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# In Situ X-ray Absorption Spectroscopy and Nonclassical Catalytic Hydrogenation with an Iron(II) Catecholate Immobilized on a Porous Organic Polymer



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The oxidation state and coordination number of immobilized iron catecholate  $EtO_2Fe(CAT-POP)$  were determined by Xray absorption spectroscopy (XAS) under a variety of conditions. We find the as-prepared material to be three-coordinate  $Fe^{2+}$  that readily oxidizes to  $Fe^{3+}$  upon exposure to air but remains three-coordinate. Both the reduced and oxidized Fe(CAT-POP) catalyze olefin hydrogenation in batch and

## Introduction

Noble metals like Pd, Pt, and Rh are typically used for both homogeneous and heterogeneous catalytic hydrogenation. The importance of this reaction has led to numerous advances through careful mechanistic study. The mechanism is generally described as consisting of oxidative addition of H<sub>2</sub> and insertion of substrate (olefin, carbonyl, imine, or other), followed by reductive elimination of the reduced product. By this paradigm, it is not surprising that hydrogenation catalysis is dominated by second- and thirdrow metals more prone to undergo two-electron redox cycles demanded by the traditional archetype. However, there is a distinct opportunity to utilize less expensive first-row metals for hydrogenation by proceeding through alternative mechanisms. Shvo catalysts<sup>[1-3]</sup> utilized by Casey and others<sup>[4–9]</sup> proceed through heterolytic H<sub>2</sub> splitting with Ru and Fe catalysts. A similar mechanism is proposed in systems which utilize the frustrated Lewis acid/base pair concept.<sup>[10]</sup> Alternatively, redox-active ligands such as pyridine bis(imides) and other related pincer ligands support Fe hydrogenation catalysts.<sup>[11-15]</sup> Many of the N-donor ligand

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flow reactors. We determined the catalytic rates for both species and also observed by means of XAS that the oxidation state of the iron centers does not change in hydrogen at the reaction temperature. Therefore, we postulate that the mechanism of hydrogenation by Fe(CAT-POP) proceeds through one of several possible nonclassical mechanisms, which are discussed.

frameworks are quite reducing,<sup>[16]</sup> and whether changing to O-donor ligands that have a lower reduction potential would promote ligand-based redox during a catalytic cycle is an open question.<sup>[17–19]</sup> In order to use O-donor ligands, the serious problem of bimolecular decomposition through ligand and/or electron exchange has to be overcome.

We have been studying porous organic polymer (POP) frameworks as tailorable supports for next-generation catalysts.<sup>[20]</sup> Ideally a POP retains the synthetic tunability of homogeneous ligands and provides a degree of environment control similar to zeolites and other structured supports. Furthermore, ligands prone to bimolecular exchange or decomposition such as catechols<sup>[21-26]</sup> can be employed by physically separating binding sites in the polymer network. Recently we reported an iron catecholate complex which is a catalyst for the hydrosilylation of ketones and aldehydes.<sup>[20]</sup> The activity and stability of our POP-supported catalyst is quite high, but it was inactive for the hydrosilvlation of olefins, a reaction catalyzed by some homogeneous Fe catalysts.<sup>[12]</sup> The Chirik and Casey systems also catalyze olefin hydrogenation, and we pursued a comparative study with our POP-immobilized Fe catalysts. Initial experiments with both batch and plug-flow systems demonstrated that the Fe(CAT-POP) system is indeed an active hydrogenation catalyst. Thus we sought to further characterize the nature of the Fe catalyst by use of X-ray absorption spectroscopy (XAS) and catalytic activation of olefins through hydrogenation.

#### **Results and Discussion**

Our method of preparing the monocatecholate iron catalyst Et<sub>2</sub>OFe(CAT-POP) within a 3-dimensional polymer

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Scheme 1. Synthesis of Et<sub>2</sub>OFe(CAT-POP).<sup>[20]</sup>

framework is summarized in Scheme 1. To summarize our previous work,<sup>[20]</sup> Et<sub>2</sub>OFe(CAT-POP) is prepared by protonation of Fe[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> in ether, and the resulting product, which is coordinated to diethyl ether is isolated after several washes to remove free hexamethyldisilazane. The resulting Fe complex was determined to be three-coordinate Fe<sup>2+</sup> on the basis of stoichiometry, Mössbauer measurements, and in analogy to the clean preparation of iron phenoxide complexes from Fe[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and phenols.<sup>[27]</sup> We also noted that the 3,6-di-*tert*-butylcatechol forms intractable solids with iron bis(hexamethylsilazide).<sup>[20]</sup>

