ACS Catalysis
Research Article
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A Remarkably Active Iron Catecholate Catalyst Immobilized in a Porous Organic Polymer

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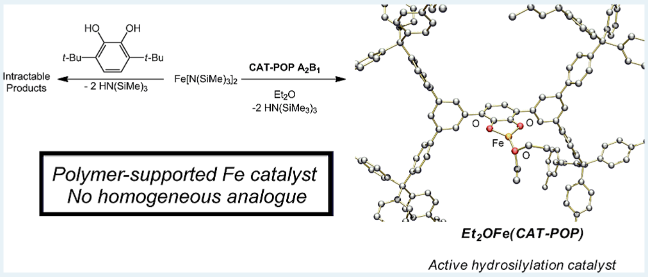
Supporting Information

ABSTRACT: A single-site, iron catecholate-containing porous organic polymer was prepared and utilized as a stable and remarkably active catalyst for the hydrosilylation of ketones and aldehydes. In some instances, catalyst loadings of 0.043–2.1 mol % [Fe] were sufficient for complete hydrosilylation of aldehydes and ketones within 15 min at room temperature. The catalyst can be recycled at least three times without a drop in catalytic activity. This system is an example of an immobilized homogeneous catalyst with no homogeneous analogue.



Polymer-supported Fe catalyst
No homogeneous analogue

Et_2OFe(CAT-POP)

Active hydrosilylation catalyst

KEYWORDS: *catalysis, hydrosilylation, iron catalysis, porous organic polymer, catechol*

INTRODUCTION

Metal containing **p**orous **o**rganic **p**olymers (POPs)[1] have gained recent interest for applications in catalysis,[1b,2] gas storage,[3] and gas separations[2d,4] because of their high surface area three-dimensional networks related to metal organic frameworks (MOFs) and zeolites. Metalated POPs have several potential advantages over MOFs and zeolites because of their greater chemical and thermal stability than MOFs combined with a more tunable ligand binding environment than zeolites. Additionally, the potential for rational synthetic variation[1b] of POP-based ligand binding sites presents an opportunity to prepare *stable and tunable* catalysts that are not accessible to traditional homogeneous systems. We hypothesized that unique coordination environment of the POP structure will stabilize catalysts capable of reactivity patterns that are not possible in homogeneous, supramolecular, or zeolitic environments.[1b]

For example, typical homogeneous metal catecholate complexes frequently form bis- or tris-chelated complexes to stabilize the metal center. Such complexes lack reactive sites and are often catalytically inactive or unstable to ligand loss or other decomposition routes.[5] The recent report of a catechol containing POP, **POP A_2B_1**, represents the opportunity for the isolation of a single catechol bound to a metal.[6] **POP A_2B_1** has been shown to coordinate divalent Mn and Mg complexes made from $Mn(OAc)_2{\cdot}4H_2O$ and Me_2Mg as neutral species without reducing pore volume below a size compatible with many organic reagents.[6] The physical separation of catechol groups in a porous network combined with the rigid support offered by **POP A_2B_1** offers a unique opportunity to attempt catalysis with low-coordinate, divalent metal centers in the absence of bulky, stabilizing ligands.[7] Single catechol site ligation is of interest as the redox noninnocent capabilities of catecholate iron complexes have made the isolation of complexes that do not participate in either intra/extradiol cleavage catalysis[5a,7a,b,e] or metal transport in natural and biomimetic siderophores difficult.[8]

