Metal complex assembly controlled by surface ligand distribution on mesoporous silica: Quantification using refractive index matching and impact on catalysis

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ABSTRACT

The catalytic activity of discrete metal complexes can be dictated by the local ligand environment. By covalently immobilizing ligands on a surface, the ability of a single metal to engage multiple ligands is controlled by the overall surface loading and distribution. Using an azide functionalized mesoporous silica prepared via co-condensation, the surface loading of 1,10-phenanthroline (phen), a bidentate chelating ligand, can be varied systematically to form preferentially mono-, bis-, or tris-phen ligated metal complexes. Solvent refractive index matching enables *in situ* transmissive spectroscopic quantification of intense metal-to-ligand charge transfer bands of the immobilized copper(I) bis-phen and iron(II) tris-phen complexes. Metal complex formation agrees well with a random distribution model of the phen ligands on the surface, providing a means to quantitatively correlate immobilized species interactions and overall catalytic performance. Rapid epoxidation catalysis is obtained with surface distributions that maximize mono- or bis-phen ligated manganese centers.

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1. Introduction

Covalent surface immobilization of discrete metal complexes is a promising strategy in catalyst design to leverage the high selectivity and ligand tunability of homogenous systems with the practical heterogeneous advantages of catalyst separation and recycling [1–4]. Moreover, surface immobilization introduces additional control over catalytic performance by modulating intermolecular interactions through both surface density and spatial distribution [5–11]. Under equilibrated homogeneous conditions, the number of ligands coordinated with a metal center is typically dictated by the thermodynamic stability of the complexes [12], and the ligation of the active catalytic species is difficult to control. Attempts to obtain coordinatively unsaturated metal complexes often rely on sterically demanding periphery groups at the ligand, but this can limit substrate accessibility and slow overall catalytic activity. In contrast, the maximum coordination on a surface is determined by the ligand spatial distribution (Fig. 1), potentially stabilizing coordination environments that exist only as minor species under equilibrated homogeneous conditions. High surface loadings result in site-dense ligand environments with significant interaction between immobilized species, whereas low surface loadings deliver ligand site-isolation. The catalytic performance of these different environments provides insight into the overall mechanism and guides further catalyst design. To apply this technique broadly to catalytic studies requires the following: (1) controllable surface loading of the covalently immobilized ligand, (2) a modular attachment method applicable to a wide range of ligands, (3) a quantitative model of surface distribution, and (4) a simple analytical tool to quantify the degree of metal complex formation.

The co-condensation synthesis of mesoporous silica is an ideal approach to incorporate functional groups on a surface in a systematic fashion. Ordered mesoporous silicas, such as SBA-15 [13], possess high surface areas, large pore diameters and hydrothermally robust silica walls. Functionalized mesoporous silica powders have been used for heterogeneous catalysis [14–19], bioimaging [20], protein immobilization [21,22], metal sequestration [23], and drug delivery [24,25]. In contrast to post-synthetic grafting techniques, which generally yield either site-dense or site-isolated surface coverages [26,27], silica co-condensation provides a precise, quantitative control over a range of target surface loadings. We have reported previously the co-condensation synthesis of azide decorated mesoporous silica SBA-15-N$_3$-x [28,29], where the azide loading is controlled by varying the molar ratio (x) of azidopropylsilane precursor. The surface-bonded azides are
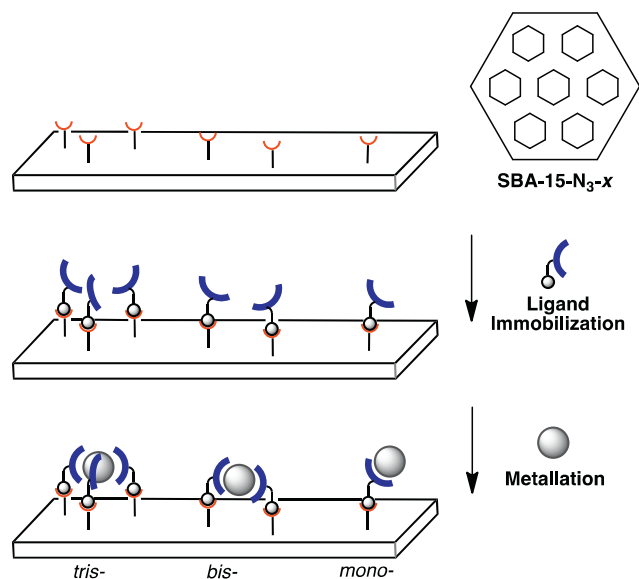
Fig. 1. The surface distribution and arrangement of immobilized ligands control the degree of metal coordination.

functionalized subsequently with ethynylated ligands via copper-catalyzed azide-alkyne cycloaddition (CuAAC), a 'click' reaction [30]. Although the surface distribution of co-condensed functionalities has been described as "well-ordered" [31], "uniform" [32–34], "regular" [35], and "homogeneous" [27,36], limited work has been done to quantitatively model the distribution [37,38]. Whether the surface coverage is statistically random or clustered will dramatically affect the average distance between immobilized species and must be determined to reasonably predict surface intermolecular interactions.

