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Controlled Loadings in a Mesoporous Material: Click-on Silica

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Surface modification of mesoporous silica materials with organosilane groups holds considerable potential for many applications, including heterogenization of discrete metal catalysts and even enzymes.[1] Beyond recycling and separation advantages, site-isolation of oxidation catalysts in such hybrid materials provides potential activity enhancements, as deleterious bimolecular catalyst interactions can be attenuated significantly.[2] Though conceptually simple, a dearth of straightforward and robust synthetic procedures are available that provide systematic loadings of catalysts within mesoporous materials. Reported here is a procedure that yields predictable and *randomly* distributed loadings of an organoazide[3] by a "direct synthesis"[4] of the mesoporous silica (ca. 2−50% surface coverage). Subsequent coupling of the organoazide with an ethynlated molecule through a Cu-catalyzed Huisgen [3 + 2] cycloaddition reaction, a "click" reaction,[5] yields expected loadings of the desired entities. Significant differences in reactivity with O_2 are demonstrated qualitatively between site-isolated and site-dense Cu(I) complexes.

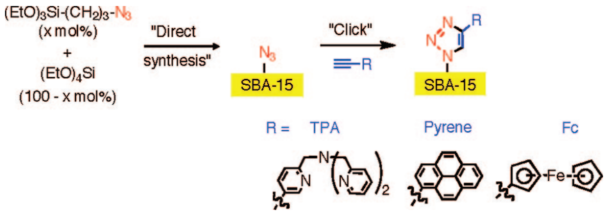
Mesoporous SBA-15 silicas are attractive as a support for oxidation catalysts with large surface areas (700−900 m^2 g^{-1}), large pores sizes (6−9 nm) and robust silica walls (3−6 nm).[6] Under forcing grafting conditions of excess (3-azidopropyl)-triethoxysilane ($Si-N_3$; >20 equiv) in refluxing toluene over several days, a near fully loaded surface (ca. 1 mmol g^{-1}) of the organoazide is possible with calcined SBA-15.[7,8] Trace amounts of water are critical, as rigorously dry conditions only yield a maximum of ca. 0.1 mmol g^{-1}. If a random distribution of organosilanes is desired at less than full coverage, water is problematic, as the monomeric organotriethoxysilanes precondense in solution, leading to clustering on the surfaces.[9]

By contrast, reproducible and predictable loadings of $Si-N_3$ within an SBA-15 were accessible by a "direct" synthetic route,[10] in which various molar amounts of $Si-N_3$ are co-condensed with tetraethoxy-orthosilicate (TEOS) in the SBA-15 preparation (Scheme 1).[8] Key to this preparative method is that the templating P_{123} organic polymer can be removed under mild Soxhlet extraction conditions rather than calcination, leaving the covalently attached organoazides in the templated pores.

The pore size and surface area of each material, SBA-15-N_3-*x*, as assessed by power X-ray diffraction and N_2 absorption isotherm measurements, are consistent fully with the ordered structure of the original SBA-15 material.[6,8] The azido-propyl groups are evident from both the CP-MAS ^{13}C solid-state NMR spectra and the IR spectra.[8] The ratio of the azide (2110 cm^{-1}) to surface-bonded H_2O bending mode (1640 cm^{-1})[11] features in the IR spectra provides a simple ratiometric assessment of the azide content. Incorporation of the $Si-N_3$ into the materials clearly scales in a linear fashion with the initial mol % used in the direct synthesis (Figure 1a).

Ethynylferrocene (R = Fc), 1-ethynylpyrene (R = pyrene), or (5-ethynyl-2-pyridylmethyl)bis(pyridylmethyl)-amine (R = TPA) were clicked to the organoazides of SBA-15-N_3-*x* to yield SBA-15-R-*x* (Scheme 1).[8,12] Ratiometric assessment of the azide IR feature of each sample decreased to ca. 20% of its original intensity (Figure 1a), suggesting that not all organoazides integrated by a direct synthesis are accessible for reaction.[13] The loadings of the Fc, pyrene and TPA materials were determined by other analytical techniques and the loadings correlated closely with the initial $Si-N_3$ mixing ratio (Figure 1b).[8] The combination of a direct synthesis of the hybrid SBA-15 material followed by click attachment allows for the efficient preparation of controlled loadings of ethynlated molecules.

Scheme 1. Preparation of SBA-15-R-*x* (*x* = 0.2−8 mol %)



The fluorescence of the SBA-15-pyrene-*x* materials provided critical information related to the distribution and density of the organic groups.[7,14] Using our lowest loaded sample (*x* = 0.2), only appreciable monomeric pyrene fluorescence is observed at 400 nm (Figure 2). Higher loaded samples produced significantly more excimer fluorescence at 480 nm resulting from interaction of two closely positioned pyrene entities with a corresponding decrease in monomer fluorescence. A direct correlation of loading and excimer fluorescence is indicated.

