Liquid-phase oxidation of alkylaromatics by a H-atom transfer mechanism with a new heterogeneous CoSBA-15 catalyst†‡

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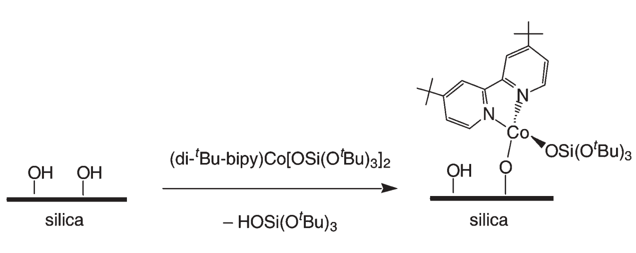
A new pseudo-tetrahedral Co(II) complex has been grafted onto the surface of SBA-15 and successfully utilized for the catalytic oxidization of alkylaromatic substrates with *tert*-butyl hydroperoxide (TBHP) *via* an H-atom transfer mechanism.

Oxygenated products are the required intermediates for many chemical feedstocks, agrochemicals, fragrances, pharmaceuticals, and polymers, but traditional methods for their preparation often require stoichiometric amounts of Cr(VI), Mn(VII) or Os(VIII) that generate large quantities of toxic metal waste.[1] A substantial amount of research has focussed on the homogeneous catalytic oxidation of alkylaromatic substrates with cobalt salts and dioxygen under corrosive conditions,[2] but a more environmentally benign and selective catalytic process is clearly desirable. Metal-supported heterogeneous catalysts that can operate in conjunction with an amenable oxidant in the liquid phase are advantageous in that they are recoverable and have minimal environmental impact.[3–7] As part of an investigation of supported transition metal siloxide complexes, *i.e.* $L_nM[OSi(O^tBu)_3]_m$, as heterogeneous oxidation catalysts, the new pseudo-tetrahedral Co(II) complex, (4,4′-di-^{t}Bu-bipy)Co$[OSi(O^tBu)_3]_2$ (**1**) was prepared, and its immobilization onto SBA-15 to yield surface-supported, site-isolated CoSBA-15 has been studied. The 4,4′-di-^{t}Bu-bipy ligand should facilitate the reversibility of the Co(II)–Co(III) redox couple.[4] Additionally, a low weight loading of **1** on SBA-15 should yield well-defined, surface-bound active sites. Previous investigations of alkylaromatic oxidations with alkylperoxides utilized catalysts with cobalt[3] and chromium[3,5] atoms incorporated throughout the silica framework. This initial investigation describes the synthesis of CoSBA-15 catalysts and their utility in the liquid phase oxidation of alkylaromatic substrates with *tert*-butyl hydroperoxide (TBHP). Since little is known about the mechanisms of such heterogeneous alkylaromatic oxidations, the oxidations described here have been studied in this context.

The Co(II) complex (**1**) was prepared by reaction of a toluene solution of $HOSi(O^tBu)_3$ (2 equiv.) with a toluene solution of $Co[N(SiMe_3)_2]_2$ and 4,4′-di-^{t}Bu-bipyridine. Analytically pure crystals were obtained in 41% yield from a mixture of pentane and toluene (1:1 v/v) at −78 °C. Complex **1** was grafted onto the SBA-15 surface *via* addition of a toluene solution of **1** (0.120 mmol) to a toluene suspension of SBA-15 (0.335 g) to yield CoSBA-15. Removal of toluene after 15 h yielded a material with 1.22 wt % cobalt as determined by inductively coupled atomic emission spectroscopy (ICPAES). Solution ^{1}H NMR spectroscopy was used to monitor the grafting reaction of **1** with the silica surface. The reaction of surface Si–OH groups with **1** resulted in elimination of 1.0 equiv of $(^tBuO)_3SiOH$ per grafted molecule of **1**. This result suggests that **1** binds to the silica surface *via* one Co–O–Si$_{surface}$ linkage (Scheme 1).

The surface area and pore volume ($520\ m^2\ g^{-1}$, $0.69\ cm^3\ g^{-1}$) of CoSBA-15 are reduced relative to that of the SBA-15 support; however, its ordered mesostructure was maintained as observed by TEM and retention of the low-angle (1 0 0) reflection in the powder X-ray diffraction pattern. The nitrogen adsorption–desorption data for CoSBA-15 corresponds to a type IV isotherm, characteristic of mesoporous SBA-15 materials, and the pore size distribution was determined to be narrow with an average pore radius of 33 Å. The FTIR spectrum for the surface-supported CoSBA-15 was difficult to obtain because of the silica background from SBA-15. However, several bands could be detected (at 2980, 1622 and 1554 cm^{-1}) that confirm the coordination of the di-^{t}Bu-bipyridine ligand to the surface bound Co(II) center. The DRUV-vis spectrum of CoSBA-15 displays a strong, broad absorption with two maxima at 267 and 295 nm that corresponds to $\pi \rightarrow \pi^*$ transitions for coordinated di-^{t}Bu-bipyridine. Additionally, three weak absorbances were observed at λ_{max} = 496, 584 and 657 nm which are characteristic of d–d transitions for pseudo-tetrahedral Co(II) species,[8,9] as also observed in the solution UV-vis spectrum of **1**. The EPR spectrum (taken at *ca.* 6 K) for CoSBA-15 gave a broad, axially symmetric signal with apparent *g* values of $g_\perp = 4.5$ and $g_\parallel = 2.3$. These *g*-values compare well with other high-spin Co(II) substituted materials (*e.g.*, CoAPO–5, CoA),[10] but differ from those for the polycrystalline powder spectrum of **1** ($g = 5.4$, 2.2 and 1.7). It is difficult, however, to distinguish between



