

Efficient Interconversion of Chemical and Electrical Energy: Electrocatalysis with Discrete Transition Metal Complexes

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Abstract

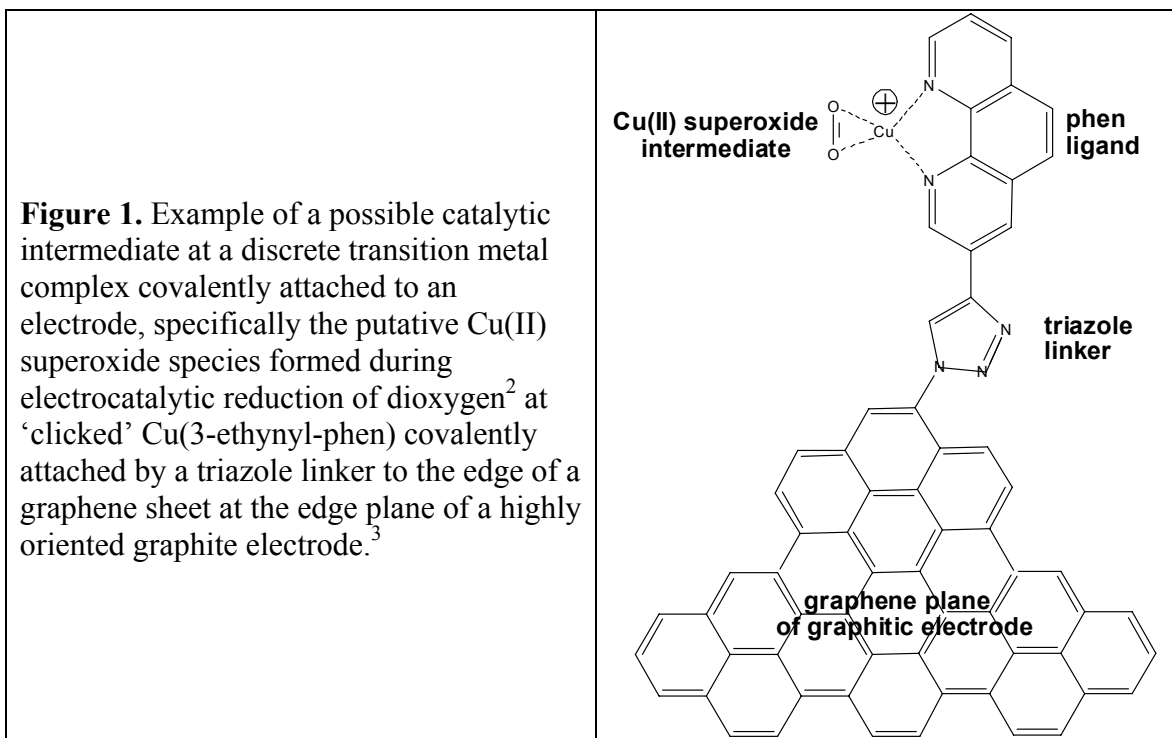
This project has worked to develop efficient electrocatalysts for the oxidation of hydrocarbons and the reduction of O₂ in polymer-electrolyte-membrane (PEM) fuel cells, which operate near ambient temperatures. This year we have further developed our recent ‘click’ strategy for the covalent attachment of discrete transition metal complexes to azide-modified graphitic electrode surfaces such as those used in ambient-temperature fuel cells and have characterized the electrocatalysis of dioxygen reduction at one of these electrodes. We have now extended the ‘click’ method to oxidatively stable metal-oxide electrodes and to high surface-area porous metal oxides and have demonstrated site isolation of species ‘clicked’ to the surfaces. We have developed partially fluorinated ligands for greater oxidation resistance in alcohol oxidation catalysts and have begun to develop complexes containing Pt dimers offering reversible electrochemistry and novel opportunities for C-H activation chemistry.

Introduction

This project has worked to develop efficient electrocatalysts for the oxidation of hydrocarbons and the reduction of O₂ in polymer-electrolyte-membrane (PEM) fuel cells, which operate near ambient temperatures. While the efficient catalysis of H₂ oxidation in these fuel cells is well established, the challenges of making, transporting and storing H₂ motivate the development of efficient catalysts for the oxidation of more easily stored and transported hydrocarbon fuels. Developing efficient electrocatalysts to use fossil fuels, renewable biofuels and solar-derived hydrocarbon fuels in such cells is an important investment for reducing net CO₂ emissions. Finally, less than optimal catalysis of O₂ reduction in these cells remains a severe problem with about a third of the available energy of the cell wasted as heat during O₂ reduction¹. This energetic inefficiency is compounded by the significant capital and operating expense of removing the waste heat across the relatively small temperature drop available in a PEM-type fuel cell. Improved electrocatalysts for O₂ reduction would thus have multiple benefits for any near-ambient-temperature fuel cell.

