ORGANOMETALLICS

Rhodium Catechol Containing Porous Organic Polymers: Defined Catalysis for Single-Site and Supported Nanoparticulate Materials

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Supporting Information

ABSTRACT: A single-site, rhodium(I) catecholate containing porous organic polymer was prepared and utilized as an active catalyst for the hydrogenation of olefins in both liquid-phase and gas-phase reactors. Liquid-phase, batch hydrogenation reactions at 50 psi and ambient temperatures result in the formation of rhodium metal nanoparticles supported within the polymer framework. Surprisingly, the Rh(I) complex is catalytically active and stable for propene hydrogenation at ambient temperatures under gas-phase conditions, where reduction of the Rh(I) centers to Rh(0) nanoparticles requires at least 200–250 °C under a flow of hydrogen gas. After hightemperature treatment, the Rh(0) nanoparticles are active arene hydrogenation catalysts that convert toluene to



methylcyclohexadiene at a rate of 9.3×10^{-3} mol g⁻¹ h⁻¹ of rhodium metal at room temperature. Conversely, single-site Rh(I) is an active and stable catalyst for the hydrogenation of propylene (but not toluene) under gas-phase conditions at room temperature.

INTRODUCTION

Current interest in metal containing porous organic polymers $(POPs)^{1-6}$ is expanding toward many different applications in catalysis,⁷⁻¹⁴ gas storage,^{6,15-20} and gas separations.^{12,21-23} This rise in research activity can be attributed to these chemical and thermal stability of these materials related to MOFs and more tunable binding environments in comparison to zeolitic environments. The tunability of these materials is reflected in recent reports concerning a variety of catalytic reactions, including hydrogenation,^{24,25} oxidation,^{7-9,26} reduction,^{10,24,27} and photochemical transformations¹¹ with a number of different metal-containing materials.

Our group is currently studying catalytic POPs containing metal catecholate functionalities, as typical homogeneous metal catecholate complexes are frequently catalytically inactive due to their propensity toward the formation of bis- or tris-chelation motifs for metal stabilization.^{28–33} Recent publications within our group and others have utilized a catechol-containing POP, **POP** A_2B_1 (monomer **A**, 3,6-linked catechol; monomer **B**, para-linked tetraphenylmethane),³⁴ and derivatives of such to stabilize catalytically active single-site metal centers of Fe,^{24,27} Ta,²⁵ and La.³⁵ These catalysts are unique because a single catechol ligand supports the metal complex and represents a

coordination environment that does not have freely homogeneous analogues.

Although rhodium is one of the most rare and costly of the transition metals, a large amount of catalysis research has been conducted with it because it often exhibits unique and extraordinary catalytic activity for hydrogenation, hydroformylation, and oxidation reactions.³⁶ Special attention must be placed on metal speciation when studying Rh catalysis to avoid confusing rhodium metal for molecular or ionic rhodium species. This is due to the relative ease of reduction of rhodium salts and organometallic complexes to rhodium metal.^{36,37} The study of the actual catalytic site within heterogeneous materials is often very challenging and can result in improper identification. The report herein highlights the use of rhodium for the hydrogenation of simple olefins and toluene supported in POP A_2B_1 for the discrimination of the oxidation state of rhodium (ionic or metallic) within this polymer support under reaction conditions.

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Figure 1. Synthesis of $[(COD)Rh(CAT)]_2$ -POP (p = extended polymer network).



Figure 2. X-ray absorption measurements of $[(COD)Rh(CAT)]_2$ -POP and standards: (orange line) as-prepared material; (green line) [{t-BuNC(Ph)CN-t-Bu}Rh(COD)]; (purple line) [(COD)_2Rh][BF_4]; (black line) Rh foil; (red line) Rh_2O_3. Calculated models are given in Table 1

RESULTS AND DISCUSSION

Addition of the convenient Rh(I) source [{t-BuNC(Ph)CN-t-Bu}Rh(COD)]³⁸ (where COD is 1,5-cyclooctadiene and{t-BuNC(Ph)CN-t-Bu is N,N'-di-tert-butylphenylamidinate) to a suspension of POP A_2B_1 in diethyl ether resulted in complete uptake of the rhodium complex within 24 h. Analysis of the washings by ¹H NMR spectroscopy reveals 95% of the expected [*t*-BuNC(Ph)CN(H)*t*-Bu] upon Rh ligation. Upon further washing, the remaining 5% is recovered. Importantly, the addition of excess [{t-BuNC(Ph)CN-t-Bu}Rh(COD)] to [(COD)Rh(CAT)]₂-POP (Figure 1) does not result in any appreciable weight change, after washing the solid to remove entrained rhodium precursor, corroborating full metalation of the catechol sites. Attempts to generate a homogeneous rhodium catechol complex in solution by the addition of 1 equiv of 3,6-di-tert-butylcatechol to 1 equiv of [{t-BuNC(Ph)-CN-t-Bu}Rh(COD)] resulted in the formation of a dinuclear rhodium complex. This complex is formed even with mixing the reagents precooled to -78 °C.