Scheme 1

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† This paper is dedicated to the memory of Professor Ian P. Rothwell.

‡ Electronic supplementary information (ESI) available: experimental details, FTIR, UV-vis, EPR and EXAFS for **1** and CoSBA-15; selected kinetic plots for ethylbenzene oxidation. See http://dx.doi.org/10.1039/b506426k

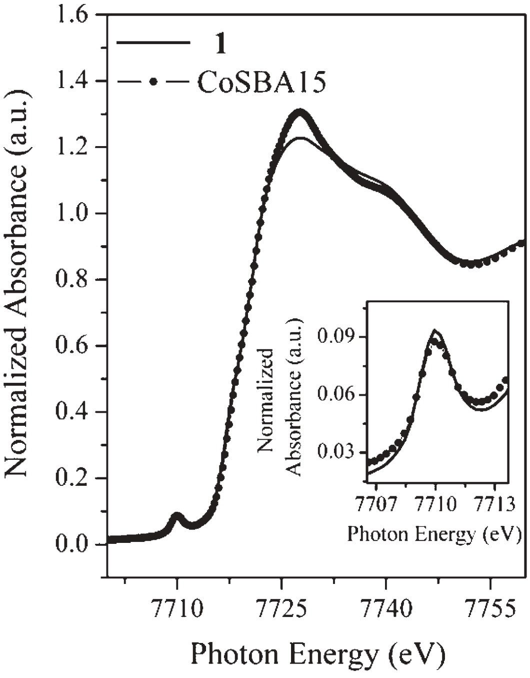

Fig. 1 Co K-edge XANES spectrum for **1** and CoSBA-15.

different coordination geometries for high-spin Co(II) by EPR spectroscopy.[11]

X-Ray absorption spectroscopy provides additional evidence for the presence of pseudo-tetrahedral Co(II) centers in the CoSBA-15. By XANES spectroscopy, Co K-edge energies of 7718.3(2) eV were calculated for both CoSBA-15 and **1** (Fig. 1), which is concordant with edge energies of other Co(II) centers in similar coordination environments.[8,12] Both samples also display a distinct pre-edge feature, assigned to a cobalt 1s → 3d transition, at 7709.9 eV. The intensity of this pre-edge feature in both samples (peak area = 9.6(2) × 10^{-2} eV for CoSBA-15 and 11.2(1) × 10^{-2} eV for **1**) is indicative of a noncentrosymmetric cobalt coordination geometry. EXAFS spectra of CoSBA-15 and **1** are very similar, which is consistent with the XANES analysis. First shell scattering in the FT $k^3\chi(k)$ patterns of both CoSBA-15 and **1** are identical in amplitude and position, suggesting a similar first coordination shell around cobalt. Based on the initial OH coverage of the support and a 1.22 wt % cobalt loading, the active sites occupy only *ca.* 14% of the available surface OH sites. Such a low weight loading should result in single-site, pseudo-tetrahedral Co(II) centers on the surface, and this is supported by the spectroscopic evidence.

Catalytic oxidation of ethylbenzene was carried out in an acetonitrile solution (2.0 mL) with *ca.* 10 mg of CoSBA-15, 2.4 × 10^{-3} mol of substrate and 1.1 × 10^{-2} mol of TBHP. The reactions were performed under a flow of air at 80 °C in a two-neck round bottom reactor fitted with a reflux condenser and septum, and aliquots were taken at regular intervals and analyzed by gas chromatography. After 24 h, a 38% conversion of ethylbenzene was achieved (Table 1), with the major product being acetophenone (83% selectivity). Ethylbenzene oxidation is generally more rapid over the first 60 min of reaction (rate of 582 TON h^{-1}), and slower over the remainder of the reaction, with deactivation likely occurring by catalyst poisoning by H_2O. It was confirmed that addition of 5 wt% H_2O to the reaction severely hampered the catalytic activity. To test for catalyst leaching, the reaction mixture was hot-filtered after 24 h and extracted with 0.10 M HCl. No cobalt was detected by ICPAES analysis of the aqueous phase, within the detection limit (<5 ppm).