The dominant approach to improving electrocatalysis in fuel cells has been the empirical optimization of the existing nanoparticulate-type catalysts dispersed on the

graphitic electrodes of the PEM fuel cell. There is a need for a sustained and focused effort to understand and to tailor the reactivity of new types of electrocatalysts that fully use each of the expensive atoms in the catalysts to bind and activate the reactants. We have explored how best to do this with stable ligands that complex individual transition metal ions in specific arrangements to optimize electrocatalytic reactions. We have also developed convenient and robust methods for covalently attaching our ligands to inexpensive and oxidatively robust graphitic electrodes and, more recently, to even more oxidatively stable metal-oxide electrodes. Figure 1 illustrates one of the putative catalytic intermediates in the reduction of dioxygen at one of the modified electrodes we have developed.



Intimate contact of the reactants with metal atoms is required for efficient electrocatalysis, but neither hydrocarbons nor O₂ are good enough ligands to displace other ligands from metal atoms. Thus, a good catalyst must have open coordination sites on the metal atoms at which the hydrocarbon or O₂ can bind and react. In this project, we have focused on ligands that maintain open coordination sites around individual copper, palladium and iron atoms. We have also explored ligands that can position two or more metal atoms in a well defined environment that maintains open coordination sites. Finally, we have explored how well our catalyst immobilization methods isolate the metal complexes from each other. Such *site isolation* prevents aggregation of the complexes, thus maintaining open coordination sites on the metal atoms.

Results

Further Development of Azide Functionalization of Graphitic Carbon Materials

Last year, we reported a new and potent method using the reagent iodine azide to attach azide ($-N_3$) groups covalently to graphitized polymer thin films as well as to the edge-plane of highly oriented pyrolytic graphite.^{3,4} We found that the reaction does not occur on the basal plane of graphite, indicating that the azide groups are installed at the edges of graphene sheets. The resulting azide-modified carbon surface can then be covalently coupled to ethynyl-terminated ($-C\equiv CH$) ligands by the recently developed Sharpless-Meldal “click” reaction^{5,6} to form hydrolytically stable, oxidatively resistant and electronically transmissive triazole linkers between the carbon surface and the ligands. We have now extended this method to carbon black powders, such as are used in the porous electrodes of PEM fuel cells. The estimated azide coverage on the powders is 5-10% of a densely packed azide monolayer, making it ideal for immobilization of catalysts that must be isolated one from the other on the surface. Azide coverage has been enhanced on all graphitic surfaces by optimization of the reaction conditions and has also now been enabled on basal plane graphite by pretreatment with iron salts and hydrogen peroxide, which presumably pits the surface, creating graphene edges at which the reaction can occur.

Covalent Attachment of Copper Complexes to Graphitic Electrodes

Last year, we reported the preparation of 3-ethynyl-phenanthroline and its covalent attachment to an azide-modified graphite surface. Initial electrochemical measurements showed that the ligand-modified surface binds Cu(II) ions, and that the resulting complex electrocatalyzes the reduction of O_2 in air-saturated aqueous solutions -- a putative intermediate is illustrated in Figure 1 above. The ‘clicked’ Cu(3-ethynyl-phen) shows a standard redox potential, E_{cat}^0 , that is 230 mV positive to that of the parent compound, Cu(phen), physically adsorbed on graphite. This positive shift may be due to the electron-withdrawing character of the triazole linker formed by the ‘click’ reaction.

As shown in Figure 2, the effective rate of O_2 reduction, k_{O_2} , in air saturated solution at E_{cat}^0 , is around 30 times slower for ‘clicked’ Cu(3-ethynyl-phen) than that for physisorbed Cu(phen). This is consistent with our previous finding that complexes with electron-withdrawing ligands, such as Cu(3,8-(CO₂Et)₂-4,7-Cl₂-phen) reduce dioxygen more slowly than the parent complex.² These results suggest that mononuclear Cu complexes of phen-based ligands retain catalytic activity when covalently attached directly to a graphite surface. However, this study also reconfirms that mononuclear Cu complexes, regardless of the attachment mechanism, are unlikely to achieve rapid O_2 -reduction rates at low overpotentials and that multinuclear complexes will be required to obtain sufficiently low overpotentials.