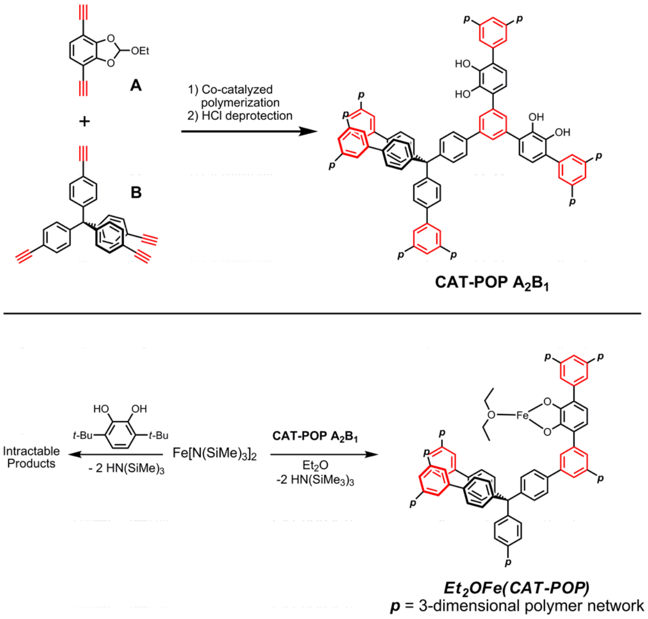
RESULTS AND DISCUSSION

The convenient Fe (II) source, $Fe[N(SiMe_3)_3]_2$,[9] rapidly reacts with proton sources, and the addition of 1 equiv of $Fe[N(SiMe_3)_3]_2$ to a suspension of **POP A_2B_1** in diethyl ether resulted in complete uptake of the iron complex within 24 h. Attempts at generating a single site catechol containing complex with addition of 1 equiv of 3,6-di-*tert*-butylcatechol to $Fe[N(SiMe_3)_3]_2$ results in complete consumption of the latter concomitant with the precipitation of insoluble and intractable products (Scheme 1).

ATR-FT-IR spectroscopy (Supporting Information, Figure S1) confirms full metalation of all catechol sites as OH stretches at 3542 cm^{-1} of **POP A_2B_1** are no longer visible. Subsequent washing with diethyl ether afforded **Et_2OFe(CAT-POP)** without any leaching of unreacted $Fe[N(SiMe_3)_3]_2$. Analysis of the washings by ^1H NMR spectroscopy reveals ~85% of the expected $HN(SiMe_3)_2$ upon Fe ligation. Upon further washing with diethyl ether, 13% of the remaining 15% of $HN(SiMe_3)_2$ bound within the material is released. The remaining 2% of expected amine remains bound in an unknown fashion within the material and is reflected in the slight

Received: January 21, 2013
Revised: March 5, 2013
Published: March 14, 2013

Scheme 1. (Top) Preparation of Porous Organic Catecholate Ligand CAT-POP A_2B_1,[6] and (Bottom) Preparation of Et_2OFe(CAT-POP)



percentage of N found in elemental analysis (1.09 wt %). Importantly, the addition of excess $Fe[N(SiMe_3)_3]_2$ to **Et_2OFe(CAT-POP)** does not result in any appreciable weight change after washing the solid to remove entrained iron precursor, corroborating full metalation of catechol binding sites.

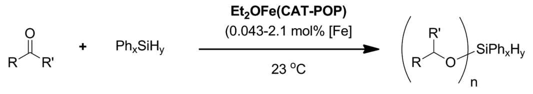
Et_2OFe(CAT-POP) is extremely O_2 sensitive and turns from its brown color to a deep black upon contact with air. Such sensitivity might be expected as iron intra/extradiol cleavage catalysts operate via oxidation in the presence of O_2 to cleave the catechol moiety.[5a,7a,b,e] Although this black product has not been successfully characterized, Brunauer−Emmett−Teller (BET) surface area measurements of as-prepared **Et_2OFe(CAT-POP)** (855 m^2/g, and pore width distribution ∼12 Å as the dominant pore size) (Supporting Information, Figure S2) do not significantly differ from the black product. This indicates that oxygen exposure does not significantly damage the POP framework. For comparison, the free POP ligand has a measured surface area of 1050 m^2/g, and the previously reported Mn and Mg complexes display a similar decrease in surface area upon metalation (BET surface areas of 600 and 610 m^2/g respectively).[6]