In order to gain insight into the Rh oxidation state and coordination environment at the Rh centers, X-ray absorption spectroscopy data (XAS) were obtained under inert conditions and in air at ambient temperature and pressure. As rhodium XAS does not contain a discernible pre-edge feature, the energy of the first derivative of the XANES curve of [(COD)Rh-(CAT)]₂-POP was compared to those of Rh(I) and Rh(III) standards, clearly showing that the as-prepared rhodium

material is in the 1+ oxidation state (Figure 2 (left) and Table 1). For clarity, the spectrum for $[(COD)Rh(CAT)]_{2}$ -

Table 1. XAS Results for	[(COD)Rh(CAT)] ₂ -POP under
Inert and Oxidizing Cond	itions	

treatment	edge energy, keV	oxidn state	CN	<i>R</i> , Å
[(COD)Rh(CAT)] ₂ -POP	23.2273	Rh(I)	4.0	2.05
(COD)Rh[^t BuNC(Ph)N ^t Bu]	23.2266	Rh(I)	6.0	2.08
$[(COD)_2Rh][BF_4]$	23.2270	Rh(I)	NA	NA
Rh foil	23.2200	Rh(0)	12	2.69
Rh ₂ O ₃	23.2295	Rh(III)	6	2.05

POP in air is not shown, as the spectrum is identical with the spectrum obtained under inert conditions. Although metal catecholate complexes are well-known to undergo oxidation of either the metal or ligand under mildly oxidizing conditions, these data indicate that the Rh(I) is not oxidized after brief exposure to ambient air.

Analysis of the extended X-ray absorption fine structure (EXAFS; Figure 2 (right)) reveals that $[(COD)Rh(CAT)]_2$ -**POP** consists of four-coordinate rhodium centers with average bond distances of 2.05 Å. Comparisons of coordination numbers and average bond lengths are given in Table 1. Such analysis indicates that the Rh centers are in a four-coordinate environment bound to an anionic oxyphenol, with a dative η^2 -olefin COD interaction. Conventional counting of

organometallic complex coordination numbers would dictate that a single olefin interaction takes up one coordination site; however, in comparison with the coordination number of the precursor, [{t-BuNC(Ph)CN-t-Bu}Rh(COD)], COD olefin interactions are counted as two neighboring atoms and not one per olefin bond. This is because the underlying physics of the XAS experiment probes the nature and number of coordinated atoms as a whole^{39,40} and both C atoms of the olefin are detected in the extended X-ray absorption fine structure (EXAFS).

Isolated Rh(I) complexes with only one olefin of the COD bound are rare,^{41,42} as these complexes typically contain chelating COD moieties. However, one of these complexes, $(\eta^2 - 1, 2, 5, 6 - \text{cyclooctadiene}) \{\eta^2 - [\text{bis}(\text{diisopropylamino}) - \theta - 1, 2, 5, 6 - \text{cyclooctadiene})\}$ phosphino][2,6-bis(trifluoromethyl)phenyl]carbene}rhodium chloride,⁴¹ was characterized by ¹³C NMR spectroscopy and contains a resonance at 71.7 ppm assigned to the olefin carbons bound to the rhodium center. For comparison and direct evidence of η^2 -COD coordination to the Rh centers, solid-state (SS) ¹H and ¹³C NMR spectroscopy was performed for [(COD)Rh(CAT)]₂-POP. The SS ¹H NMR data (Figure S2, Supporting Information) reveals an upfield shift of the aromatic protons within the material consistent with Rh(I) coordination to catechol sites. Resonances for the COD protons are observed but are rather broad and nondiscernible as to the number of varied electronic environments. However, the SS ¹³C NMR spectrum (Figure 3; a fully deconvoluted spectrum is



Figure 3. Solid-state ${}^{1}H/{}^{13}C$ cross-polarized NMR spectra overlay of POP $A_{2}B_{1}$ and $[(COD)Rh(CAT)]_{2}$ -POP, highlighting the COD–Rh association.

given by Figure S3 in the Supporting Information) shows clearly defined resonances for olefin carbons bound to Rh(I) at 70.7 ppm consistent per the previous report.⁴¹ The unbound olefinic carbon resonances are observed at 130.6 ppm, and this asymmetry in the SS NMR spectrum corroborates the XAFS analysis describing Rh(I) centers with η^2 -COD interactions.

