 3D entrapment and 2D adsorptions are completely different processes, and the pattern of performance in the reported applications was witnessed solely in the entrapped 3D case.

We return now to the third direction, where both the metal and the dopant are catalysts. This stimulating possibility already yielded some interesting observations. For instance, exceptional synergism between dopant and metal-a rhenium complex entrapped within a silver was recently reported for alkene epoxidations.^[16] Yet another demonstration of the horizon opened by this direction has been the report on a one-pot dual catalytic reaction from the hybrid catalytic material, Nafion@Pd,^[11a] where the Nafion acts as an acidic catalyst and the palladium as a hydrogenation and disproportionation catalyst in a two catalytic step process. Here we widen the scope of catalyst@catalyic-metal concept to two new aspects: First, we introduce the option of entrapment of an organometallic catalytic complex in a catalytic metal. Specifically we demonstrate this concept by entrapping a rhodium complex - Wilkinson's catalyst $[(RhCl(TPPS)_3]$ (TPPS = triphenylphosphine-3-sulfonic



acid sodium salt)) within metallic Pd, [Rh]@Pd in short. Second, we aimed at increasing the number of one-pot reactions, and report here a four step sequence, including reduction of nitrobenzene to aniline, hydroformylations of phenyl acetylenes, carbonyl-amine condensations forming imines, and imine reductions. The main synthetic challenge has been how to tailor reaction conditions that will accommodate in one pot both the oxo-reaction and the hydrogenation. Although hydrogenation is usually a straightforward reaction of molecular hydrogen addition and is known to be catalyzed by both palladium and rhodium, hydroformylation is a more complex reaction of addition of CO and hydrogen to a carbon-carbon double or triple bond resulting in linear and branched aldehydes. Hydroformylation of alkynes and specifically aryl alkynes and unsymmetrical alkynes is especially difficult, as usually the selectivity towards hydroformylation rather than hydrogenation is challenging; here is how we solved it:

Results and discussion

As the multiple activity of [Rh]@Pd is dictated by the material characteristics of this doped metal, we begin with this aspect of the study, and then move on to its reactivity. SEM images, Figure 1, display the typically aggregated porosity of the matrix, an important feature that allows substrate molecules to penetrate and reach the entrapped Rh catalyst, and allows product molecules to diffuse out.



Figure 1. SEM images of the dual catalyst $[Rh(TPPS)_3CI]@Pd$, ([Rh]@Pd). Left bar, 2 µm; right bar 200 nm.

Further characterization of this porosity is provided by the shape of the nitrogen adsorption-desorption isotherm (Figure 2, top) which is typical of a mesoporous material; indeed, the BJH-calculated average pore diameter is ≈ 10 nm (see the Supporting Information) and the calculated BET surface area is $13.5 \text{ m}^2 \text{g}^{-1}$ (for comparison purposes with classical catalysts supports such as carbon and alumina, recall that the weight of Pd is much higher than C or Al, that is, in terms of per mol atoms, the comparative surface area is higher). An important observation is that the compliance to the BET equation is excellent (Figure 2, bottom)—this indicates the homogeneity of the physisorption sites, and, therefore, also the homogeneity of the composite material, that is, of good dispersion of the dopant in the metal.



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Figure 2. Top-Adsorption-desorption isotherms of nitrogen is indicative of the mesoporosity of [Rh]@Pd. Bottom-Shown is the compliance to the BET equation: The perfect compliance is indicative of the homogeneity of the composite material.



Figure 3. XRD analysis of the composite [Rh]@Pd.

X-ray diffraction (XRD) analysis indicates clearly that the FCC crystal nature of the palladium nanocrystallites is not affected by the entrapment (Figure 3). Notably, the XRD spectrum shows no signs of zinc and palladium oxide, and likewise not seen are metallic rhenium crystals. The average size of the Pd nanocrystals, as determined by the Scherer equation is ≈ 2.8 nm, somewhat smaller than, but in agreement with previous reports.^[11a] The presence of the Rh complex was confirmed by EDAX analysis (Figure 4). The EDAX analysis also reveals the ligand's phosphorous, as well as oxygen and zinc (which probably originate from small amounts of PdO and ZnO on the surface, but as these are not seen by XRD, they are apparently residual).





Figure 4. EDAX analysis of [Rh]@Pd.

As described above, our aim has been to combine in one catalytic material the ability to hydroformylate and to hydrogenate. As metallic palladium catalyzes hydrogenation, but practically does not catalyze hydroformylation, it was selected as the entrapping metal of choice. On the other hand, rhodium complexes are widely used to catalyze hydroformylation reactions,^[17] but the efficiency of Willkinson-type catalysts in hydrogenations is greatly decreased as the number of the triphenylphosphine groups increases,^[18] and thus this complex was selected as the organometallic complex to be entrapped. Although combinations of rhodium (both as metal particles and in the form of a complex) and palladium were anchored onto silica to explore hydrogenation and hydroformylation separately,^[19] their one-pot competition over hydrogen was not explored.