Since the origin of the stability and catalytic ability of  $Et_2OFe(CAT-POP)$  remains an open question, and given the inability to utilize traditional homogeneous characterization methods, we pursued in situ X-ray absorption spectroscopy (XAS) at the Advanced Photon Source located at Argonne National Laboratory. Though XAS has been employed with great success to study enzyme active sites<sup>[28,29]</sup> and heterogeneous nanoparticles,<sup>[30]</sup> its application to homogeneous and homogeneous-like systems such as ours is less common, but capabilities are growing rapidly.<sup>[31]</sup> Therefore, the  $Et_2OFe(CAT-POP)$  system presents an opportunity to study the structure of physically isolated iron catecholates as well as to screen them as truly heterogeneous catalysts: in suspended liquid/catalyst batch and plug-flow systems.

XAS data were obtained under inert conditions, in  $H_2$ and propylene at 150 °C. The energy of the XANES (X-ray absorption near edge structure) pre-edge peak of Et<sub>2</sub>-OFe(CAT-POP) was compared to Fe<sup>II</sup> and Fe<sup>III</sup> standards and clearly shows that the as-prepared iron is in the 2+ oxidation state (Figure 1, top). The latter is oxidized to Fe<sup>3+</sup> in Et<sub>2</sub>OFe(CAT-POP) upon exposure to air at room temperature with the expected pre-edge shift in energy. The clear evidence for the oxidation of iron from 2+ to 3+ upon air exposure in this species is in agreement with our previous Mössbauer studies.<sup>[20]</sup>

Analysis of the extended X-ray absorption fine structure (EXAFS; Figure 1, bottom) reveals that both the as-prepared and oxidized Fe(CAT-POP) species are three-coordinate iron complexes. The bond lengths refine to 1.81 and 1.78 Å for the Fe<sup>2+</sup> and Fe<sup>3+</sup> forms, respectively (errors are estimated to be  $\pm 0.02$  Å). Bond lengths and iron coordination numbers are shown in Table 1. The refined Fe–O bond



Figure 1. X-ray absorption measurements of  $Et_2OFe(CAT-POP)$ . The red, solid lines are for the as-prepared material, and the blue, dashed lines are for the material after exposure to ambient conditions. The calculated models are listed in Table 1.

lengths are similar to the value of 1.83 Å in three-coordinate dimer [Fe(3,5-tBu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O)<sub>2</sub>]<sub>2</sub><sup>[27]</sup> but significantly shorter than typical Fe–O single bonds in higher-coordinate iron complexes, for example, 1.99 Å in  $Fe(acac)_3$  (acac = acetylacetonate), 1.95 Å in Fe<sub>2</sub>O<sub>3</sub>, or 2.06 Å in Fe<sub>3</sub>O<sub>4</sub>. Alternatively, these distances are significantly lengthened as compared with those in  $[FeIV(O)(TMC-Py)]^{2+}$  {TMC-Py = 1-(2-pyridylmethyl)-4,8,11-trimethyl-1,4,8,11-tetraazacyclotetradecane}<sup>[32]</sup> [FeIV(O)(TMG<sub>3</sub>tren)]<sup>2+</sup> and  $\{TMG_3 tren = 1, 1, 1-tris-2-[N^2-(1, 1, 3, 3-tetramethylguan$ idino)] ethylamine},<sup>[33]</sup> which exhibit Fe=O double bond lengths of 1.667(3) and 1.661(2) Å, respectively. Although these species contain tetravalent Fe centers, such short bond lengths indicate that as-prepared and oxidized Fe(CAT-



Sample	Pre-edge energy [eV]	Oxidation state	Non-H <sup>[a]</sup>	Bond length [Å] <sup>[b]</sup>
Et <sub>2</sub> OFe(CAT-POP)	7112.9	Fe <sup>II</sup>	3.2	1.81
Et <sub>2</sub> OFe(CAT-POP) <sup>[c]</sup>	7114.4	Fe <sup>III</sup>	3.0	1.78
Fe(acac) <sub>2</sub>	7112.9	Fe <sup>II</sup>	NA	NA
$Fe(acac)_3$	no pre-edge	Fe <sup>III</sup>	6	1.99
Fe <sup>III</sup> oxalate	7114.8	Fe <sup>III</sup>	NA	NA

Table 1. XAS results for Et<sub>2</sub>OFe(CAT-POP) under inert and oxidized conditions.

[a] Coordination numbers ( $\pm 10\%$ ). [b] Numbers are  $\pm 0.02$  Å. [c] Air-exposed.