The mechanism for ethylbenzene oxidation occurs *via* a radical process, as evidenced by inhibition of the reaction upon addition of a low concentration of radical trap (*i.e.*, 3 × 10^{-6} mol 2,6-di-*tert*-butyl-4-methylphenol). Two different initiation steps for benzyl radical formation can be envisioned: (1) an electron transfer from the arene to Co(III) to yield an arene radical cation, which yields a benzyl radical upon H^+ loss, or (2) H-atom transfer through abstraction of benzylic hydrogen atoms by radical species.[13] The rate of benzylic hydrogen abstraction, *via* H-atom transfer, should not correlate with the electron density in the aromatic system, in contrast to a cobalt-catalyzed electron transfer mechanism. There was no relationship observed between the relative rates of oxidation and electron density in the aromatic substrates by surveying various *para*-substituted ethylbenzenes (Table 1). If the mechanism occurs *via* H-atom transfer, the relative rates should, however, correlate with the benzylic C–H bond strengths of the substrates.[13] Examining primary, secondary and tertiary C–H bond reactivity by the oxidation of toluene,

Table 1 CoSBA-15-catalyzed oxidation of alkylaromatics with TBHP (80 °C, reaction time = 24 h)

Substrate	Major product (% selectivity)	Conversion (%)	TON[f]	k_H/k_D[g]
Ethylbenzene[a]	Acetophenone (82.5)	38.0	582	15.6
Ethylbenzene[b]	Acetophenone (96.6)	14.3	24.5	
Ethylbenzene[c]	Acetophenone (49.1)	25.8	438	
Ethylbenzene[d]	Acetophenone (48.8)	41.5	257	
Ethylbenzene[e]	Acetophenone (86.2)	12.8	…	
4-Ethylnitrobenzene[a]	4-Nitroacetophenone (100)	30.8	252	
4-Bromoethylbenzene[a]	4-Bromoacetophenone (100)	33.3	338	
1,4-Diethylbenzene[a]	4-Ethylacetophenone (76.5)	78.4	335	
4-Ethylmethoxybenzene[a]	4-Methoxyacetopheneone (100)	63.7	349	
Toluene[a]	Benzaldehyde (63.8)	7.97	103	9.2
Cumene[a]	2-Phenyl-2-propanol (75.9)	68.0	759	
sec-Phenethyl alcohol[a]	Acetophenone (100)	100	611	

[a] Substrate/catalyst (wt) ≈ 26; oxidant/substrate (mol) = 4.4; oxidant/cobalt (mol) ≈ 5200; CH_3CN solvent. [b] 25 °C. [c] With 2.8 × 10^{-6} mol 2,6-di-*tert*-butyl-4-methylphenol. [d] Homogeneous reaction with 3.6 × 10^{-6} mol of **1**. [e] No catalyst. [f] TON = mol products/mol Co, taken at 60 min. [g] Measured by initial rates of product formation (slope of the tangent to the plot of conc. *vs.* time at t = 0) in separate experiments under identical conditions.

$$\mathrm{Co(II)} + {}^{t}\mathrm{BuOOH} \longrightarrow \mathrm{Co(III)OH} + {}^{t}\mathrm{BuO}\bullet \qquad (1)$$

$$\mathrm{Co(III)OH} + {}^{t}\mathrm{BuOOH} \longrightarrow \mathrm{Co(II)} + {}^{t}\mathrm{BuOO}\bullet + \mathrm{H_2O} \qquad (2)$$

$$\mathrm{Ar\text{-}CH_2Me} + {}^{t}\mathrm{BuO}\bullet \longrightarrow \mathrm{Ar\text{-}(CH\bullet)Me} + {}^{t}\mathrm{BuOH} \qquad (3)$$

Scheme 2

ethylbenzene and cumene gave a statistically corrected, relative C–H bond reactivity of 1:8.5:22.1, respectively. This is in excellent agreement with the relative reactivity reported for benzylic C–H bond abstraction by various radical species for toluene, ethylbenzene and cumene (1:5–20:10–35) that occur *via* H-atom transfer.[13,14] Thus, the function of the CoSBA-15 catalyst is probably to generate free radicals from TBHP (Scheme 2, eqns. (1) and (2)). Based on the relative reactivity of benzylic C–H bonds, a ${}^{t}\mathrm{BuO}\cdot$ radical most likely abstracts a benzylic hydrogen from the substrate to yield a benzyl radical *via* H-atom transfer (Scheme 2, eqn. (3)). The large kinetic isotope effects for ethylbenzene (k_H/k_D = 15.6) and toluene (k_H/k_D = 9.2) oxidation, measured by initial rates of reaction, strongly suggest an important role for benzylic C–H cleavage in the rate determining step. These kinetic isotope effects cannot be taken as conclusive evidence for an H-atom transfer mechanism; however, they are in good agreement with those measured in homogeneous systems that occur *via* H-atom transfer (k_H/k_D = 10–20).[15,16] Under identical conditions, oxidation of *sec*-phenethyl alcohol occurred at a similar rate (611 TON h^{-1}) to that of ethylbenzene. Only small initial amounts of *sec*-phenethyl alcohol were observed in the oxidation of ethylbenzene; therefore, it appears that a majority of ethylbenzene oxidation occurs *via* a direct pathway from ethylbenzene to acetophenone.

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