New metal-ion modifications of silicas; catalysed liquid-phase oxidations

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A new means is reported for producing transition-metal ion modified silicas with exceptional catalytic activity for phenolic type liquid-phase catalytic oxidations at temperatures as low as 25 °C.

Metal-ion modifications of silicas and related materials are important in industry[1,2] and geochemistry.[2–4] Transition-metal ion association with high-performance liquid chromatographic (HPLC) silica packings can impart catalytic properties and alter retention behaviour.[5–11] A new approach applicable to attaching various transition-metal ions onto silicas is reported here whereby several types of new catalytic silicas can be prepared, as well as others with desirable features (*e.g.* optical properties).

Methods for applying metal ions to oxide supports generally involve chemisorption, impregnation, or ion exchange. (See refs. 1,12–14 and references therein.) Chromatographic silica packings have been frequently modified for selective separations[5,11,15] using these techniques. Chemisorption[10] effective with monovalent cations such as Cs^+ and Li^+ is less successful for adsorbing multivalent cations such as Co^{2+} and Al^{3+}. Stability has been a concern with impregnation or precipitation methods[5,15,16] since metal salt ions may be removed by mobile phases or interactive solutes. Silica surface treatment at higher temperatures with volatile metal halides[17] is undesirable for heat sensitive HPLC silicas.

The two-stage attachment method described here accommodates characteristic silica properties and exploits solvent environments. It is highly effective for multivalent cation attachment to silica and similar types of materials. It involves controlled initial ion exchange with alkali-metal ion (*e.g.* potassium) to form an Si–O–M salt in aqueous solution, followed by exchange with the desired transition-metal salt in a favourable, non-aqueous organic solvent such as propan-2-ol. Column pressure drops for comparable HPLC columns did not change after packing treatment.

The procedure is based on the ion exchange capacity of silica surface silanol groups[18,19] and general silica stability in the pH range 2–9. Silica gel has an isoelectric point at about pH 2.2, with pK_a values of 7.1 ± 0.5.[18–21] Above the isoelectric pH, significant cation exchange is feasible and aqueous exchanges have been performed for a variety of cations[22] without concern for changes in physical properties. Cation exchange studies[23–25] show that non-hydrolysed ions such as potassium sorb rapidly, while ions which tend to hydrolyse [*e.g.* iron(III)] sorb slowly. Controlled silica treatment with KO_2CMe solution (sometimes with added dilute acetic acid to adjust pH) facilitates rapid K^+ ion exchange first, while providing for pH control, critical to silica stability. The second stage is ion replacement of surface alkali-metal ions with dissolved cations in an organic solvent. This circumvents H^+ exchange competition in aqueous solutions. Such H^+ exchange can result from transition-metal salt hydrolysis in aqueous solutions. Silica is stable in the organic solvent. Favourable kinetics allows control and shortens the exchange time reducing mechanical particle breakdown from stirring.[8] The resulting ion-modified silicas are stable to water washing and can be reproducibly synthesised with unique and useful catalytic properties.

A Co^{II}-modified silica preparation illustrates the new procedure.† SEM showed that the metal ion-modified silica particle sizes were the same as the original Spherisorb (10 μm spherical particles). Specific surface area measurements (single-point BET method[27]) indicated that Spherisorb silica surface area (190 $m^2\ g^{-1}$) was not changed by ion modification (within 5% of the original value). Since silica surface area is a sensitive parameter to modification,[19] the structural properties would appear to be retained in this two-stage procedure.

X-Ray powder diffraction patterns showed only a broad peak (at $2\theta = 20°$), typical of amorphous silica, without indication of a secondary crystalline phase from modification.

The Co^{II}-modified silica was packed in a 10 cm HPLC column (4.6 mm id) for testing as a liquid chromatographic reactor[7,9,11] with organic mobile phases. Significant catalytic activity for phenol type oxidations with liquid phase dissolved oxygen was found, providing an alternative to traditional cobalt Schiff-base and phthalocyanine type complexes as catalysts.[28–30] The concerted reaction with separation in the reactor resulted in high selectivity to *p*-benzoquinones for phenol and its *ortho*- and *meta*-methyl and chloro derivatives. Illustrative reactor chromatograms for *o*-chlorophenol with a UV detector (245 nm) at 45 °C are shown in Fig. 1. Altered chlorophenol retention and change in product formation with flow rate (residence time) [Fig. 1(*b*), (*c*)] demonstrate the catalytic activity of the immobilized cobalt ion which was maintained unchanged for months. Hydroquinone which is usually readily oxidized by Fe^{III}[6,7] was only slightly oxidized.

Our HPLC Fe^{III}-modified silica showed substantial catalytic activity for hydroquinone oxidation to quinone in the presence of dissolved oxygen, as did Cr^{III}-modified silica.