To gain insight into the electronic and coordination environment at the Fe centers, Mössbauer spectra were obtained at 90 K for both the air free and the O_2 exposed **Et_2OFe(CAT-POP)** materials (Supporting Information, Figure S3). The spectrum of **Et_2OFe(CAT-POP)** was fitted to two symmetric quadrupole doublets with isomer shifts of 0.32 and 0.34 mm/s and quadrupole splittings of 1.47 and 0.89 mm/s respectively. Although two different iron environments could be fit, the small difference in isomer shift indicates their oxidation state and coordination environment are practically the same. Thus, while there is a degree of irregularity in the POP polymer structure, the local environment of the Fe sites is virtually identical according to the Mössbauer spectrum. Exposure of the material to air results in a very small change in the isomer shifts to 0.35 mm/s, but significant quadrupole splitting shifts to 0.69 and 1.15 mm/s. No significant change in isomer shifts between the inert and the air exposed samples indicates that oxidation may not occur at the iron center, but rather within the catechol POP framework itself. This is also consistent with changes in the quadrupole splitting as coordination environment around the iron center would result from catechol oxidation to semiquinone ligands. The deep color change from brown to black for the air-free POP to O_2-exposed POP without any change in the formal oxidation state of the iron center is characteristic of oxidized redox-active semiquinone metal complexes previously reported and corroborates these results.[10] Regardless of the Fe or catechol oxidation state, the air-exposed **Et_2OFe(CAT-POP)** is inactive for hydrosilylation catalysis under conditions where the initial material is operative.

In the absence of O_2 **Et_2OFe(CAT-POP)** is stable whether suspended in solution or stored as a solid at room temperature for longer than one week. Solid samples can be heated to 175 °C in vacuo and also retain identical catalytic properties to unheated material. In contrast, our Fe(II) source $Fe[N(SiMe_3)_3]_2$ is a catalyst for the hydrosilylation of ketones and aldehydes,[11] but it is unstable in solution at room temperature for extended periods resulting in precipitation of insoluble iron-containing material.[11]

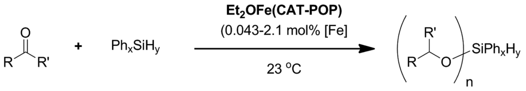
Et_2OFe(CAT-POP) was screened as a catalyst for hydrosilylation reactions, important for fine chemical synthesis and industrially relevant silicon containing materials.[12] Rapid conversion of aldehydes and ketones to the corresponding silyl ether was observed with catalyst loadings of 2.1 mol % [Fe] in C_6D_6 when monitored via ^1H NMR spectroscopy (Scheme 2). The results for a variety of substrates are collected in Table 1.

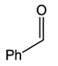
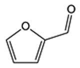
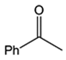
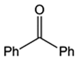
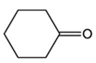
Scheme 2. Catalytic Hydrosilylation by Et_2OFe(CAT-POP)



Within 20 min benzaldehyde was fully converted to a mixture of $PhCH_2OSiHPh_2$ and $(PhCH_2O)_2SiPh_2$ (28:72) upon reaction with 1 equiv of diphenylsilane (Table 1, entry 1). The full catalytic potential was observed upon addition of phenylsilane to a mixture of **Et_2OFe(CAT-POP)** and benzaldehyde in benzene-d_6, resulting in a sufficiently exothermic reaction to boil the mixture within 10 s (Table 1, entry 2). Within 2 min the reaction mixture cooled, and analysis by ^1H NMR spectroscopy revealed complete conversion to $(PhCH_2O)_2SiHPh$ and $(PhCH_2O)_3SiPh$ (48:52). Despite the thermal output of this reaction, **Et_2OFe(CAT-POP)** retains its catalytic ability, and further addition of benzaldehyde to these mixtures resulted in full conversion of the silane to the highest order alkoxysilane products. Decreased catalyst loadings to as low as 0.043% with an *average* turnover frequency (TOF) of 1.11 s^{-1} is possible. Complete conversion of benzaldehyde with **Et_2OFe(CAT-POP)** and phenylsilane was achieved rapidly for catalyst loadings of 0.43 and 0.043 mol % (Table 1, entries 3 and 4). Both these reactions are noticeably exothermic and are complete upon cooling after 10 and 15 min respectively yielding $(PhCH_2O)_2SiHPh$ and $(PhCH_2O)_3SiPh$ (75:25 and 80:20 for 0.43 and 0.043 mol % respectively). The TOF for the hydrosilylation of aldehydes is remarkable for iron-based catalysts, and is considerably more

