Letter

Silicate xerogels containing cobalt as heterogeneous catalysts for the side-chain oxidation of alkyl aromatic compounds with *tert*-butyl hydroperoxide

Marina Rogovin, Ronny Neumann [*]

Casali Institute of Applied Chemistry, Graduate School of Applied Science, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel

Abstract

New transition metal substituted silicate xerogels, ML_n–SiO_2, have been prepared by the sol–gel technique and have been used as heterogeneous catalysts for the side-chain oxidation of alkyl arenes with anhydrous *t*-butylhydroperoxide. The cobalt substituted silicates were the most active and selective, for example, ethylbenzene was cleanly oxidized to acetophenone at 65% conversion and $> 99\%$ selectivity. The metal salt precursor used was a key factor in determining the activity of the metallosilicate. Diffuse reflectance UV-vis and IR measurements indicated that when using $Co(OAc)_2$ as metal precursor, the acetate group was detached from the metal and Co(II) was tetrahedral and site substituted in the silicate network. Addition of the oxidant led to stabilization of a Co(III) oxidation state and/or retention of the tetrahedral configuration. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic oxidation; Metallosilicates; Peroxide; Side-chain oxidation; Alkyl arenes

The discovery of the titanium-substituted silicalite of the MFI structure, TS-1, as a versatile oxidation catalyst [1] has led to a flurry of research into oxidative transformations of organic compounds catalyzed by 'redox molecular sieves' [2]. Side-chain oxidation of alkyl aromatic compounds catalyzed by such heterogeneous catalysts using cleaner peroxide oxidants is an especially attractive goal since classical synthetic laboratory procedures preferably use permanganate or acid dichromate as stoichiometric oxidants. Although titanium substituted silicalites usually are thought to catalyze ring hydroxylation of arenes, substitution of vanadium [3–10], tin [7–11] and chromium [12–14] into a variety of zeolite and aluminophosphate structures has led to favored oxidation at the side chain. Most notably, the chromium substituted aluminophosphate, CrAPO-5, catalyzes formation of ketones from alkyl arenes with TBHP as oxidant in moderate yields with selectivity generally $> 90\%$ [14]. Another much less studied approach to redox metal containing heterogeneous oxidation catalysis has been to use amorphous metallosilicate aerogels [15,16] and xerogels [17,18] prepared by the sol–gel synthesis. However, the use of amorphous metallosilicates has been limited to the substitution of
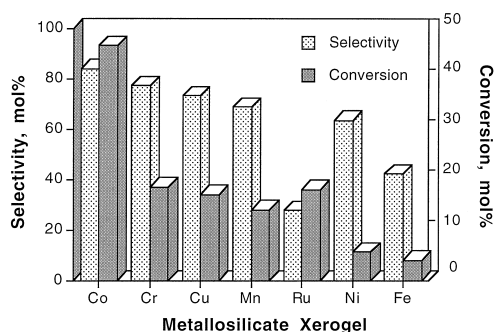
---

[*] Corresponding author

Fig. 1. Oxidation of ethylbenzene by TBHP catalyzed by various $MCl_n–SiO_2$ metallosilicate xerogels. Reaction conditions: 1 mmol ethylbenzene, 6 mmol 3 M TBHP in isooctane, 5 mg 5% $MCl_n–SiO_2$, 90°C, 24 h, ambient atmosphere. Selectivity is for acetophenone given as mol% acetophenone/mol% all products. The only other product was the mixed peroxide $PhCH(CH_3)OOC-(CH_3)_3$ except in the case of $CuCl_2–SiO_2$ where 12 mol% of an unidentified product was formed.

high-valent metals ($M = Ti^{IV}$, V^V, Mo^{VI}, and W^{VI}) and the oxidation of alkenes and alcohols. We have now utilized the sol–gel technique to prepare macroporous silicates containing a variety of low-valent transition metals. The cobalt containing silicate, $Co–SiO_2$, was especially active and selective for the oxidation of alkyl aromatic compounds with *t*-butyl hydroperoxide.

