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Discovery of Highly Selective Alkyne Semihydrogenation Catalysts Based on First-Row Transition-Metallated Porous Organic Polymers**

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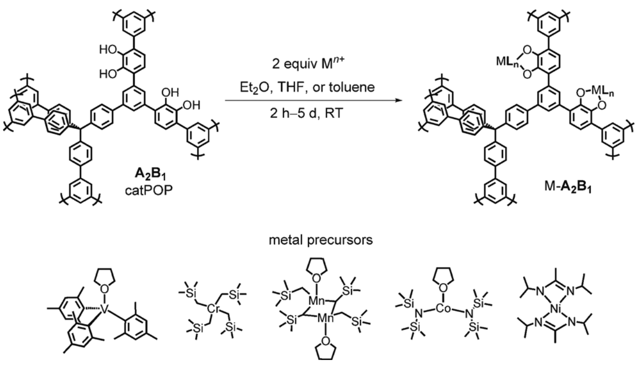
Abstract: *Five different first-row transition metal precursors (V^{III}, Cr^{III}, Mn^{II}, Co^{II}, Ni^{II}) were successfully incorporated into a catechol porous organic polymer (POP) and characterized using ATR-IR and XAS analysis. The resulting metallated POPs were then evaluated for catalytic alkyne hydrogenation using high-throughput screening techniques. All POPs were unexpectedly found to be active and selective catalysts for alkyne semihydrogenation. Three of the metallated POPs (V, Cr, Mn) are the first of their kind to be active single-site hydrogenation catalysts. These results highlight the advantages of using a POP platform to develop new catalysts which are otherwise difficult to achieve through traditional heterogeneous and homogeneous routes.*

Porous organic polymers (POPs) containing well-defined transition-metal catalysts are emerging as designer materials which combine the best features of traditional heterogeneous and homogeneous catalysts.[1] Like solid catalyst supports, POPs have good thermal and chemical stability, thereby enabling them to withstand the high temperatures and pressures generally employed in heterogeneous catalytic reactions.[2] Similar to homogeneous catalysts, POPs inherit the excellent physical and chemical tunability afforded by the wide range of functionalized organic ligands used in their construction.[3] Importantly, the micropore environment of POPs can isolate reactive, low-coordinate species which are not stable as freely soluble complexes, thus enabling new and unexpected reactivities. By combining all these features into one framework, one can design and tune a POP to have combinations of functionalities and interactions which are not trivially achieved with traditional heterogeneous and homogeneous systems.[4]



Scheme 1. General metallation procedure of catPOP $\mathbf{A_2B_1}$. The notation $\mathbf{A_2B_1}$ refers to the ratio of the two comonomers used to synthesize the POP (**A** = catechol structure, **B** = tetraphenylmethane node).

Recently, we[5] and others[6] reported POPs with isolated single-site transition-metal centers in an effort to generate unique catalytic species. We were particularly interested in the broad potential of catPOP $\mathbf{A_2B_1}$[7] (Scheme 1), which can be post-synthetically metallated to obtain well-defined, low-coordinate species which are unattainable through traditional homogeneous routes. In one report, the metallation of $\mathbf{A_2B_1}$ with [(tBuCH$_2$)$_3$Ta=CHtBu] yielded a material with [catecholato(tBuCH$_2$)$_3$Ta^V] single sites which are capable of hydrogenating cyclohexene and toluene with greatly improved activity and thermal stability over its molecular analogue.[5a] Incorporation of [Rh(tBu-PhAMD)(cod)] (AMD = amidinate,[8] cod = 1,5-cyclooctadiene) into $\mathbf{A_2B_1}$ gave a supported [Rh^I(cod)] complex which can hydrogenate propylene to propane in the gas phase at room tempera-

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ture.[5d] In another example, metallation of **A_2B_1** with [Fe{N-($SiMe_3$)$_2$}$_2$] gave coordinatively unsaturated [catecholato-(Et_2O)Fe^{II}] centers which are highly active hydrosilylation catalysts at room temperature.[5b] This material is also an active catalyst for the gas-phase hydrogenation of propylene at 150 °C,[5c] a temperature which is rarely seen for homogeneous iron(II) complexes.