Table 1. Hydrosilylation of Aldehydes and Ketones with Et_2OFe(CAT-POP)[a]



Entry	Cat [mol%/Fe]	Substrate	Silane	t [min][b]	Products	Product Distribution [%][c]
1	2.1		Ph_2SiH_2	20	$PhCH_2OSiHPh_2$; $(PhCH_2O)_2SiPh_2$	28:72
2	2.1		$PhSiH_3$	2	$(PhCH_2O)_2SiHPh$; $(PhCH_2O)_3SiPh$	48:52
3	0.43		$PhSiH_3$	10		75:25
4	0.043		$PhSiH_3$	15		80:20
5	2.1		$PhSiH_3$	2	$[(C_4H_3O)CH_2O]_2SiHPh$; $[(C_4H_3O)CH_2O]_3SiPh$	0:100
6	0.43		$PhSiH_3$	4		27:73
7	0.043		$PhSiH_3$	n.r.		n.r.
8	2.1		Ph_2SiH_2	20	$PhMeCHOSiHPh_2$	100
9[d]	2.1		$PhSiH_3$	2	$(PhMeCHO)_2SiHPh$	100
10	2.1		Ph_2SiH_2	90	$Ph_2CHOSiHPh_2$; $(Ph_2CHO)_2SiPh_2$	88:12
11	2.1		$PhSiH_3$	5	$(Ph_2CHO)_2SiHPh$	100
12	2.1		Ph_2SiH_2	90	$(Cyclohexyl)OSiHPh_2$; $[(Cyclohexyl)O]_2SiPh_2$	94:6
13	2.1		$PhSiH_3$	2	$[(Cyclohexyl)O]_2SiHPh$	100

[a] Reaction conditions: substrate (0.356–3.56 mmol), silane (1 equiv), 23 °C, C_6D_6. [b] Reaction times were determined via ^1H NMR spectroscopy after complete consumption of substrate. [c] Product distribution listed in order of products column. [d] All three stereoisomers were observed.

active than our precursor, $Fe[N(SiMe_3)_2]_2$, which exhibits a TOF of ~0.007 s^{-1} at similar reaction conditions.[11] **Et_2OFe(CAT-POP)** can be recovered as a solid, and qualitatively identical catalytic reactivity was observed upon catalyst recycling by filtration, drying, and reuse (3 times). Also, the notable stability of **Et_2OFe(CAT-POP)** can be demonstrated by heating solid samples to 175 °C in the absence of O_2 or storing suspensions for 1 week with no loss of catalytic activity. Furthermore, the catalyst can be separated from the reaction mixture, and the filtrate is not active for hydrosilylation.

Although no molecular analogue to **Et_2OFe(CAT-POP)** is available we treated $Fe[N(SiMe_3)_2]_2$ with 3,6-di-*tert*-butyl catechol in C_6D_6, diethyl ether, or toluene, and the resulting separable but intractable mixture of brown solid (36%) and brown solution (64%) was tested for catalytic hydrosilylation. Addition of a mixture of benzaldehyde and phenylsilane to the two materials provided no hydrosilylation products after 30 min. However, full conversion of benzaldehyde to $(PhCH_2O)_2SiHPh$ and $(PhCH_2O)_3SiPh$ was observed after a 24 h period for both materials at room temperature. Unlike **Et_2OFe(CAT-POP)**, however, these mixtures are no longer active for catalysis after isolation and addition of fresh substrate, having transformed further to catalytically inactive material. The slow reaction time of these mixtures and their inability to be recycled validates the catalytic role of **Et_2OFe(CAT-POP)**, which is far faster kinetically and stable to decomposition under reaction conditions. Such a rapid hydrosilylation of benzaldehyde is atypical for iron-based hydrosilylation catalysts, which generally catalyze aldehydes with modest rates at ambient temperature[11] and require higher catalyst loading (5 mol %) to achieve similar speeds[13] or elevated temperatures.[14]