POP) species contain singly bound catecholate species in unusually low-coordinate environments for these ligand species.

The XANES and EXAFS of  $Et_2OFe(CAT-POP)$  under flowing  $H_2$  at 150 °C were also obtained (Figure 2). Under these conditions the air-exposed  $Fe^{3+}$  shows no sign of reduction, and there is no statistical change in iron coordination number or bond length; however, XAS is sensitive only



Figure 2. X-ray absorption measurements of  $Et_2OFe(CAT-POP)$ under a hydrogen atmosphere. The red, solid lines are for the asprepared material, and the blue, dashed lines are for the material after exposure to atmospheric air. Oxidation states are presented in Table 2.

to non-hydrogen atoms. More importantly, the oxidation state of iron clearly remains  $Fe^{2+}$ . Therefore, it is reasonable to say that no oxidative addition to a hypothetical "Fe<sup>4+</sup>" dihydride occurs under conditions where Et<sub>2</sub>OFe(CAT-POP) shows catalytic hydrogenation activity (vide infra).

Given the example of active iron hydrogenation catalysts that are also active hydrosilylation catalysts,<sup>[12,13]</sup> we screened Et<sub>2</sub>OFe(CAT-POP) for hydrogenation activity with the simple substrate cyclohexene. After 17 hours under approximately 1380 kPa of hydrogen, approximately 50% conversion was obtained in [D<sub>6</sub>]benzene solution. However, it proved troublesome to obtain true catalytic rates in batch experiments. Also, given the propensity of arenes to coordinate to the related bis(imine)Fe catalyst.<sup>[13]</sup> we tested Et<sub>2</sub>O-Fe(CAT-POP) and air-exposed, oxidized Et<sub>2</sub>OFe(CAT-POP) for catalytic propene hydrogenation in plug-flow mode. Turnover frequencies (TOF) and conditions are summarized in Table 2. In direct contrast to the results we obtained for catalytic hydrosilylation, both the Fe<sup>2+</sup> and Fe<sup>3+</sup> materials are active hydrogenation catalysts (Table 2). Although Fe<sup>3+</sup>(CAT-POP) is a less active catalyst by about a factor of forty in rate, hydrogenation catalysis utilizing an Fe<sup>3+</sup> center is rare. Previous Mössbauer results showed that the coordination environment of the iron was relatively unchanged upon oxidation, which corroborates the observed XAS results. The XANES result also indicates the oxidation state of iron to be 3+ in the air-exposed catalyst and discounts any reduction of the iron center to Fe<sup>2+</sup> during catalysis.

Oxidation of the iron occurs immediately upon contact with air to the limit of our detection (ca. 5%); however, it is theoretically possible that a small amount of Fe<sup>2+</sup> is responsible for the catalytic behavior. However, air-exposed Fe(CAT-POP) is completely inactive for hydrosilylation catalysis.<sup>[20]</sup> Since Fe<sup>2+</sup>(CAT-POP) is an extremely efficient catalyst for this reaction (1000 turnovers in < 10 min in ideal cases), we can rule out catalytically competent amounts of remaining Fe<sup>2+</sup> in air-exposed Fe(CAT-POP). Furthermore, samples of Fe<sup>3+</sup>(CAT-POP) stored in open

Table 2. Propene hydrogenation rates for Et<sub>2</sub>OFe(CAT-POP) measured in a steady state plug-flow reactor.

Sample <sup>[a]</sup>	XANES [eV]	Oxidation state <sup>[b]</sup>	<i>T</i> [°C]	H <sub>2</sub> TOF [min <sup>-1</sup> ] <sup>[c]</sup>
Et <sub>2</sub> OFe(CAT-POP)	7112.9	Fe <sup>II</sup>	150	0.42
Et <sub>2</sub> OFe(CAT-POP)	7112.9	Fe <sup>II</sup>	175	0.56
Et <sub>2</sub> OFe(CAT-POP) <sup>[d]</sup>	7114.2	Fe <sup>III</sup>	150	0.01
Et <sub>2</sub> OFe(CAT-POP) <sup>[e]</sup>	n.d.	Fe <sup>III</sup>	150	0.01

[a] Average of 3 runs. [b] Determined by energy of the pre-edge in XANES. [c] Rate after 1 h time-on-stream. [d] Air-exposed (5 min) followed by  $H_2$  at 150 °C. [e] Air-exposed (1 month).





Figure 3. Possible mechanisms for  $H_2$  activation for  $Et_2OFe(CAT-POP)$  via heterolytic cleavage into a Fe–H and a ligand-based H (A), molecular oxidative addition (B), and ligand oxidation/metal addition (C).

air for up to a month display identical hydrogenation rates to materials exposed to air and immediately tested.