Given the hydrogenation activity demonstrated by the iron(II) POP, we questioned whether other low-oxidation-state, first-row transition-metal species (V, Cr, Mn, Co, Ni) could display new activities once stabilized and constrained within the pores of **A_2B_1**. Up until now, the majority of hydrogenation studies with metallated POPs and similar microporous systems generally have employed traditional precious metals such as ruthenium,[9] rhodium,[10] palladium,[11] and platinum.[12] There have been very few examples utilizing earth-abundant metals (e.g., V, Cr, Mn, Co, Ni). Iron,[13] cobalt,[14] and nickel[15] are active for hydrogenation, but the majority of homogeneous catalysts based on these metals utilize phosphine- and nitrogen-based ancillary ligands. Alternatively, hydrogenation catalysts with vanadium,[16] chromium,[16a,17] and manganese,[16a,18] are limited to a few homogeneous examples and mixed-metal systems on solid supports. Herein, we report a series of catalytically active, low-coordinate, first-row transition-metal species stabilized within a catechol POP. By using alkyne hydrogenation as a probe reaction, we demonstrate how studying structurally similar, but diversely metallated POPs can lead to the discovery of unique catalytic activities and lend insights into catalyst design and substrate activation.

Similar to our earlier work,[5a,b,d] we procured metal precursors with ligands that cleanly protonate upon chelation with catechol moieties. Thus, [V(Mes)$_3$thf],[19] [Cr-(CH_2SiMe_3)$_4$],[20] [{Mn(μ-CH_2SiMe_3)(CH_2SiMe_3)thf}$_2$],[21] [thf{Co(N($SiMe_3$)$_2$}$_2$],[22] and [Ni(*i*Pr-MeAMD)$_2$],[23] (Mes = mesityl, thf = tetrahydrofuran) were selected as the precursors (Scheme 1). NMR-scale reactions between **A_2B_1** and the metal precursors in C_6D_6, [D$_8$]toluene, and [D$_8$]THF were used to quantify the release of the expected protonated byproduct (e.g., mesitylene, $SiMe_4$, HN($SiMe_3$)$_2$, and diisopropylacetimidamide, respectively). Upon scaling up these reactions, the metallated POPs ([M]-**A_2B_1** for brevity) were isolated in good yields.

Analysis of all the POPs by attenuated total reflectance infrared (ATR-IR) spectroscopy showed consumption of the characteristic catechol OH stretch (ca. 3500 cm^{-1}; see Figure S1 in the Supporting Information). No IR stretches corresponding to the starting metal precursor were found for [Cr]-, [Mn]-, and [Co]-**A_2B_1**, and is consistent with complete reaction. New aliphatic C–H stretches were present and attributed to coordinated solvent (see the Supporting Information). [V]-**A_2B_1** had distinct C–H stretches consistent with the mesityl group and solvent, while [Ni]-**A_2B_1** had IR stretches indicative of a coordinated *i*Pr-MeAMD ligand.

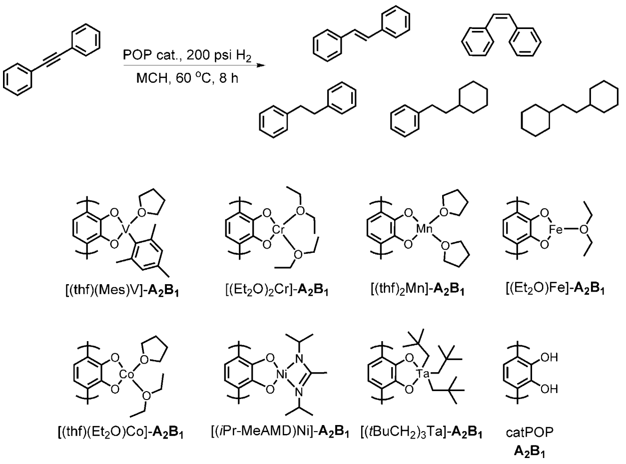
The oxidation state and coordination number of the metal species in the [M]-**A_2B_1** POPs were determined using X-ray absorption spectroscopy (XAS).[24] XANES analysis confirmed the oxidation states of the metal species in the [M]-**A_2B_1** POPs to be V^{III}, Cr^{III},[25] Mn^{II}, Co^{II}, and Ni^{II}, while EXAFS analysis showed monomeric sites with coordination numbers of four (Table 1). Complete details of the POP characterizations can be found in the Supporting Information (Figures S2–S11 and Tables S1–S5).