With a firm picture of the precatalyst Rh structure and the recent development of hydrogenation catalysts contained within porous materials,^{43,44} catalytic activity toward the hydrogenation of the simple arene toluene was explored. Reactions were first performed in deuterated tetrahydrofuran (THF- d_8) under a 50 psi H₂ atmosphere at ambient temperature, where full conversion to methylcyclohexane was observed within 4 h. However, upon reaction completion, a color change from orange to black occurred for [(COD)Rh-

 $(CAT)]_2$ -POP. As mild reduction of rhodium complexes to rhodium metal has been well established,^{36,37,45,46} a color change from orange to black is indicative of such phenomena. Analysis by scanning transmission electron microscopy (STEM) spectroscopy shows 1.5–7.0 nm particles of rhodium metal with a mean size of 3.4 ± 1.0 nm (Figure 4) after liquidphase batch reactions were performed, and the material **Rh(NP)(CAT-POP)** (NP = nanoparticle) was isolated. Such reduction is typical of supported Rh complexes in solution.^{17,18} Additionally, a similar reduction of metal occurs in the hydrogenation of olefins (i.e., cyclohexene and tetramethylethylene) and benzonitrile under identical reaction conditions.

To determine the source of nanoparticle formation during liquid-phase hydrogenation reactions of toluene and unsaturated substrates in THF- d_8 , the reactions were performed in deuterated cyclohexane. Upon a change in solvent a drastic increase in reaction completion time to 8 h occurs for the hydrogenation of toluene at 50 psi of H₂. Additionally, reactions performed in THF- d_8 at 50 psi of H₂ lose ~10 psi of H₂ within 1.5 h, indicative of an induction period for nanoparticle formation. Alternatively, such a pressure consumption does not occur for reactions with deuterated cyclohexane until ~4 h of reaction time, indicating that solvents play a major role in the time of reduction of [(COD)Rh(CAT)]₂-POP to nanoparticles. Indeed, when the reaction in deuterated cyclohexane is halted before the consumption of ~ 10 psi of H₂ (at 3 h reaction time), $[(COD)Rh(CAT)]_2$ -POP is still orange with no conversion of toluene to methylcyclohexane. These data may seem contradictory, but it is reasonable to hypothesize that the more coordinating solvent THF- d_8 helps to reduce the energy barrier to rhodium metal reduction. However, solvent alone is not sufficient for Rh reduction, since [(COD)Rh(CAT)]₂-POP treated with 50 psi of H_2 in only THF- d_8 with no aromatic substrate present does not reduce to rhodium metal: i.e. there is no visual change in the material and no particles are observed by STEM. Thus, while coordinating solvent aids in the reduction of rhodium to metal, the substrate is also necessary for the reduction of rhodium to metal under liquid-phase reaction conditions.

Because liquid-phase hydrogenation reactions of toluene produced nanoparticles with solvent-dependent formation kinetics, we also tested the hydrogenation of propene and toluene under gas-phase and solvent-free plug-flow hydrogenation conditions. Propene hydrogenation was performed first as a test of the material to perform hydrogenation of a simple olefin. The results obtained at ambient temperature are summarized in Table 2. A slight induction period occurs for the material over the course of 2.5 h, probably due to the removal of entrained solvent molecules in the POP framework, but the activity remains stable for over 24 h on stream at maximum conversion with a TOF of 22.5 $h^{-1}\!,$ assuming all rhodium(I) centers are active (or 2.2×10^{-3} mol h⁻¹ g⁻¹). Exposure to oxygen and reentry into catalysis does not result in oxidation of the Rh centers or catalyst deactivation, but the conversion tested over three recycling periods remains the same. In accordance with Bayram et al.,47 poisoning studies were attempted with PMe₃ to determine the actual number of active rhodium centers under reaction conditions. However, addition of PMe₃ to [(COD)Rh(CAT)]₂-POP results in leeching of rhodium(I) out of the polymer, not allowing such studies, thus resulting in the assumption that all rhodium centers are active for hydrogenation.



Figure 4. (top) Representative STEM images of Rh(NP)(CAT-POP) as prepared (left) and after liquid-phase batch hydrogenation reactions of toluene with $[(COD)Rh(CAT)]_2$ -POP in THF- d_8 (middle and right). (bottom) Graph of particle size distribution counting for this material.

Table 2. Propylene Hydrogenation Results for Plug-Flow Reactions with [(COD)Rh(CAT)]₂-POP

time (min)	Rh TOF_{av} at room temp (h^{-1})
0	15.9
60	20.3
150	22.1
max conversion ^a	22.5
^a 24 hours on-stream.	