The POP framework proves to be a difficult environment for vibrational spectroscopy, and thus far no diagnostic stretches (e.g. O–O or OH) have been observed in the airexposed Fe<sup>3+</sup>(CAT-POP). Such details would provide insight to a marked change in the overall rate of reaction between the Fe<sup>2+</sup> and Fe<sup>3+</sup> materials. At present, the precise nature of the oxidized Fe<sup>3+</sup>(CAT-POP) remains unclear, so we will discuss potential mechanisms for hydrogen activation with the Et<sub>2</sub>OFe<sup>2+</sup>(CAT-POP) catalyst exclusively.

The overall mechanism for hydrogenation with Et<sub>2</sub>-OFe(CAT-POP) must involve activation of dihydrogen, transfer to olefin, and regeneration of the starting iron active site. We consider mechanisms that begin with initial olefin activation to be less likely at this time. Thus, let us first consider the hydrogen activation. We propose three likely and precedented mechanisms for the initial activation of dihydrogen, pictured in Figure 3. All result in iron hydrides, which would be poised for olefin insertion.

Option **A** consists of a heterolytic cleavage of  $H_2$  to form an iron hydride and one protonated catechol oxygen that remains datively bonded to the iron center. This possibility finds precedent in the iron catalysis described by Casey et al.<sup>[9]</sup> and is based on frustrated Lewis acid/base pairs.<sup>[10]</sup> Notably, **A** also does not involve any electron transfer from the catechol aromatic system or the iron center. This mechanism is attractive because it requires little reorganization of the ligand environment around iron, which is consistent with the EXAFS results.

Option **B** is best described as a molecular oxidative addition in which an iron hydride is formed along with addition of the other H atom to the catechol ring. Such a dearomatization reaction has been demonstrated by Milstein et al. for an iron PNP pincer complex that catalytically hydrogenates carbonyl substrates.<sup>[14]</sup> Addition of substrates to the  $\alpha$ -carbon of a catechol has also been observed in reversible dioxygen activation by a triphenylantimony complex.<sup>[34]</sup> Mechanism **B** does require the transfer of electron density from the catechol aromatic ring to the dihydrogen molecule. One alternative description would be protonation of the *iron* and hydride addition to the *catechol*.

We have termed option **C** "ligand oxidation/metal addition" and it consists of a two-electron transfer from the catechol but addition of the resulting hydrides to the iron center. This case is intriguing, because it can be inferred from the solution reactivity of many metal catechol and related species; however, in homogeneous solution the quinone is a poorly binding ligand prone to dissociation. Thus we are not aware of definitive examples of this pathway. Heyduk and others have shown that, by changing from catechol to phenylenediamine backbones, stronger nitrogen donors and more addition of sterically encumbering peripheral groups do form stable complexes.<sup>[17–19]</sup>

Although there is some precedent for all three proposed hydrogen activations, we favor option **A** on the basis of the minor perturbation of the iron coordination environment upon hydrogen treatment. Although such addition of  $H_2$ across redox-active ligands has been observed, it is unlikely that option **B** would be supported in a catalytic cycle as ligand rearrangement would lie relatively high in energy as compared to that for option **A**. As no loss in catalytic activity is observed when the catalyst is recycled, activation route **C** seems even more unlikely, as the mobility of iron centers within fully oxidized quinone-based ligand environments is well-documented (i.e. siderophore binding).<sup>[35–37]</sup>

#### Conclusions

The polymer-supported iron catecholate,  $Et_2OFe(CAT-POP)$ , is an active olefin hydrogenation catalyst. The complex is three-coordinate both as-prepared and after exposure to oxygen, which oxidizes the iron from the 2+ to the



3+ oxidation state. The Fe<sup>3+</sup> is not active for hydrosilylation but remains active for hydrogenation and does not get reduced back to Fe<sup>2+</sup> under dihydrogen at the reaction temperature as determined by in situ X-ray absorption spectroscopy. Thus, the activation of hydrogen does not seem to involve electron transfer from the iron center. Of the several possible mechanisms for hydrogen activation by Et<sub>2</sub>O-Fe(CAT-POP), we favor heterolytic cleavage into an iron hydride and protonated catechol ligand. Further studies are on-going.