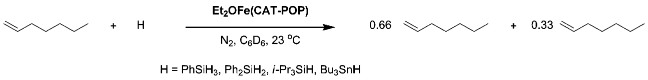
We also pursued the less common hydrosilylation substrate, 2-furaldehyde. It is produced by the treatment of pentoses derived from hemicellulose biomass, which itself is an undesirable fuel source.[15] However, selective reduction of 2-furaldehyde to furfuryl alcohol is an important industrial process as it is used to produce resins, rubbers, and alternative chemical feedstocks.[16] Hydrosilylation is a model reaction for selective reduction to the alcohol as direct hydrogenation can result in coking or reduction of the olefin to furan derivatives.[17] Alternatively, the hydrosilylation product can be hydrolyzed easily to form the desired alcohol.[15a] 2-Furaldehyde was treated with **Et_2OFe(CAT-POP)** and phenylsilane; an exothermic reaction resulting in full conversion to $[(C_4H_3O)CH_2O]_3SiPh$ was again observed within 2 min (Table 1, entry 5). A decrease in catalyst loading to 0.43 mol % yielded complete conversion within 240 min generating $[(C_4H_3O)CH_2O]_3SiPh$ and $[(C_4H_3O)CH_2O]_2SiHPh$ in a ratio 73:27 (Table 1, entry 6). However, when the catalyst loading is decreased to 0.043 mol % the reaction does not progress, most likely because of commercial impurities in 2-furaldehyde (Table 1, entry 7). This activity for 2-furaldehyde is considerably higher than typical Ni[18] and Fe[19] catalysts for this process that exhibit slower TOFs. Moreover, this activity is on the order of the capability of recently reported lanthanide hydride complexes which are some of the fastest reported for this reaction.[15a]

Finally, we studied more sterically encumbered ketone substrates. Acetophenone reacts with diphenylsilane (average TOF ~ 0.04 s^{-1}) at a comparable rate to that of benzaldehyde (average TOF ~ 0.04 s^{-1}) with diphenylsilane and generates a sole product, $PhMeCHOSiHPh_2$ (Table 1, entry 8). The formation of a sole product is consistent with that of $Fe[N(SiMe_3)_3]_2$; however, a much faster reaction occurs with **Et_2OFe(CAT-POP)** *than with this iron precursor* (average TOF ~0.015 s^{-1}).[11] In contrast, phenylsilane generates the purely bis-1,2-addition products of $(PhMeCHO)_2SiHPh$ and its diastereomers when reacted with acetophenone which differs from the 1:6.5 ratio of $PhMeCHOSiH_2Ph$ to $(PhMeCHO)_2SiHPh$ that is observed with $Fe[N(SiMe_3)_3]_2$ (Table 1, entry 9).[11] Ketone hydrosilylation is exothermic like the corresponding reaction of benzaldehyde and was complete within 2 min. Unlike hydrosilylation of benzaldehyde and 2-furaldehyde, the addition of a subsequent equivalent of acetophenone in either reaction does not result in complete consumption of Si−H, and is most likely due to the large steric bulk imparted by the methyl groups in the resulting alkoxysilanes.

A further increase in substrate size to benzophenone resulted in longer reaction times (1.5 h) with diphenylsilane generating $Ph_2CHOSiHPh_2$ and $(Ph_2CHO)_2SiPh_2$ (88:12) (Table 1, entry 10). However, decreasing the silane size by using smaller phenylsilane resulted in complete conversion of benzophenone within 5 min, producing $(Ph_2CHO)_2SiHPh$. The rate of this reaction is surprising (average TOF ~ 0.009 s^{-1}; Table 1, entry 11) since this is typically a slow reaction.[20] Hydrosilylation of cyclohexanone with diphenylsilane shows a similar trend, with longer reaction times (1.5 h) needed with bulkier diphenylsilane leading to $(Cyclohexyl)OSiHPh_2$ and $[(Cyclohexyl)O]_2SiPh_2$ (94:6) ((Table 1, entry 12), but phenylsilane was complete within 2 min producing $[(Cyclohexyl)O]_2SiHPh$ (Table 1, entry 13). Although few homogeneous iron hydrosilylation catalysts perform ketone hydrosilylation with similar catalyst loadings within 1−3 h at room temperature,[11,21] many require elevated temperatures and/or much longer reaction times than the observed reactivity with this system.[13,14,22] We speculate that the slower qualitative rates of bulky substrates are consistent with the catalysis occurring within the pore structure of the POP, rather than exclusively on the surface; however, more detailed experiments are required to explicitly address the impact of mass-transport effects and count active catalytic sites. In addition, the exothermicity of hydrosilylation severely complicates quantitative kinetic experiments.