Table 1: XAS characterization data for [M]-**A_2B_1** POPs.

Metal	V	Cr	Mn	Fe[b]	Co	Ni
Oxidation state	3	3[a]	2	2	2	2
Coordination number	4	4	4	3	4	4

[a] Also confirmed by EPR analysis (see Figure S11). [b] This material was previously characterized (Ref. [4c]).

The [M]-**A_2B_1** POPs were tested for catalytic activity and selectivity with alkyne hydrogenation. Over-reduction is a current challenge for alkyne hydrogenation catalysts, and selective semihydrogenation of an alkyne to an alkene is an important reaction in organic chemistry.[26] The [M]-**A_2B_1** POPs were tested using Freeslate's CM3 automation platform and pressure reactor (SPR; see Figure S12) with diphenylacetylene as a substrate because of its multiple possible hydrogenation products (Scheme 2). In a typical experiment, the robotic platform was programmed to weigh out the six [M]-**A_2B_1** POPs at varying catalyst loadings along with three controls: catalyst-free alkyne stock solution and **A_2B_1**, both of which should not be catalytically active, as well as [Ta]-**A_2B_1**, which has been previously shown to be active for hydrogenation.[5a] All reactions were carried out at 60 °C for 8 hours (200 psi H_2) and subsequently analyzed by GC-MS and GC-FID (see the Supporting Information).



Scheme 2. The high-throughput catalytic evaluation of [M]-**A_2B_1** POPs using diphenylacetylene as the substrate. [Ta]-**A_2B_1** and catPOP **A_2B_1** serve as positive and negative controls, respectively.

All six of our [M]-**A_2B_1** POPs were found to be catalytically active for diphenylacetylene hydrogenation, with *cis*-stilbene, *trans*-stilbene, and bibenzyl being the main products. As expected, no hydrogenation activity was observed for either the alkyne stock solution or **A_2B_1** (see Table S6). Thus, the observed catalytic activities for these materials must be occurring with the POPs. Sampling at different time intervals is not practical with our high-throughput setup so the activity profile for each catalyst was determined as a function of catalyst loading (1, 3, 5, 7, 10 mol %) at a fixed time (see Figures S13 and S14). At a 5 mol % catalyst loading, [V]- and [Cr]-$\mathbf{A_2B_1}$ led to about 99 % conversion of diphenylacetylene while [Mn]-$\mathbf{A_2B_1}$ afforded about 15 % conversion (see Table S7). To the best of our knowledge, these are the first examples of active, neutral vanadium(III), chromium(III), and manganese(II) single-site hydrogenation catalysts.

All six [M]-$\mathbf{A_2B_1}$ POPs display very high selectivity for stilbene [> 80 %, both *cis* (major) and *trans* (minor) isomers] at up to 80 % diphenylacetylene conversion (total stilbene and bibenzyl combined; Figure 1). This conversion is in stark contrast to the [Ta]-$\mathbf{A_2B_1}$ control, which begins to overhydrogenate stilbene to bibenzyl at very low conversion. Indeed, bibenzyl production was only detected for the first-row [M]-$\mathbf{A_2B_1}$ POPs once conversions of greater than 90 % were achieved, thus suggesting that stilbene hydrogenation only occurs when diphenylacetylene is nearly depleted in the reaction. None of the first-row [M]-$\mathbf{A_2B_1}$ POPs exhibited arene hydrogenation activity compared to the aromatic ring hydrogenation observed for the Ta-$\mathbf{A_2B_1}$ control (see Table S6).