Indeed, the main problem which was solved in this study has been to carefully find the right hydrogen pressure that will allow hydroformylation *and* hydrogenation at the same time too much reduces all of the starting substrates and prevents hydroformylation, and too little allows partial hydroformylation and partial hydrogenation. Thus, we regard the extraction of the two competing reactions from the same catalyst, as shown below, as a non-trivial result of this study. Specifically, as mentioned above, we performed the hydroformylation reaction on terminal aryl-alkynes resulting in the corresponding branched and linear aldehydes, the reduction of nitrobenzene to aniline, the condensation of both products to the corresponding imines, and their reduction to the substituted amines (Scheme 1). Under the optimal conditions described in the Experimental Details none of the potential hydroamination prod-

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ucts is obtained, and, interestingly, no styrene is observed as potential intermediate. The most successful reactions were performed when the reaction vessel was charged with hydrogen/ carbon monoxide molar ratio of 1:4 at pressures of 100 and 400 psi (total reaction pressure of 500 psi; 1 psi = 68.9 mbar). The large excess of CO ensured the successful progress of the hydroformylation rather than hydrogenation. The optimized temperature was 95 °C—at lower temperatures, hydrogenation to ethylbenzene was the preferred reaction. Solvent selection was also critical: In addition to the other factors mentioned, selection of the right polar solvent is important for the success of a hydroformylation reaction;^[20] chlorinated solvents were found to be more useful than methanol and hexanes.

Duration of 48 h was needed for the completion of the full reaction set under optimal conditions. Although reduction was the fastest process, hydroformylation was slow, and so was the condensation reaction. The ratio of linear: branched products (*N*-phenylbenzenepropanamine and β -methyl-*N*-phenylbenzeneethanamine), under the optimal conditions was 1:1.9. When a blank hydroformylation reaction was performed with no nitrobenzene in the reaction vessel, hydrogenation of phenylacetylene to ethylbenzene was observed as well (35%). Another important aspect of the four-step sequence is that the final reduction of the imine to amine pulls the whole sequence to completion. This is so because the imine formation is an equilibrium reaction which releases water as a by-product. The shifting of the imine formation is assisted by water removal, and therefore several beads of molecular sieves were added to the reaction vessel.

Shown in Figure 5 are the details of the optimization experiments (average of at least four repetitions), which led to the optimal conditions of 100:400 psi of hydrogen to CO. To compare the results of the experiments under different pressures, the experiment was allowed to run for 6 days to reach near completion under the different conditions. Depending on the CO/H₂ ratio, the linear branched products ratio varied in the range 1:1.5-1:2. Additional hydrogen pressures of 400, 200, and 50 psi, as well as the use of hydrogen at atmospheric pressure (15 psi), all with CO pressure of 400 psi were tested. When hydrogen at atmospheric pressure was used, the hydroformylation reaction did not take place at all and hydrogenation of nitrobenzene to aniline took place only in part. If hydrogen is scarce, the reduction processes are slowed down, due to occupation of the catalyst pores by CO molecules. This is why even after a long reaction time of 6 days phenylacetylene was still observed at pressures of 50 psi and lower. The fact that at low levels of hydrogen of 50 psi reduction of phenylacetylene to



Scheme 1. Typical reactions sequence of the hybrid catalyst. Molecular sieves were added to assist in pulling the reaction towards the imine.



Figure 5. Dependence of products and intermediate distributions on the hydrogen pressure at fixed CO pressure of 400 psi.

styrene does take place may indicate that the hydroformylation process passes though initial reduction to styrene in this particular system. Here the branched product begins to form at a 5% level. The hydroformylation of acetylene was slightly greater at 100 psi compared to 200 psi of hydrogen. The main by-product was ethylbenzene, and the percentage of this product grows as the pressure of hydrogen increases. At high levels of hydrogen, reduction to ethylbenzene occurs (as is the reduction of nitrobenzene to aniline) that is, reduction of the double bond takes place rather easily and other reactions, such as hydroamination or hydroformylation are observed to a lesser degree. When the ratio was increased to 400:400 (a total of 800 psi), hydrogenation to ethyl benzene with little hydroformylation took place.

To assure that the observed reaction sequence is not due to leached [Rh], the supernatant solution was tested for possible catalytic effects according to the same procedure for 6 days under heating. No hydroformylation was observed, but the presence of some palladium nanoparticles was detected by minor reduction to styrene, ethyl benzene and aniline, and also some hydroamination—the first and the last do not form with the hybrid catalyst. Finally, the ability to affect the reactions sequence of Scheme 1 was additionally tested on three substituted phenylacetylenes: 4-chlorophenlacetylene, 4-fluorophenlacetylene, and 4-methodxyphenlacetylene. Indeed, it was found to work as well, and the results are summarized in Table 1.

Table 1. Yields of final products for various acetylenes.				
Substrate	Branched	Yield [%] Linear	Total	Ratio
phenylacetylene 4-fluorophenylacetylene 4-chlorophenylacetylene 4-methoxyphenylacetylene	54.3 48.9 25.7 25.6	28.6 17.2 6.8 19.6	82.9 66.1 32.5 45.2	1.9 2.8 3.8 1.3

Recyclability experiment was performed with a focus on the performance of the entrapped [Rh]: the second cycle showed a slight reduction in yield from 80% down to 72%; interestingly only the branched product was obtained. Further recycles do not yield satisfactory values.