# **Experimental Section**

**General Considerations:** All manipulations were carried out under inert conditions unless otherwise noted. Et<sub>2</sub>OFe(CAT-POP) was prepared as previously reported.<sup>[20]</sup> Multiple batches of CAT-POP, Fe starting material, and Fe(CAT-POP) were prepared and compared for consistency. The iron concentration was determined by ICP-MS and is reproducible. Batch hydrogenations were conducted in a pressure vessel with typically 5 mg (0.005 mmol, 5 mol-%) catalyst in 0.6 mL [D<sub>6</sub>]benzene with 40 equiv. of substrate.

Plug-Flow Catalyst Testing Procedures: The catalyst performance testing was conducted in a vertical quartz tube reactor equipped with mass flow controllers, and the products were determined by on-line gas chromatography (J&W scientific #115-3552, GS-Alumina, 50 m  $\times$  0.530 mm). Et<sub>2</sub>OFe(CAT-POP) (ca. 0.100 g) was diluted with  $SiO_2$  (ca. 0.800 g) and supported on quartz wool, and an internal thermocouple was placed at the top of the catalyst bed. Because of its air sensitivity, the sample was packed and sealed in a Vacuum Atmospheres glovebox under N2. Initially, the catalyst was purged with H<sub>2</sub> (UHP Grade, Airgas USA, LLC) at 50 mL/ min at room temperature and then for 15 min at either 150 or 175 °C. The reaction mixture was 4% H<sub>2</sub>/Ar mixture at a flow rate of 30 mL/min and 4% propene/Ar at a flow rate of 15 mL/min. Generally the conversions were under differential conditions, i.e., less than 10%. Air-exposed samples were treated in the same manner as those not exposed to air in order to observe the catalytic activity of Fe<sup>3+</sup>(CAT-POP). The catalyst was exposed to air for ca. 5 min, then loaded into the reactor, heated to reaction temperature, and tested. Fe<sup>3+</sup>(CAT-POP) was also tested after storage in air for about 1 month, and rates were the same as those with the freshly oxidized sample. Product composition was determined by using gas calibration standards and analyzed by a flame ionization detector (FID) using H<sub>2</sub> (99.999%, Airgas USA, LLC) and air (< 2 ppm H<sub>2</sub>O, Airgas USA, LLC). Turnover rates were calculated by assuming that all Fe sites are active.

In Situ XAFS Measurements at the Fe K-Edge (7.112 keV): X-ray absorption measurements were conducted with the bending magnet beamline of the Materials Research Collaborative Access Team (MRCAT, 10-BM) at the Advanced Photon Source (APS), Argonne National Laboratory. Ionization chambers were optimized at the midpoint of the Fe spectrum for the maximum current with linear response (ca.  $10^{10}$  photons detected per second) by using 30% He in N<sub>2</sub> (15% absorption) in the incident X-ray detector and a mixture of ca. 30% Ar in N<sub>2</sub> (70% absorption) in the transmission X-ray detector. A third detector in the series simultaneously collected a Fe foil reference spectrum with each measurement for energy calibration. A cryogenically cooled double-crystal Si(111) monochromator was used and detuned to 50% in order to minimize the presence of harmonics. The X-ray beam was  $0.5 \times 1.5$  mm and data was collected in transmission geometry in

10 min in step scan mode. The catalyst was pressed into a 4 mm self-supporting wafer and placed in a stainless steel holder. The reactor consisted of a straight quartz tube (1'' OD, 10'' length) with an Ultra-Torr<sup>®</sup> fitting equipped with shut-off valves. At both ends of the reactor were Kapton windows sealed with O-rings. The reactor has an internal thermocouple at the sample, which controls the clamshell furnace. After treatment with gas flows (3.5% H<sub>2</sub> in He; 50 sccm) at elevated temperature, the catalysts were cooled in the flowing gas and re-measured at room temperature without exposure to air.

**X-ray Absorption Analysis at the Fe K-Edge:** The XANES pre-edge energy was obtained from the data calibrated with the Fe foil obtained simultaneously with each spectrum. EXAFS fits of the Fe(CAT-POP) catalysts were modeled from experimental phase shift and backscattering amplitudes, which were obtained from Fe<sup>III</sup> acetylacetonate (6 Fe–O at 1.99 Å). Standard procedures based on WINXAS 3.1 software were used to fit the XAS data. The EXAFS coordination parameters were obtained by a least-squares fit in *r*-space of the first shell nearest neighbor,  $k^2$ -weighted Fourier transform data ( $\Delta k = 2.8$ –10.5 Å<sup>-1</sup> and  $\Delta R = 1.1$ –1.9 Å).

**Supporting Information** (see footnote on the first page of this article): A description of the XAS fitting procedure and a table of calculated XAS parameters for Fe(CAT-POP) catalysts and standards.

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