One barrier to widespread use of surface immobilization as a tool for analyzing discrete molecular catalysts is the unsuitability of various spectroscopic techniques used in homogeneous solution characterization. UV–vis spectroscopy is an ideal probe into ligand coordination, as the absorption spectra of metal complexes are extremely sensitive to the ligation environment [39]. Light scattering due to the silica particles, however, prevents quantitative transmission measurement. Quantitative diffuse reflectance spectroscopy requires precise corrections for sample thickness, spatial architecture, and inhomogeneity of the surface, and is a static characterization technique performed without solvent, dissimilar to homogenous reaction conditions [40,41]. Alternatively, light scattering is attenuated using solvent refractive index matching, whereby the suspension of silica in a matched solvent minimizes light scattering at the particle–solvent interface. These conditions provide a quantitative, dynamic probe of surface immobilized species *in situ*. Refractive index matching has been applied to aid in characterizing flow mechanics [42,43], microfluidics [44], hydrogels [45], immobilized chromophore-quencher assemblies [46], optical rotation of insoluble polymers [47] and Raman of solids [48]. To the best of our knowledge, such a technique has not been applied to surface immobilized catalysts, where quantitative spectroscopic characterization would provide valuable insight into the ligand environments.

Here we report the surface immobilization of 1,10-phenanthroline (phen) for the formation of multi-ligand metal complexes as a function of surface loading. Surface immobilized metal complexes with phen have shown catalytic activity that is sensitive to the surface coverage [11,49], making phen an ideal target to probe a systematic variation in the formation of mono-, bis-, and tris-ligated sites. Phen compounds are also ideal for UV–vis characterization of the coordination environment, as judicious metal selection can provide intense

metal to ligand charge transfer (MLCT) bands in the visible range. The correlation of catalytic performance with surface-dictated coordination demonstrates the power of this approach to provide insight into catalyst design.

2. Results

2.1. Material synthesis and refractive index matching

5-Ethynyl-1,10-phenanthroline [50] was prepared on the multi-gram scale from 1,10-phenanthroline via bromination [51] and subsequent Sonogashira C–C coupling (Scheme 1). Phen-Tz-*t*Bu was prepared by CuAAC of the ethynylated phen with *tert*-butyl azide, N_3-*t*Bu, and serves as a homogeneous electronic analog for surface-immobilized phen. A range of SBA-15-N_3-*x* materials were prepared with azide incorporation *x* = 0.1–4.0% of the silane precursor (up to 30% total surface coverage) as described previously [28]. Incorporation of the azide species at these levels during synthesis does not impact appreciably the SBA-15 overall structure. 5-Ethynyl-1,10-phenanthroline was immobilized covalently to SBA-15-N_3-*x* materials through CuAAC to yield SBA-15-phen-*x* (Table 1). Phen loadings range from 0.008 to 0.344 mmol g^{-1} SBA-15, consistent with previously reported yields for surface CuAAC immobilization. These materials provide a broad range of surface coverages for probing intermolecular interactions.

Refractive index (n_D) matching for the SBA-15-phen-*x* materials was determined from the light scattering of silica suspensions in solvent mixtures under constant stirring. Combinations of dimethyl sulfoxide (DMSO, n_D = 1.478), acetonitrile (MeCN, n_D = 1.344), and benzonitrile (BzCN, n_D = 1.528) provide fine control over the solvent refractive index. The baseline scattering at 525 nm was measured and normalized by the suspension concentration (γ, mg SBA mL^{-1} solvent), and the scattering was fit as a parabolic function of solvent n_D (Fig. 2). For example, scattering from SBA-15-phen-3 (0.180 mmol g^{-1}) is minimized in solvent with n_D = 1.499. Ideal solvent n_D values for all SBA-15-phen-*x* and SBA-15-N_3-*x* materials are summarized in Table 1. Azide incorporation has only a minor impact on the SBA-15 refractive index, with an overall range of 0.5% in matching value. For the SBA-15-phen-*x* materials prepared, refractive indices vary by 3%. Even with optimal matching, a limited amount of residual light scattering is observed, *ca.* 0.005 a.u. γ^{-1} for SBA-15-N_3-*x* materials and *ca.* 0.02 a.u. γ^{-1} for SBA-15-phen-*x* materials. With this approach, the optimal solvent matrix can be determined easily, providing a high degree of light transmission and the opportunity to quantitatively monitor metal complex absorption *in situ*.

2.2. Metal coordination

Ligand site-isolation was quantified by the binding of copper(I) to SBA-15-phen-*x* systems. [Cu^I(phen)$_2$]$^{1+}$ has a characteristically intense absorption at 450 nm, whereas the [Cu^I(phen)]$^{1+}$ does not absorb appreciably at this wavelength [52]. Suspensions of an effective "0.15 mM" phen solution concentration were prepared for all SBA-15-phen-*x* materials in the appropriate n_D matched solvents. The absorbance *ca.* 450 nm of a vigorously stirred suspension was monitored while performing a titration with [Cu^I(MeCN)$_4$]SbF$_6$. The difference UV–vis absorbance was compared to that obtained with the homogeneous analog phen-Tz-*t*Bu under identical solvent conditions (Fig. 3). In the example case of SBA-15-phen-2 (0.131 mmol g^{-1}), the maximum absorbance at 450 nm was 60% of that obtained with phen-Tz-*t*Bu, indicating 40% of phen is site-isolated. The formation of the bis-phen copper(I) species is sensitive to excess copper both on the surface and in solution, with maximum complex formation at a 1:2 metal:ligand ratio (Figs. S1 and