The first step in procedure for the preparation of metal containing silicates consisted of partial pre-hydrolysis of silicon tetraethoxide, TEOS. Thus, 40 mmol TEOS was reacted with 1.45 ml 0.15 M HCl (80 mmol water) in 15 ml ethanol for 1.5 h at 60°C. After this pre-hydrolysis, the mixture was cooled to room temperature and 2 mmol (5 mol%) of a metal salt, ML_n ($M =$ Co(II), Ru(III), Cr(III), Cu(II), Fe(III), Ni(II) and $L = Cl^-$, NO_3^- and CH_3COO^-), dissolved in 1.5 ml 0.15 M HCl was added over a period of 15 min without interruption of the stirring. The mixture was then left standing in an open beaker and the excess solvent was allowed to evaporate off. The resulting brittle xerogel was subsequently dried in air at 100°C for 12 h. Initially, the catalytic efficiencies of the metal containing silicates derived from the corresponding metal chlorides, $MCl_n–SiO_2$, was

tested in the oxidation of ethylbenzene with *t*-butyl hydroperoxide, TBHP (Fig. 1). Clearly, the cobalt containing silicate, $CoCl_2–SiO_2$, was much more active and a some what more selective catalyst for oxidation of ethylbenzene to acetophenone and therefore additional research was devoted to cobalt containing silicates.

The next stage of the research involved the optimization of the xerogel preparation and the choice of the preferred cobalt salt precursor. Three cobalt salts were tested, $CoCl_2$, $Co(NO_3)_2$ and $Co(OAc)_2$ at a 1.25-mol% (0.5 mmol salt/40 mmol TEOS) incorporation level and the xerogel preparation was varied by extending the evaporation time of the excess ethanol solvent from 12 to 48 h, yielding $CoL_2–SiO_2(f)$ and $CoL_2–SiO_2(s)$, respectively. BET measurements showed surface areas of 650–750 m^2/g and average pore diameters of ~ 1.5 nm. The catalytic activity of the cobalt silicates were tested showing that the $Co(OAc)_2–SiO_2(s)$ metallosilicate was significantly more selective compared to the other silicates with a 65% conversion at $> 99\%$ selectivity to acetophenone being observed (Fig. 2).

In order to understand the differences between the various cobalt silicates and correlate
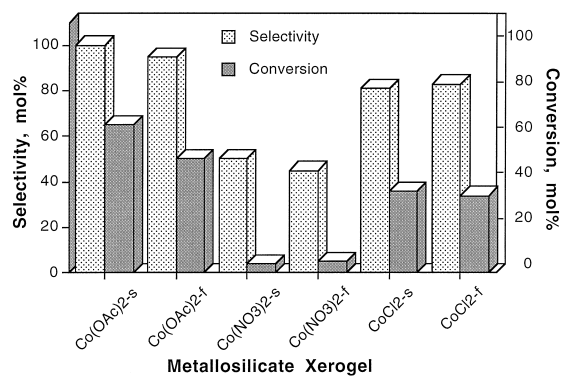

Fig. 2. Oxidation of ethylbenzene by TBHP catalyzed by various $CoL_n–SiO_2$ metallosilicate xerogels. Reaction conditions: 1 mmol ethylbenzene, 6 mmol 3 M TBHP in isooctane, 5 mg 1.25% $CoL_2–SiO_2$, 90°C, 24 h, in an ambient atmosphere. Selectivity is for acetophenone given as mol% acetophenone/mol% all products and the only other product was the mixed peroxide $PhCH(CH_3)OOC(CH_3)_3$.

catalytic activity with the different salts used, both the diffuse reflectance UV-vis and IR spectra were measured (Fig. 3). From the UV-vis spectrum one can learn that for the lilac $Co(NO_3)_2-SiO_2$, $\lambda_{max} = 544$ nm, the cobalt(II) is incorporated into the silicate with an octahedral coordination sphere, whereas for the blue $Co(OAc)_2-SiO_2$ and $CoCl_2-SiO_2$, $\lambda_{max} = 627$ and 676 nm, a tetrahedral coordination is observed for cobalt(II). The IR spectra besides showing the typical peaks for amorphous silicates via the sol–gel method at 1080, 950 and 790 cm^{-1}, additionally show that for $Co(NO_3)_2-SiO_2$ the nitrate ligand ($\lambda = 1383$ cm^{-1}) is retained in the silicate. For $CoCl_2-SiO_2$ the presence of the Cl^- ligand could not be verified due to the low energy of absorption of the Co–Cl bond. However, for $Co(OAc)_2-$