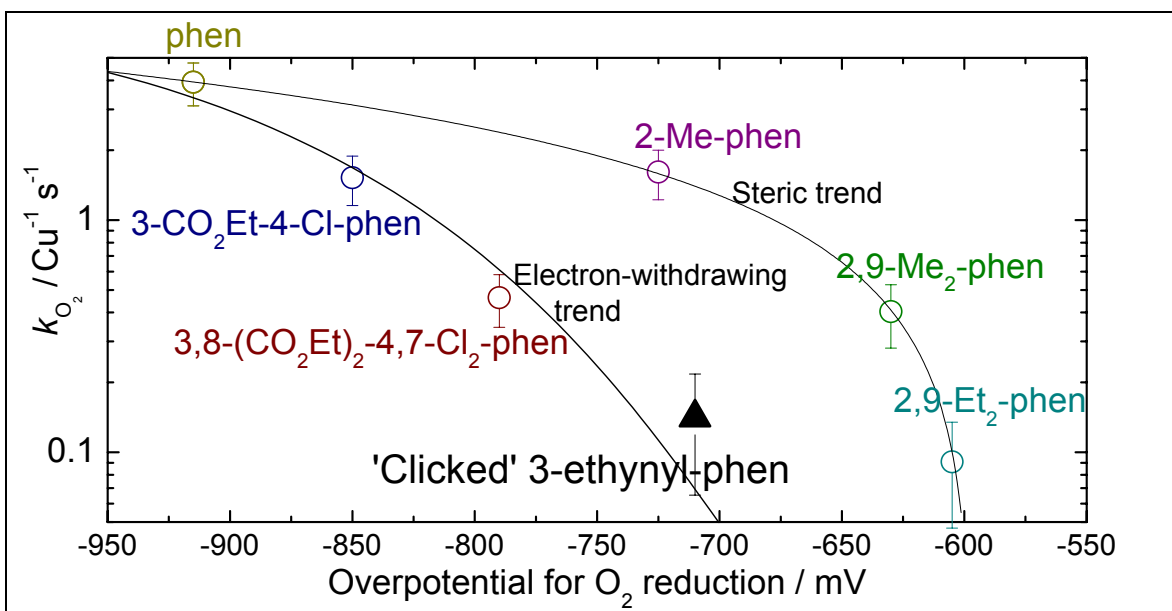
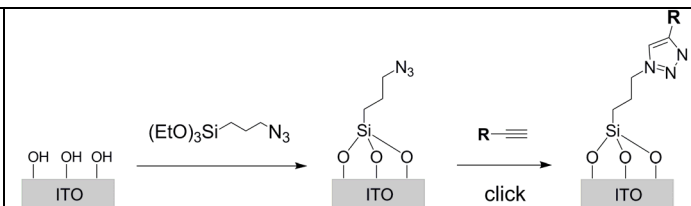


Figure 2. Catalyst-limited rate of O_2 reduction from air with Cu complexes of the given ligands measured at E_{cat}^0 . Complexes were physisorbed onto an edge-plane graphite surface² except for 3-ethynyl-phen, which is covalently attached directly to the graphite surface. The lines are guides to the eye for two observed trends – decreasing k_{O_2} with increasingly electron-withdrawing ligands, and decreasing k_{O_2} with increasing steric bulk near the Cu-binding site. Conditions: 25°C in air saturated aqueous solutions with 0.1M $NaClO_4$ and a buffer of 0.02M sodium acetate and 0.02M acetic acid at pH 4.8.

Covalent Attachment of Metal Complexes to Indium-Tin-Oxide Electrodes

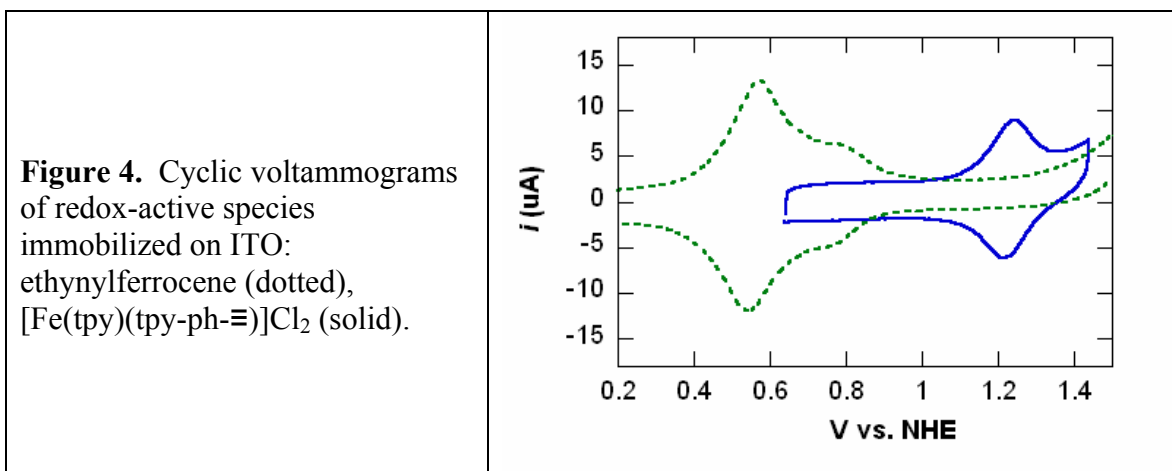
In order to provide the maximum range of electrical potentials for stable functioning of electrocatalysts, it is advantageous to have even more oxidatively stable and inert electrodes than provided by the graphitic materials used in conventional PEM fuel cells. Conducting metal oxides are a suitable class of materials for this purpose, and we have begun to develop an electrocatalytic system using one such metal oxide, indium tin oxide (ITO). Our immobilization strategy uses an azide-terminated alkoxy silane covalently attached to the hydroxyl-terminated oxide surface (Fig. 3). The azide group is available for Cu(I)-catalyzed ‘click’ reaction with a terminal ethynyl group appended to any ligand we want to attach to the surface. In a complete electrocatalytic system, the ligand will then be coordinated to one or more metal ions with open coordination sites.