Thus, we explored the ability of **Et_2OFe(CAT-POP)** to hydrosilylate less polar bonds. The hydrosilylation of phenylacetylene was attempted with diphenyl-, phenyl-, and triisopropyl- silanes. Mixtures of silane, **Et_2OFe(CAT-POP)**, and phenylacetylene resulted in the formation of an unidentified polymer most likely assigned as polyphenylacetylene. Since a relatively small amount of the polyacetylene could potentially block the POP pores, we also screened diphenylacetylene and benzonitrile as substrates, but no reaction occurred after 24 h. Attempts to hydrosilylate 1-hexene were also unsuccessful, but upon stirring for 3 h 2-hexene was observed. Stirring the suspension of catalyst with silanes for 48 h yields the complete isomerization of 1-hexene to the thermodynamic equilibrium ratio of 2-hexene and 3-hexene (2:1) (Scheme 3) at far slower rates than $Fe(CO)_5$.[23] The slow isomerization progresses to completion within a similar time frame when diphenylsilane, phenylsilane, triisopropylsilane, or tributyltin hydride are present, but not in the absence of a hydride or H atom source. This is in contrast to the catalytic activity of $(^iPrPDI)Fe(N_2)_2$ reported by Chirik[24] which performs olefin isomerization in the absence of silane, but is capable of hydrosilylation of olefins in the presence of silane.

Scheme 3. Isomerization Reactions of 1-Hexene



As alluded to earlier **Et_2OFe(CAT-POP)** can be recycled at least three times yielding the same product selectivity and rate of reaction. Notably, material used in hydrosilylation reactions (any listed in Table 1) can be reused to perform the isomerization of 1-hexene and vice versa without activity loss as circumstantial support for a common catalytic intermediate. Although recyclability is commonplace among heterogeneous catalysts, the observed stability of our low-coordinate single site metal catecholate is extremely rare, and such results reported herein highlight their stability imparted by unique porous environments within a POP framework.

■ CONCLUSION

Initial studies have proven site-isolated iron catecholates in **Et_2OFe(CAT-POP)** are stable, extremely active catalysts for the hydrosilylation of carbonyl groups. Hydrosilylation of aldehydes and ketones with phenylsilane are rapid with this system resulting in exothermic reactions completed within minutes with obtainable catalyst loadings of as low as 0.043 mol % [Fe] and an average TOF of 1.11 s^{-1}. Although hydrosilylation of these substrates with diphenylsilane are relatively slower, full conversion of substrates are achieved with catalyst loadings of 2.1 mol % [Fe] on the order of 20 to 90 min. The catalyst is reusable, recyclable for at least three reaction cycles, and thermally robust allowing catalytic activity after treatment to 175 °C. Currently, the synthesis of other catalytic POP materials, exploration of **Et_2OFe(CAT-POP)** as a catalyst for other transformations, and elucidation of the origin of stability are all ongoing.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental conditions and synthetic methods for this Article. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge funding by the U.S. Department of Energy, under Contract No. DE-AC02-06CH11357. R.H.S. acknowledges CONACYT (Consejo Nacional de Ciencia y Tecnología) and Fundación México for doctoral fellowship. We would like to thank Ted Betley, SonBinh Nguyen, and Marc Johnson for helpful discussions.

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