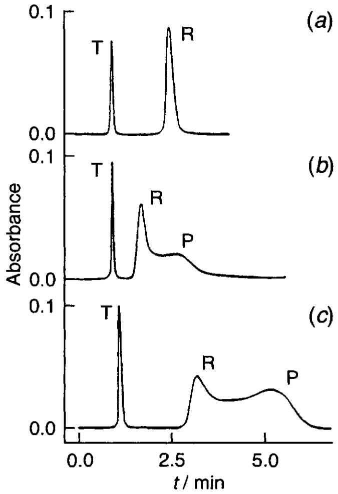

Fig. 1 Reactor chromatograms of 0.89 mmol dm^{-3} 2-chlorophenol at 45.0 °C in (*a*) a bare silica column at flow of 1.0 ml min^{-1}, (*b*) Co^{II}-modified silica column at flow rate of 1.0 ml min^{-1}, and (*c*) Co^{II}-modified silica column at flow rate of 0.5 ml min^{-1}. Mobile phase: 1% 2-methylpropan-2-ol in hexane; sample size: 20 μl. T: toluene inert. R: 2-chlorophenol reactant. P: 2-chlorobenzoquinone product from reactant oxidation.

Mn-modified silica (990 ppm) was prepared by a variation of the Co preparation procedure in which dissolved KO_2CMe (0.1 mol dm^{-3}) and $MnCl_2$ (0.01 mol dm^{-1}) concentrations were increased and treatment with each solvent was repeated. With propanol-2-ol, the silica developed a tan colour, indicative of higher Mn oxidation states. Oxide surfaces are known to promote heterogeneous Mn^{II} oxidation in the presence of dissolved oxygen.[31] This modified silica was more active for phenol type oxidations than cobalt for 2-chlorophenol oxidation to 2-chlorobenzoquinone at 45 °C. More than 95% conversion was achieved with less than 2.5 min column residence. Furthermore, even *para*-substituted materials such as *p*-chlorophenol could be oxidized (giving mainly *o*-chlorobenzoquinone and *p*-benzoquinone).

Conventional bulk type chromatographic silica packings (Absorbosil 100–200 mesh, Altech) with metal-ion modification procedures similar to those described here were active for phenol oxidations in batch operations (closed 22 ml glass vials with 0.1 g silica, 23 °C), but tended to be fouled because of insoluble yellow–brown oxidation product accumulation on the catalyst surface. The solution products were the same as in our chromatographic reactor, but required longer reaction times (up to several weeks) and further reaction to maleic acid was observed with our Mn-modified Spherisorb silica. Disappearance of benzoquinone over Mn and Co silicas indicated further oxidation. The availability of stable, modified catalytic silicas gives access to a new tool for controlled phenol type oxidations as well as uses with environmentally undesirable materials. Although Co- and Mn-type silicas were sufficiently catalytic to oxidize benzoquinone in batch processes over several weeks, other means such as biodegradation are available where desired.[32]

Success of the silica modification procedure above led to modification studies of porous Vycor type glass tubing (Corning #7930; 96% silicon dioxide, 3% B_2O_3, *ca.* 0.4% Al_2O_3). Controlled surface modification is of interest because of the potential for special optical properties through ion isolation on the silica surface.[33] Initial testing with $CoCl_2$ to give aqueous-stable blue tinted product demonstrated modification feasibility. $Eu(NO_3)_3$ (0.022 mol dm^{-3} in propan-2-ol) treatment of porous glass tubing (1.5 cm length) after aqueous KO_2CMe conversion gave a colourless product which exhibited Eu^{3+} fluorescence upon dye laser excitation (575–580 nm) illustrating the potential of this approach in optical material preparation. The width of spectral features with fluorescence line narrowing spectroscopy at 26.5 K was consistent with an amorphous silica environment. Small spectral changes over a narrow range of excitation wavelengths are indicative of fluorescence line narrowing and a tendency for cluster inhibition.[33]

Direct surface attachment of transition-metal ions described here makes it possible to produce silicas with catalytic properties comparable to complex metal-ion coordination compounds, useful for catalytic conversions or destruction of environmentally undesirable materials in packed beds as well as providing special optical properties. Additional liquid-phase catalytic reactions can be anticipated in the future using ion-modified silicas and similar materials.

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Footnote

† *Experimental procedure*: Two grams of Spherisorb S10W (Phase Separations) chromatographic silica were added to 75 ml of 40 mmol dm^{-3} aqueous KO_2CMe solution at pH 8.4 (adjusted with dilute acetic acid) in a glass beaker. After magnetic stirring at medium speed (room temp.) for 4 h followed by centrifuge separation, the silica was washed three times with water, followed by a rinse with propanol-2-ol. The product contains *ca.* 3000 ppm K$^+$ {< 100 ppm K$^+$ originally present [inductively coupled plasma (ICP) analyses]}. The product was then stirred in glass with 50 ml of 2.9 mmol dm^{-3} $CoCl_2$–propan-2-ol at ambient temperature for 3 h. The Co^{II}-modified product was separated by centrifugation, washed with propan-2-ol (8 ×), water twice, then propanol-2-ol three times to remove water. No Cl$^-$ was detected with $AgNO_3$ in the aqueous wash. The silica product, typically light purple, contained *ca.* 1000 ppm cobalt (ICP analysis). The metal ion exhibited solvatochromism,[26] changing from light blue in propan-2-ol to colourless in water, suggesting coordinative changes.

Using similar procedures Fe^{III} (2000 ppm), Cr^{III} (1000 ppm), and Cu^{II} (1000 ppm) ion-modified 10 μm HPLC silicas (Spherisorb S10W, Phase Separations) were prepared. Additional batches of the four examples above were reproducible.

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