Figure 3. Immobilization of azidosilane linker on an indium-tin oxide (ITO) surface and subsequent ‘click’ attachment of an ethynyl-terminated species.



To validate this immobilization platform using a known and reversible redox probe, the azide-functionalized ITO surface was first clicked with ethynylferrocene. The voltammetry of the resulting surface (Fig. 4) shows a fully reversible oxidation wave for

the immobilized ethynylferrocene near the normal redox potential of ferrocene. Additionally, XPS analysis of the surface shows the presence of iron in the ferrocene.



Next an ethynyl-terminated chelating ligand (tpy-ph- \equiv = 4'-(4-ethynyl)phenyl-2,2':6',2''-terpyridine) in the substitutionally inert complex $[\text{Fe}(\text{tpy})(\text{tpy-ph-}\equiv)]\text{Cl}_2$ was immobilized on the ITO surface and observed electrochemically. The reversible oxidation wave for this species appears at +1.2 V vs. NHE, and shows the symmetric peak shape and small peak-to-peak separation characteristic of a surface-immobilized complex (Fig. 4). The surface coverage of the immobilized $[\text{Fe}(\text{tpy})(\text{tpy-ph-}\equiv)]^{2+}$ complex is measured from the voltammogram to be $\sim 2 \times 10^{13} \text{ cm}^{-2}$, which is ca. one fifth the coverage of ethynylferrocene 'clicked' to identically prepared surfaces. This smaller coverage is currently the subject of study. Possible causes are the larger size of the $[\text{Fe}(\text{tpy})(\text{tpy-ph-}\equiv)]^{2+}$ complex and the electrostatic repulsion among the dicationic complexes at the electrode surface.

These results demonstrate the ability to immobilize ethynylated derivatives of a polydentate ligands on a conductive metal oxide. We are currently taking the next step in this strategy and working to produce electrode-immobilized, metal complexes with open coordination sites that will provide electrocatalytic activity.

Covalent Attachment of Metal Complexes to Porous Metal-Oxide Electrodes

In order to obtain the high surface area needed for effective electrocatalysis on metal oxide electrodes in fuel cells, we have begun studies of covalent attachment of ligands to porous metal oxides. Initially, we have focused on the well-known porous silica system SBA-15. However, we will soon extend this work to porous versions of conductive metal oxides like ITO. We have focused on controlling the density of reactive sites in the porous material in order to enforce site isolation and thus maintain open coordination sites in our catalysts. Convenient modification methods with controllable loadings are needed for this purpose. Modification methods of porous materials are generally classified as either "direct synthesis" or "post grafting".⁷ The "post grafting" method has the advantage of allowing for full surface coverage and results in well characterized materials, but it is difficult to control the loading of the grafted species. In contrast, the "direct synthesis" method can easily control the loading of the added species by adjusting the mixing ratio of the reagents. To develop well characterized and easily modifiable materials for heterogeneous catalysts, we have prepared SBA-15 materials with variable

azide loadings by “direct synthesis” (Figure 5). We have further demonstrated quantitative “click” surface modification of the materials using the Cu(I)-catalyzed azide-alkyne coupling reaction. In addition, using pyrene fluorescence and oxygen binding to TPA-Cu, we have demonstrated two functional applications of the materials that depend on the density of the surface modification sites.

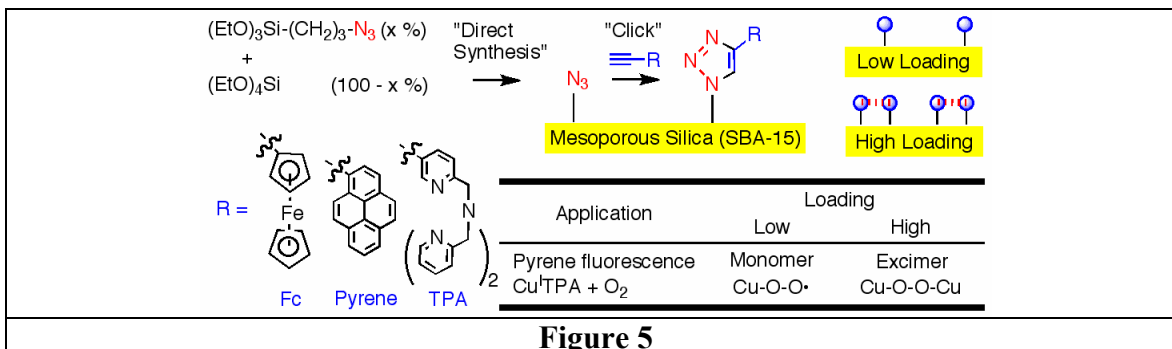


Figure 5

Ordered mesoporous SBA-15 silica materials with controlled azide loadings (SBA-15-N₃-x) were prepared by “direct synthesis” with different molar ratios of (3-azidopropyl)triethoxysilane (Si-N₃, x mol %) and tetraethoxyorthosilicate (TEOS, 100-x mol %) in the presence of the P₁₂₃ templating polymer in acidic media.⁸ The mesoporous structure of the material was characterized by powder X-ray diffraction (XRD) and N₂ adsorption-desorption isotherms to confirm the large, hexagonal pores structure characteristic of SBA-15 materials. The infrared spectroscopic signal area of the N₃ stretching increases with the Si-N₃ loading (Fig. 6).