Table 1
Oxidation of alkyl arenes by TBHP catalyzed by various $Co(OAc)_2-SiO_2$

Substrate	Product	Yield (mol%)
Ethylbenzene	Acetophenone[a]	65
4-Nitroethylbenzene	4-Nitroacetophenone	60
Diphenylmethane	Benzophenone	58
Cumene	Acetophenone[a]	57
Toluene	Benzoic acid	27
4-Methoxytoluene	4-Methoxybenzoic acid	39
4-Nitrotoluene	4-Nitrobenzoic acid	17

Reaction conditions: 1 mmol ethylbenzene, 6 mmol 3 M TBHP in isooctane, 5 mg 1.25% $Co(OAc)_2-SiO_2$, 90°C, 24 h, in an ambient atmosphere. Yields are isolated.
[a] Yields from GLC analysis.

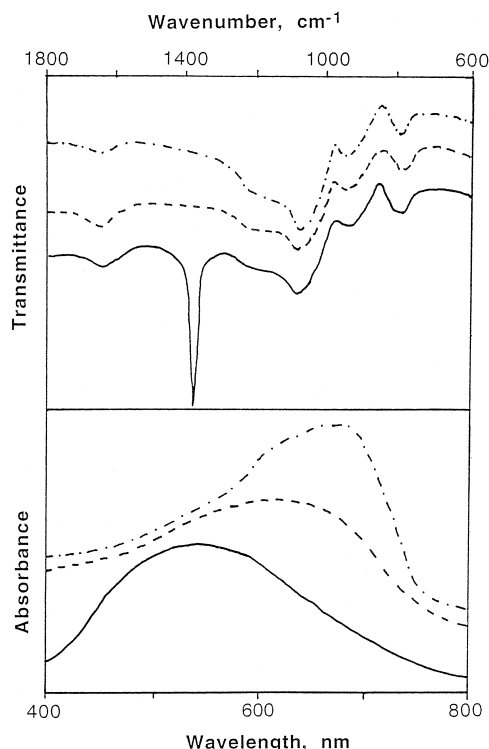SiO_2 the acetate ligand is clearly lost as the typical carbonyl absorption is not observed. The UV-vis and IR spectra that indicate that for $Co(NO_3)_2-SiO_2$ the cobalt(II) center is not incorporated into the tetrahedral silicate framework and the metal silicate obtained is essentially a mixture of $Co(NO_3)_2$ and SiO_2. This probably accounts for the poor catalytic performance of $Co(NO_3)_2-SiO_2$. For $Co(OAc)_2-SiO_2$ and $CoCl_2-SiO_2$ it would appear at first approximation from the UV-vis spectra that it is possible that the cobalt(II) center is incorporated into the tetrahedral silicate framework. In the case of $Co(OAc)2-SiO_2$, the absence of the original acetate ligand in the metallosilicate is especially supportive of such a conclusion. Further investigation revealed that upon addition of TBHP to $CoCl_2-SiO_2$, the metallosilicate turns pink, $\lambda_{max} = 540$ nm. Thus, here under reaction conditions the cobalt is clearly octahedral Co(II). On the other hand addition of TBHP to $Co(OAc)_2-SiO_2$ gives a dark green metallosilicate, $\lambda_{max} = 615$ nm. This observation indicates stabilization of a Co(III) oxidation state and/or retention of the tetrahedral configuration. Either or both possibilities may explain the higher activity and selectivity observed in ethylbenzene oxidation catalyzed by $Co(OAc)_2-SiO_2$.