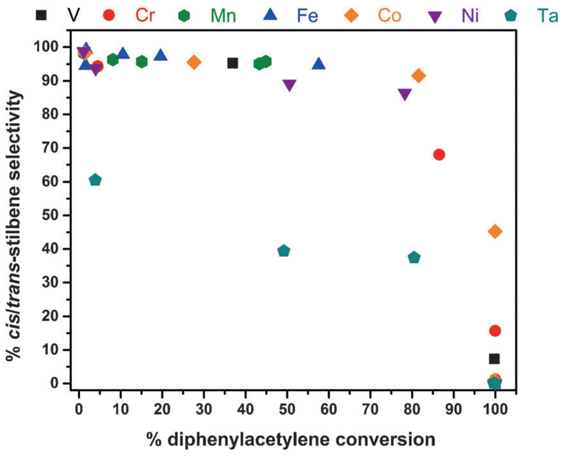


Figure 1. *cis/trans*-Stilbene selectivity versus diphenylacetylene conversion. Reaction conditions: 1, 3, 5, 7, 10 mol % of [M]-$\mathbf{A_2B_1}$, 0.25 M diphenylacetylene stock solution in methylcyclohexane, 60 °C, 200 psi H_2, 8 h. % Diphenylacetylene conversion = % conversion to stilbene and bibenzyl.

The high activities of the early-first-row metal POPs [V]- and [Cr]-$\mathbf{A_2B_1}$ are apparent when one compares their relative rates (TOF, h^{-1}) to those of the late-first-row metal POPs (see Table S8). At a 1 mol % catalyst loading, the TOFs for [V]- and [Cr]-$\mathbf{A_2B_1}$ are 4 and 0.6 h^{-1}, respectively, and much higher than those for [Mn]-, [Fe]-, [Co]-, and [Ni]-$\mathbf{A_2B_1}$ (TOF = 0.1–0.2 h^{-1}). While homogeneous complexes of iron,[13] cobalt,[14] and nickel[15] have been more extensively studied for catalytic reduction, their catecholato POP derivatives are less active when compared with vanadium and chromium. Moreover, [V]- and [Cr]-$\mathbf{A_2B_1}$ are more active compared to known homogeneous V and Cr catalysts. For example, a [V-(bisimido)] catalyst does hydrogenate alkynes, but moderate conversions could only be achieved at 20 mol % catalyst and over 24 hours.[16b] In another report, [(triallyl)Cr] is a precatalyst for 1-alkene hydrogenation when decomposed at 85 °C.[17a] Given that the overall pore-size distribution profiles of the [M]-$\mathbf{A_2B_1}$ POPs are quite similar to that of catPOP, such high reactivities of [V]- and [Cr]-$\mathbf{A_2B_1}$ can be attributed to the unique coordination environment supported inside the POP.[27] This feature highlights the effectiveness of the POP platform for supporting unprecedented reactivity of monocatecholato complexes of low-oxidation-state, first-row transition-metal species.

Given the excellent selectivity and high activity exhibited by our [M]-$\mathbf{A_2B_1}$ catalysts for diphenylacetylene semihydrogenation, phenylacetylene and 3-hexyne were also briefly examined. Under similar reaction conditions, the semihydrogenation of both of these alkynes shows similar olefin selectivity (*cis/trans*-2/3-hexene and styrene) of up to greater than 90 % conversion of the starting alkyne (see Scheme S1 and Figures S15 and S16). [M]-$\mathbf{A_2B_1}$ POPs are also active for alkene hydrogenation (see Scheme S2 and Table S9), thus suggesting that the high selectivity of our [M]-$\mathbf{A_2B_1}$ catalysts is due to preferential binding of the alkyne (versus the alkene). None of the [M]-$\mathbf{A_2B_1}$ POPs performed arene hydrogenation under these conditions and [V]-, [Cr]-, [Mn]-, and [Fe]-$\mathbf{A_2B_1}$ all catalyzed some isomerization of *cis*- to *trans*-stilbene.

In conclusion, we discovered that first-row transition metals are active and selective catalysts for alkyne semihydrogenation when stabilized inside a POP environment. Three POPs (V, Cr, Mn) represent a class of hydrogenation catalysts which have little precedent in literature. Ultimately, this study demonstrates the tremendous potential of a POP to support a wide range of low-coordinate, highly reactive catalytic sites. The high semihydrogenation selectivities observed with these first-row [M]-$\mathbf{A_2B_1}$ POPs demonstrates that exploring structurally similar but diversely metallated POPs can lead to the discovery of new catalytic activities. Additional studies are currently in progress to elucidate the mechanism of H_2 activation, the impact of ligand choice on metal activity and selectivity, and the role (if any) that the potentially redox-active catecholate ligand plays in catalytic function.

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[27] A comparison between three of the metallated POPs (Ta, V, and Fe) indicates that they have similiar pore size distributions (see Figures S4 and S5).