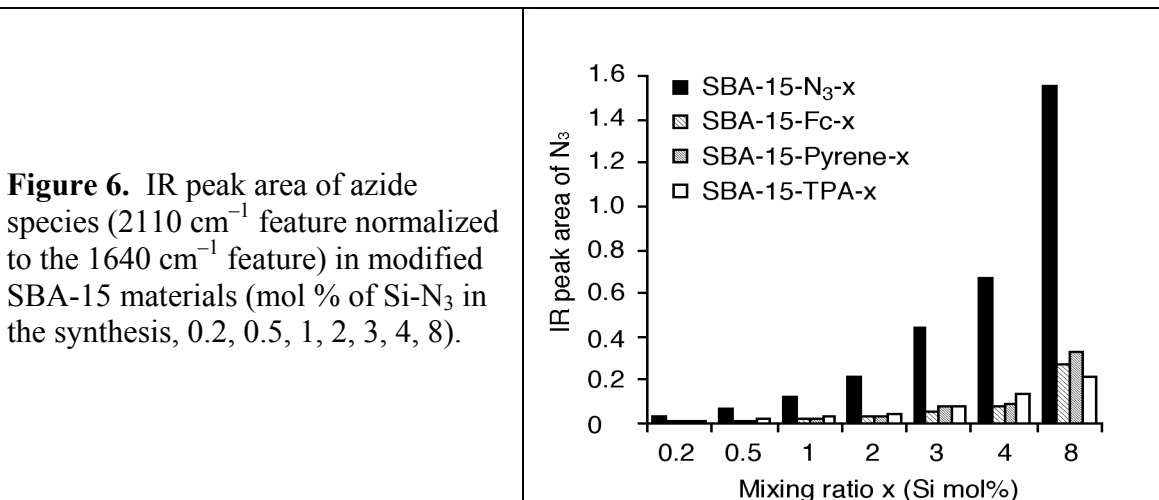


Figure 6. IR peak area of azide species (2110 cm⁻¹ feature normalized to the 1640 cm⁻¹ feature) in modified SBA-15 materials (mol % of Si-N₃ in the synthesis, 0.2, 0.5, 1, 2, 3, 4, 8).

Click modification of SBA-15-N₃-x was carried out separately with ethynylferrocene (R = Fc), 1-ethynylpyrene (R = Pyrene) and (5-ethynyl-2-pyridylmethyl)bis(2-pyridylmethyl)amine (R = TPA). Azide disappearance was monitored by the IR absorption of the residual azide (Fig. 6). In all cases, the decrease in the azide intensity was ca. 80 %, suggesting that ca. 20% of residual azide is accessible for the click reaction. The anticipated loadings of SBA-15-Fc and SBA-15-TPA molecules from the Si-N₃ content less than 20% were confirmed by ICP analysis of the Fe content of SBA-15-Fc and the UV-vis absorption of TPA at 261 nm of SBA-15-TPA, respectively (Table 1).

We conclude that the combination of “direct SBA-15-N₃ synthesis” and covalent attachment ethynylated molecules provide controlled loadings in SBA-15 materials.

R	x = 0.2	0.5	1.0	2.0	3.0	4.0	8.0
Fc	0.02	0.05	0.09	0.17	0.26	0.34	0.62
TPA	0.03	0.06	0.10	0.18	0.26	0.33	0.53

To explore the degree of site isolation of the covalently clicked ligands, the fluorescence of the SBA-15-Pyrene-x materials at different loadings were measured (Fig 7a, Fig. 8).⁹ From low to high loadings of pyrene, the features characteristic of the pyrene monomer emission (ca. 400 nm) give way to the emission of the pyrene excimer (ca. 470 nm).

We also found that the nature of the binding of O₂ to surface immobilized Cu^ITPA depended on loading (Fig. 7b). It is known that upon expose to air at -90 °C in homogeneous EtCN solution, the [Cu^I(TPA)]⁺ complex immediately forms a purple dicopper(II) trans-μ-1,2-peroxospecies [(TPA)Cu^{II}-O-O-Cu^{II}(TPA)]²⁺.¹⁰ By contrast, a green-colored monocopper(II) superoxo species [(TPA)Cu^{II}-O-O•]⁺ has been detected as an intermediate species by stopped-flow methods and also isolated by CO/O₂ gas exchange. In the case of our materials, the yellow complex of Cu^I with SBA-15-TPA-4 (higher loading) immediately turned purple upon expose to air at -90 °C. The similar yellow complex of Cu^I with SBA-15-TPA-0.5 (lower loading) turns brilliant green immediately after expose to air at -90°C. This striking difference in color suggests that the monocopper superoxo species is indeed stable at low enough surface coverage and that true site isolation and protection against μ-peroxo bridging between metal sites is achieved. While further characterization of these species is needed, these initial results clearly highlight the role of surface loading in controlling the chemistry that occurs.