The use of $Co(OAc)_2-SiO_2(s)$ as catalyst for the oxidation of alkyl aromatic compounds was finally extended to additional substrates

Fig. 3. Diffuse reflectance UV-vis (bottom) and IR (top) spectra of CoL_n-SiO_2 metallosilicate xerogels. ——— $Co(NO_3)_2-SiO_2$; --- $Co(OAc)_2-SiO_2$; ·--·- $CoCl_2-SiO_2$.

(Table 1). As one may observe good yields and very high selectivities were obtained in the oxidation of substrates with secondary benzylic carbons to ketones. Interestingly, the presence of a nitro group on the aromatic ring hand no significant effect on the yield. For cumene, oxidation was accompanied by scission of a methyl group leading to acetophenone as major product with < 5 mol% cumyl alcohol being formed. Methyl substituted arenes were somewhat less reactive, however, the carboxylic acids could easily be isolated from the reaction mixture after removing the catalyst by filtration and the isooctane and *t*-butyl alcohol by evaporation. Although possibility for catalyst recycle was not extensively studied, leaching of cobalt into the reaction mixture was tested [2]. Thus, a hot reaction mixture was filtered after reacting 10 mmol ethylbenzene, 20 ml of 3 M TBHP in isooctane, 50 mg 1.25% $CoL_2–SiO_2$ at 90°C for 24 h in an ambient atmosphere. The filtrate was cooled and treated with 20 ml of 0.15 M aqueous HCl for 1 h with vigorous stirring of the two phases. Atomic absorption analysis of the aqueous phase revealed that no cobalt was leached into solution. It is notable that use of either 30% H_2O_2 or 70% TBHP led to considerable leaching. The lack of leaching when using 3 M TBHP in isooctane is explained by the high hydrophobicity of the homogeneous phase; such a solvent is not conducive to dissolution of cobalt ions.

References

[1] B. Notari, Adv. Catal. 41 (1996) 253.
[2] I.W.C.E. Arends, R.A. Sheldon, M. Wallau, U. Schuchardt, Angew. Chem., Int. Ed. Engl. 36 (1997) 1143.
[3] P. Kumar, R. Kumar, B. Pandey, Synlett (1995) 289.
[4] K.R. Reddy, A.V. Ramaswamy, P. Ratnasamy, J. Catal. 143 (1993) 275.
[5] T. Sen, M. Chatterjee, S. Sivasanker, J. Chem. Soc., Chem. Commun. (1995) 207.
[6] A. Bhaumik, M.K. Dongare, R. Kumar, Microporous Mater. 5 (1995) 173.
[7] P. Ratnasamy, R. Kumar, Stud. Surf. Sci. Catal. 97 (1995) 501.
[8] R. Vetrivel, P.R. Hari Prasad Rao, A.V. Ramaswamy, Stud. Surf. Sci. Catal. 83 (1995) 109.
[9] T. Selvam, A.P. Singh, J. Chem. Soc., Chem. Commun. (1995) 883.
[10] K.R. Reddy, A.V. Ramaswamy, P. Ratnasamy, J. Chem. Soc., Chem. Commun. (1992) 1613.
[11] N.K. Mal, V. Ramaswamy, S. Gonapathy, A.V. Ramaswamy, Appl. Catal. 125 (1995) 233.
[12] J.D. Chen, R.A. Sheldon, J. Catal. 153 (1995) 1.
[13] J.D. Chen, H.E.B. Lempers, R.A. Sheldon, J. Chem. Soc., Faraday Trans. 92 (1996) 1807.
[14] J.D. Chen, M.J. Haanepen, J.H.C. van Hooff, R.A. Sheldon, Stud. Surf. Sci. Catal. 84 (1994) 973.
[15] R. Hutter, T. Mallat, D. Dutoit, A. Baiker, Top. Catal. 3 (1996) 421.
[16] R. Hutter, T. Mallat, A. Baiker, J. Catal. 153 (1995) 165–177.
[17] R. Neumann, M. Levin-Elad, Appl. Catal. A 122 (1995) 85.
[18] R. Neumann, M. Levin-Elad, J. Catal. 166 (1997) 206.