In conclusion, the independent reactions of hydrogenation and hydroformylation, catalyzed by a hybrid catalyst of a rhodium complex entrapped within palladium was demonstrated and investigated. We showed that consecutive catalytic reactions using one combined catalyst can lead to interesting ways in which multiple step processes are performed; we believe these observations are of interest in the general context of heterogeneous catalysis.

Experimental Section

Preparation of the [Rh]@Pd catalyst: Synthesis of the catalyst: Rh atoms (9×10⁻⁴ mol) in the form of $[(RhCICOD)_2]$ (COD = cyclooctadiene) were placed in a round bottom flask along with TPPS (triphenylphosphine-3-sulfonic acid sodium salt, 2.7×10^{-3} mol) and dissolved with methanol (55 mL). The mixture was stirred overnight at 55 °C and evaporated to dryness, resulting in [Rh(TPPS)₃Cl], denoted [Rh] for short. Entrapment of [Rh] in Pd: [Rh] was dissolved in triply distilled water (160 mL) and then $PdCl_2$ (9× 10^{-3} mol) was added, the temperature was set to 40° C and Zn granules (0.01 mol) were added. The mixture was stirred for five days during which the slurry blackened, and then the product, [Rh]@Pd, was filtered, washed with water three times and then with HCl (0.1 M, 30 mL), and dried overnight in a desiccator. Before use, the catalyst was ground using an agate mortar and pestle for several minutes, until the metal crumbs were homogeneous to the eye. TGA analysis average indicates a Rh/Pd weight ratio of 1:8 in the final product, [Rh]@Pd.^[21]

The one-pot, four step multiple catalytic reaction: The dried catalyst (0.13 g, 1.1×10^{-3} mol Pd, 9.8×10^{-5} mol Rh) was placed in a pressure vessel. Nitrobenzene (0.1 mL, 9.8×10^{-4} mol) and phenylacetylene (0.1 mL, 9.1×10^{-4} mol), and 1,2-dichloroethane (3.0 mL) were added along with \approx 10 beads of molecular sieves (4 Å). A feed of H_2 (100 psi) and CO (400 psi) was inserted to the reaction mixture, which was heated to 90 °C for 2 days. The reaction components were identified by NMR spectroscopy and gas chromatography. NMR was measured after evaporation and compared, when possible, to known spectra, or an NMR prediction tool was used.^[21] **Recyclability test:** The dried catalyst (0.13 g, 1.1×10^{-3} mol Pd, 9.8×10^{-5} mol Rh) was placed in a pressure vessel. Nitrobenzene (0.1 mL, 9.8×10^{-4} mol) and phenylacetylene (0.1 mL, $9.1 \times$ 10^{-4} mol), and 1,2-dichloroethane (3.0 mL) were added along with \approx 10 beads of molecular sieves (4 Å). A feed of H₂ (100 psi) and CO (400 psi) was inserted to the reaction mixture, which was heated to 90 °C for 2 days. Then, the supernatant was poured off, centrifuged at 50000 rpm for 20 min and evaporated for measurement. The remaining catalyst was collected back into the reaction vessel for further use.

Instrumentation: For SEM measurements a Sirion (FEI) microscope was used, operating at 5 kV, fitted with an EDS free detector. Samples were prepared by placing the air-dried powder on an aluminum stub suitable for SEM using carbon double side tape. Thermogravimetric analysis was performed by using a Mettler–Toledo TGA/SDTA 851e from 50 to 800 8C at a heating rate of 10 °C min⁻¹ in flowing N₂. Specific surface area was calculated from nitrogen adsorption/desorption isotherms obtained by using a Micromeritics ASAP 2000 surface analyzer, using the BET equation. Gas chromatographs were measured by using an Agilent 7890A GC, fitted with an HP-5 column. Solution analysis was performed by introducing



sample solutions by direct spitless injection (1 µL by volume). For the chromatography procedure, the oven temperature was elevated from 80 °C to 220 °C at 2.5 °C min⁻¹, then to 260 °C at 20 °C min⁻¹ and held at the final temperature for 10 min. Helium carrier gas flow was 1.5 mL min ^{<-M>1}. X-ray diffraction (XRD) measurements were performed with a Philips automated powder diffractometer (with a PW1830 generator, PW1710 control unit, PW1820 vertical goniometer, 40 kV, 30 mA, Cu_{Ka1} (1.5406 Å), stepscan mode 0.02 s⁻¹). NMR spectra were recorded with Bruker DRX-400 in CDCl₃.

Acknowledgements

We acknowledge the support of the Einstein Foundation, Berlin, and the Israel Science Foundation (grant no. 703/12).

Keywords: heterogeneous catalysis • mesoporous materials • multiple catalysis • organic–inorganic hybrid composites • supported catalysts

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Received: March 6, 2015 Revised: April 17, 2015 Published online on June 18, 2015