The gas-phase hydrogenation of propene with $[(COD)Rh-(CAT)]_2$ -POP is rapid, and there is no change in color; however, visual observation does not preclude the possibility of reduction of the Rh(I) to Rh(0). Thus, the catalyst was analyzed by in situ XAS with hydrogen, propylene, and a mixture of propylene and hydrogen. All three of these experiments resulted in no change of the spectrum of the material, as shown in Figure 1, indicating that Rh(I) activates H₂ without the formation of a Rh(III) intermediate or the equilibrium lies far to the Rh(I) oxidation state. Moreover, XAS does not show any reduction of the metal at ambient temperature or up to 175 °C with reactant gases. These observations are in contrast to those of Gates' Rh(III) species Rh(allyl)₂SiO₂,³⁷ which reduces to rhodium metal after 5 h of H₂ exposure on stream at ambient temperature.

Analysis of $[(COD)Rh(CAT)]_2$ -POP by XAS at elevated temperatures under hydrogen gas (3.5% in helium) revealed that the formation of nanoparticles does not occur below 200 °C. Complete conversion to nanoparticles occurs in 30 min at 250 °C to generate Rh(NP)(CAT-POP), as shown in Figure 5.





A comparison of the XAFS spectrum (Figure 5 (right)) with the Rh foil indicates the presence of nanoparticles \sim 5 nm in size, which corroborates the particle sizes measured by STEM of [(COD)Rh(CAT)]₂-POP after batch hydrogenation reactions.

However, it is still possible that a small percent (<5%) of the rhodium centers, which is below the detection limit of XAS, have reduced to metal and are the catalytically active species for olefin hydrogenation in the gas phase. The ability of Rh(0)nanoparticles to catalytically saturate aromatics provides a convenient way to test for the onset of metal reduction. Thus, the Rh(I) single-site catalyst [(COD)Rh(CAT)]₂-POP under conditions where it rapidly hydrogenates propene was also tested for toluene hydrogenation in the gas phase: i.e., without solvent. A saturator was attached to the plug-flow system filled with toluene. The reaction was run at ambient temperature with a flow of 15 mL/min of 4% H₂/96% Ar through the toluene saturator at 22 Torr. For the same [(COD)Rh-(CAT)]₂-POP catalyst used for propylene hydrogenation, there was no toluene hydrogenation at room temperature. After hightemperature reduction of the Rh(I) metal centers to nanoparticles, the catalyst was cooled to room temperature, where Rh(NP)(CAT-POP) converted toluene quantitatively at 25 °C to methylcyclohexadiene (TOF of 9.3 \times 10⁻³ mol g⁻¹ h⁻¹). Methylcyclohexadiene was observed as the product because the current reactor setup only allows the ratio of H₂ to toluene to be approximately 1:1 under steady-state conditions at this temperature. Finally, infrared analysis of the Rh(NP)(CAT-**POP**) catalyst after toluene saturation shows that the C=Cregion is unchanged. Thus, the Rh NPs within the polymer pores are unable to hydrogenate the bulk POP network.

Given the propensity for POP materials to entrain guest molecules, the effect of physisorbed toluene on the reduction and catalysis was explored. Interestingly, the toluene is not removed by the high-temperature H₂ treatment used to reduce the Rh(I) to nanoparticles, but toluene does not appear to affect the reduction temperature. Presumably, the entrained toluene concentration is not high enough to produce a truly "solvated" environment. Furthermore, entrained toluene in the porous material is saturated by flowing hydrogen through the Rh(NP)(CAT-POP), resulting in the release of fully converted methylcyclohexane in flowing H2. These results are consistent with our assertion that Rh(I) centers are active for roomtemperature, gas-phase propylene hydrogenation and that Rh(0) NPs are not the active catalytic material in this case. In liquid-phase hydrogenation with high concentrations of solvent, Rh(I) centers are much more easily reduced to nanoparticles, perhaps by an autocatalytic mechanism.⁴⁴

CONCLUSION

The studies reported herein indicate that site-isolated Rh(I) centers of $[(COD)Rh(CAT)]_2$ -POP are active toward the hydrogenation of propylene to propane under vapor-phase plug-flow reaction conditions with a TOF of 22.5 h⁻¹ or 2.2 × 10⁻³ mol h⁻¹ g⁻¹. The single-site Rh(I) catechol POP is thermally robust, resulting in no change in catalytic activity after treatment to 175 °C. Under gas-phase plug-flow conditions the Rh(I) centers are not active for arene hydrogenation. These single-site Rh(I) catalysts reduce to Rh(0) nanoparticles readily at 250 °C under H₂ and are then active for the hydrogenation of toluene to methylcyclohexadiene with a TOF of 9.3 × 10⁻³ mol g⁻¹ h⁻¹ at 25 °C. Single-site Rh(I) centers under batch (solution) reaction conditions

are easily reduced to Rh(0) nanoparticles, which have high hydrogenation activity for olefins and arenes. The reducibility of Rh(I) in the liquid phase is dependent on both solvent and substrate; however, under gas-phase conditions Rh(I) is the active catalyst species for olefin hydrogenation.

ASSOCIATED CONTENT

Supporting Information

Text and figures giving full details of the syntheses and procedures used and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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