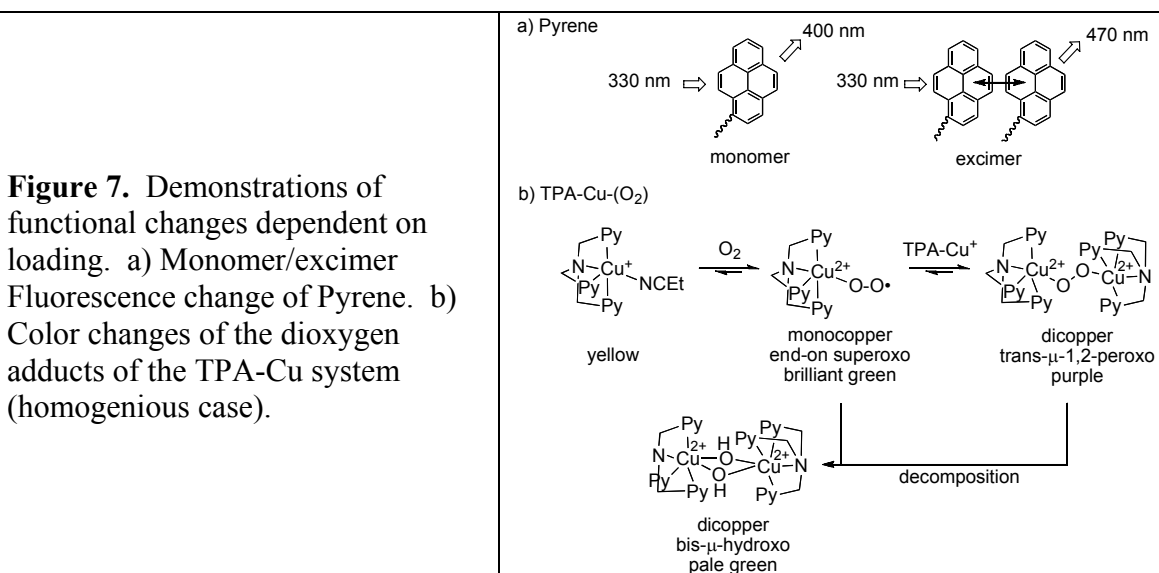
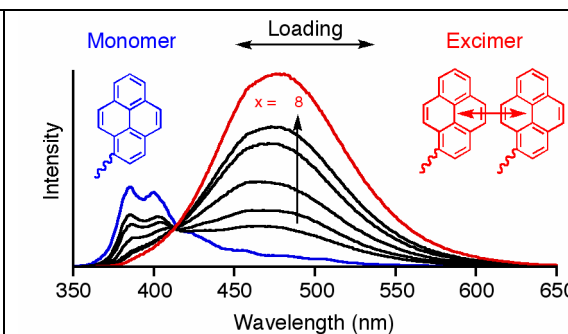


Figure 8. Fluorescence spectra of SBA-15-Pyrene-x (mol % Si-N₃: x = 0.2, 0.5, 1, 2, 3, 4, 8) suspended in CHCl₃ excited at 330 nm. The intensity of spectra were normalized at 415 nm. The intensity ratios of excimer (480 nm) to monomer (385 nm) (I_{exc}/I_{mon}) for the materials are 0.14 (x = 0.2), 0.74 (x = 0.5), 1.29 (x = 1), 2.95 (x = 2), 7.84 (x = 3), 10.6 (x = 4) and 28.5 (x = 8), respectively.