Assuming a 15 Å tether length of each surface immobilized pyrene along with the ca. 700 m^2 g^{-1} surface area, a loading of ca. 0.2 mmol g^{-1} is possible with idealized hexagonal packing; only monomer fluorescence would be anticipated from this ordered distribution. Assuming both a random distribution and excimer fluorescence at any level of pyrene overlap, a 10-fold greater surface area per pyrene is needed to ensure ca. 90% site-isolation.[8] The I_{mono}/I_{exc} ratio of SBA-15-pyrene-0.2 (0.03 mmol g^{-1}), shows

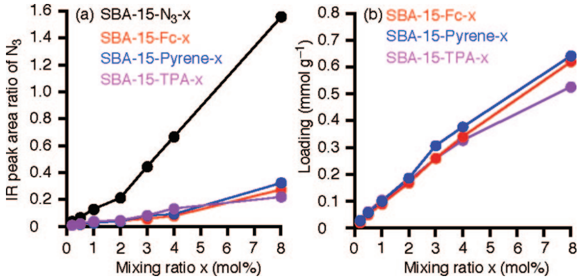


Figure 1. (a) IR peak area of azide (2110 cm^{-1} normalized to the signal at 1640 cm^{-1}) of the SBA-15 materials as a function of the mixing ratio *x* of $Si-N_3$. (b) Loading amounts (mmol g^{-1}) of SBA-15-R-*x* (R: Fc, Pyrene and TPA. *x*: mol % mixing ratio of $Si-N_3$). Fc loading was determined by ICP Fe analysis of digested samples. Pyrene and TPA loadings were determined by UV−vis analysis of digested samples.

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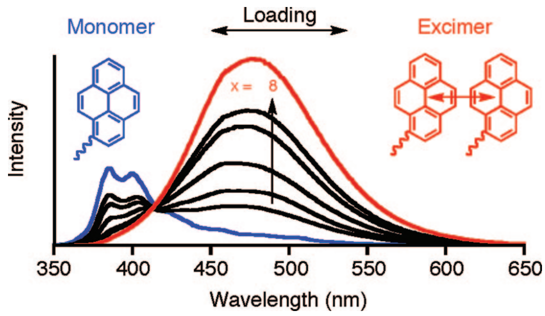
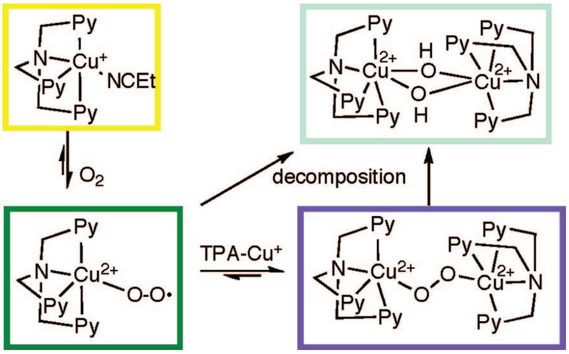


Figure 2. Fluorescence spectra of SBA-15-pyrene-*x* ($x = 0.2$, 0.5, 1, 2, 3, 4, 8 mol %) suspended in $CHCl_3$ ($\lambda_{ex} = 330$ nm). For comparison the spectra were normalized at 415 nm.

Scheme 2. Dioxygen Adducts of $[Cu^{I}TPA]^{1+}$



predominant monomer fluorescence. The correlation of the decrease of the I_{mono}/I_{exc} ratio with loading is also consistent with a cumulative density function for randomly distributed objects.[8] These data suggest that the pyrene and thus the original organoazide distribution is *random* and that site-isolation of similarly sized metal complexes will be achieved at loadings in the 0.03 mmol g^{-1} range or less.[8]

Oxygenation of $[Cu^{I}TPA]^{1+}$ in a homogeneous propionitrile (EtCN) solution at −90 °C generates a green monomeric superoxide complex initially, which rapidly reacts with a second equivalent of $[Cu^{I}(TPA)]^{+}$ to form a purple dimeric peroxo complex (Scheme 2).[8,15] This rapid dimerization precludes any investigation of the superoxide species reactivity. Site-isolation of $[Cu^{I}TPA]^{1+}$ allows the formation of this mononuclear species; SBA-15-TPA-0.5, loaded with 0.9 equiv of $[Cu^{I}(MeCN)_4](SbF_6)$ per TPA ligand, turns brilliant green upon oxygenation at −90 °C in EtCN. The more densely loaded material, SBA-15-TPA-4, oxygenates to form a purple material. These color changes are consistent with the homogeneous chemistry. Unfortunately, the instability of both complexes at −90 °C precludes reactivity studies and suggests that passivation of the silica surface may be needed. These initial results indicate, however, that sensitive metal-based homogeneous chemistry can be translated efficiently into mesoporous silicas at variable loadings and highlights heterogenization as a strategy for site-isolation of reactive, monomeric species.

We have synthesized and characterized a series of mesoporous silica materials (SBA-15-N_3-*x*) with controlled, *randomly* distributed azide loadings for quantitative click modification. Given the simplicity and predictability of these material preparations, we anticipate the materials will be widely adopted in applications needing to heterogenize homogeneous chemistry.

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Supporting Information Available: Sample preparation and characterization of SBA-15 materials. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) SBA-15-Fc-*x*: Sodium ascorbate (25 μmol/0.5 mL H_2O) was added to a mixture of SBA-15-N_3-*x* (100 mg), ethynyl-ferrocene (100 μmol), $CuSO_4$ (10 μmol), and TPA (10 μmol) in dimethylformamide (5 mL) and stirred for 24 h under N_2. The silica was filtered and extensively washed with a 0.1 M Et_2NCS_2Na/MeOH and sodium acetate/MeOH.
(13) By contrast, the azide signal of a traditionally grafted SBA-15-N_3 (0.1 mmol g^{-1}) effectively disappears (>95%) upon the reaction with 1-ethynl-pyrene.
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