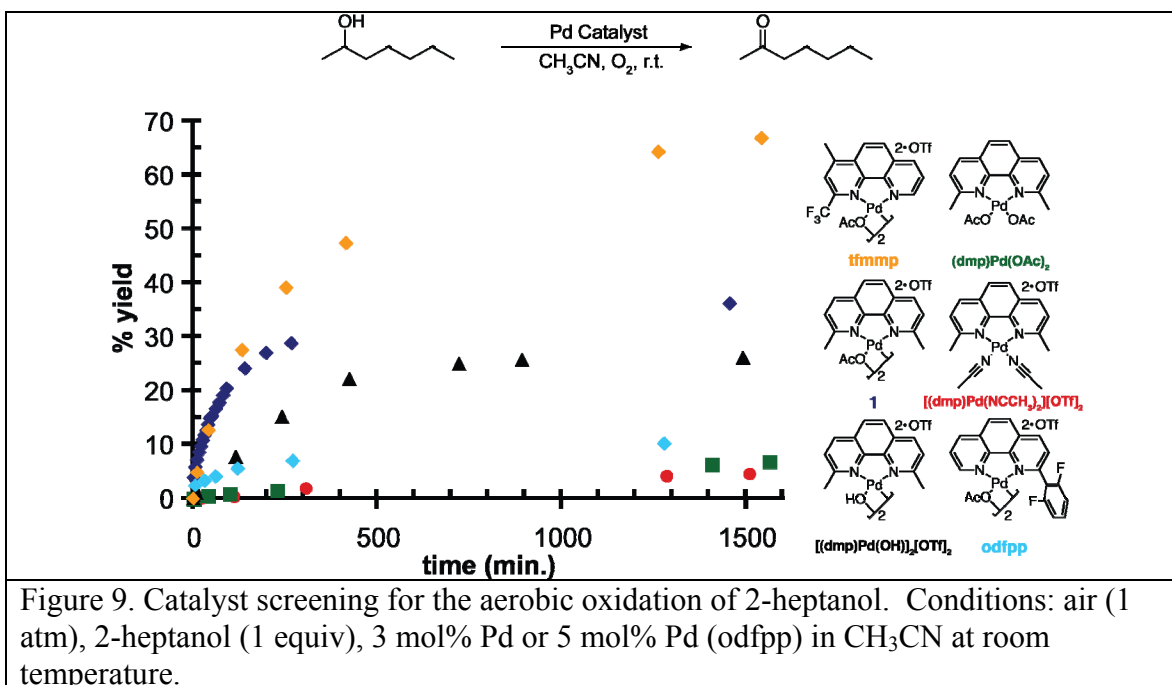


In conclusion, building on the well studied porous silica system SBA-15, we have synthesized and characterized SBA-15-N₃-x, we have modified it with several species using the “click” method, and we have achieved “site-isolation” at low loadings. We will next adapt this methodology to less well studied porous conductive metal oxide systems such as mesoporous porous ITO.

Oxidation Resistant Pd Ligands for C-H Oxidation

Last year, we reported that the metal complex [(dmp)Pd(OAc)]₂(OTf)₂ (dmp = 2,9-dimethyl-1,10-phenanthroline) exhibited as a remarkably fast catalyst for oxidation of alcohols by dioxygen at room temperature.¹¹ We have identified two key requirements in mononuclear Pd catalyst design necessary to achieve high rates: the active catalyst must (a) be cationic to afford an open coordination site for alcohol binding and (b) contain a basic counterion for intramolecular deprotonation of the bound alcohol species. Despite the fast initial rate of catalyst **1**, the turnover number was only 12 after 24 h due to substantial slowing of the reaction rate over the course of the reaction. Palladium black formation and catalyst inhibition by products were ruled out. Oxidation of one of the methyl groups on the phenanthroline ligand to a chelating carboxylate was identified as the deactivating process.

To combat this deactivation of the catalyst, we have worked to develop oxidation-resistant ligands with fluorine substituted for hydrogen at positions where oxidation chemistry has been shown to occur. Despite extensive efforts, we were not able to form a palladium complex with the phenanthroline in which both methyl groups were fully fluorinated. However, removal of one trifluoromethyl (Fig. 9, tfmmp), allowed for complexation. Complexation was also successful with a fluorinated phenyl-substituted phenanthroline (Fig. 9, odfmp). We have tested these complexes as alcohol oxidation catalysts under reaction conditions to favor the cationic monomers of these species in analogy to our initial success with (dmp)Pd(OAc)⁺. Figure 9 documents the time course of the oxidation of a model alcohol, 2-heptanol, under aerobic oxidation conditions with various ligands.



As shown in Figure 9, the putative (tfmmp)Pd(OAc)⁺ species has similar reactivity as (dmp)Pd(OAc)⁺ but has an extended lifetime, completing almost twice as many turnovers. Conversion slows significantly after 22 turnovers suggesting catalyst decomposition. We have not yet identified the reason for catalyst decomposition but we suspect it may be due to ligand dissociation. The odfpp complex was significantly slower achieving only 2 turnovers after 24h, possibly due to the increased steric bulk of the phenyl group.

Synthesis of Metal Dimer Complexes for Electrochemical Oxidation of Hydrocarbons

Several of the above mononuclear Pd catalysts have been physically adsorbed onto graphite. The 3-ethynyl-1,10-phenanthroline complex with Pd has also been covalently attached to azide functionalized graphite. However, to date we have not been able to verify electrocatalytic behavior with any of these species. Moreover, we have not been able to detect an electrochemically reversibly change of the oxidation state of the Pd. The lack of electrochemical activity is presumably due to large reorganization barriers between different oxidation states of Pd in these mononuclear complexes.

We have thus turned our attention to a more elaborate catalytic system involving a dinuclear metal center, a class of metal-metal dimers that show reversible electrochemistry while also participating in many organic oxidation reactions including C-H activation and olefin oxidation.^{12,13} Pt dimers held together by two bridging amide ligands maintain catalytic activity when supported on a variety of surfaces.^{14,15} We have synthesized one of the known compounds with two amines coordinated to each platinum center providing a cationic complex with reversible electrochemistry (Fig. 10). Current efforts are focused on derivatives of these complexes containing metal carbon bonds to couple the reversible redox chemistry with hydrocarbon activation.

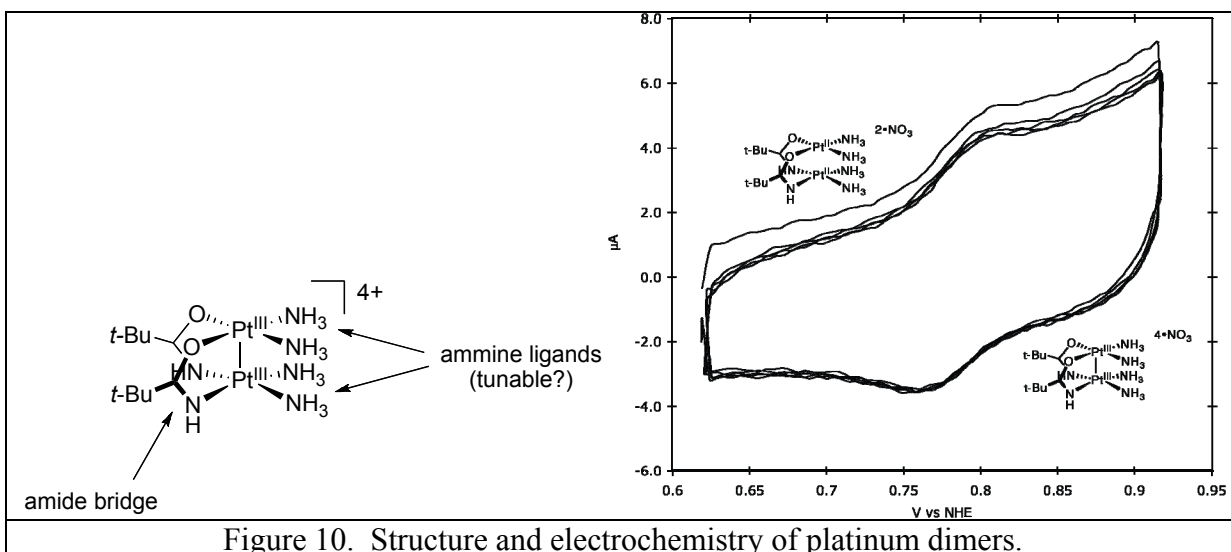


Figure 10. Structure and electrochemistry of platinum dimers.

We have also synthesized a chelating diamide ligand (Fig. 11) that will allow covalent attachment to azide-functionalized surfaces. The use of a chelating diamide as our bridge should improve the stability of these species. We are currently working develop means to prepare the complex after ‘clicking’ the ligand to an electrode surface and also to prepare the dimer in solution to be followed by ‘click’ attachment.

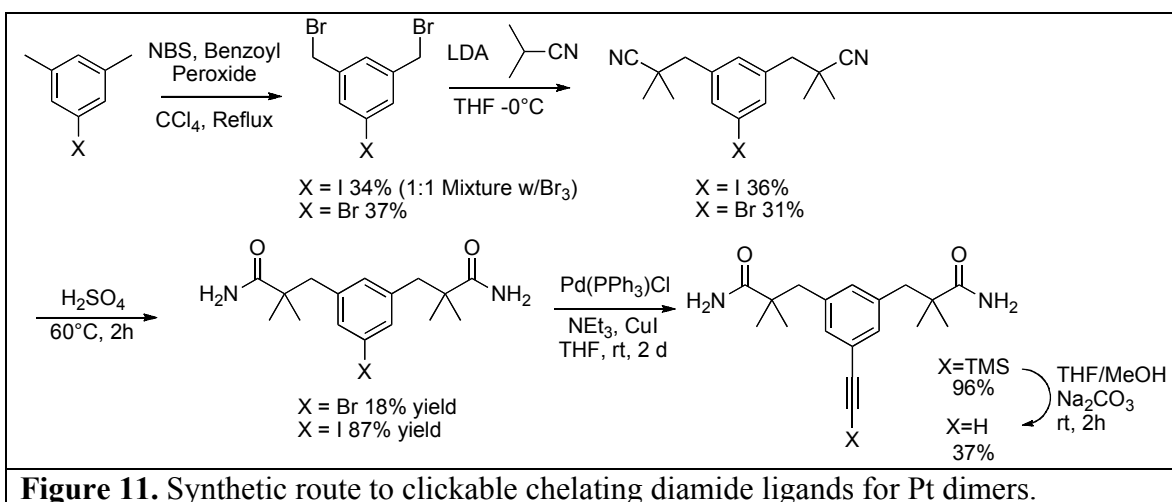


Figure 11. Synthetic route to clickable chelating diamide ligands for Pt dimers.

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