

Environmentally friendly catalysis using supported reagents: catalytic epoxidation using a chemically modified silica gel¹

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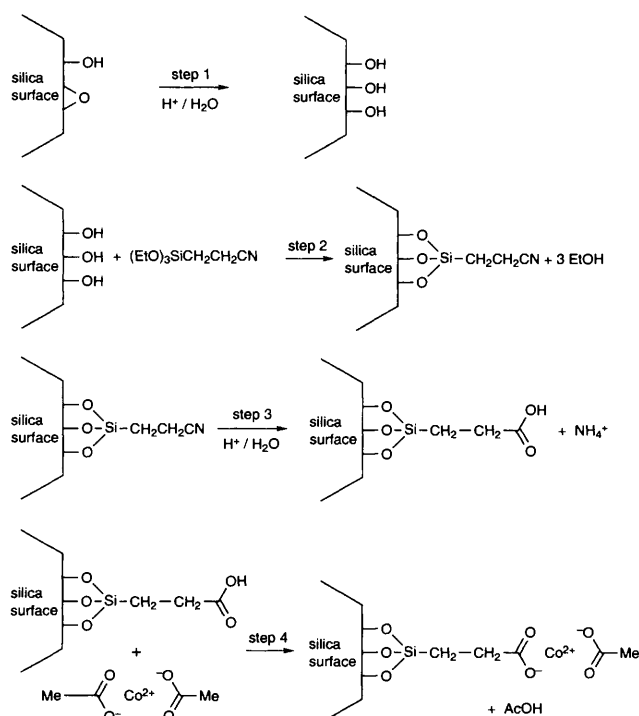
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A new heterogeneous catalyst based on a chemically modified mesoporous silica gel possessing immobilised cobalt ions is developed and successfully applied to the epoxidation of alkenes.

The epoxidation of alkenes is important both in industrial processes and in organic synthesis due to the utility of epoxides as synthetic intermediates.² Numerous epoxidation systems based on the use of peracids, hydrogen peroxide, alkyl peroxides or molecular oxygen and a catalyst which is commonly a ruthenium, molybdenum or titanium complex have been developed.³ One of the main disadvantages with most of these methods is poor selectivity to the epoxide with further reaction to the diol and even cleavage products often being observed. Apart from designing catalytic systems that maximise epoxide formation, the use of air/oxygen is preferred on economic and safety grounds and the use of heterogeneous catalysts is preferred on environmental grounds. The heterogenisation of inorganic reagents and catalysts useful in organic reactions is an important goal in clean technology.⁴ Recent examples of effective heterogeneous catalysts in epoxidations include titanium-silica materials (using hydroperoxides as the source of oxygen)^{5,6} and a cobalt-substituted Keggin-type heteropolytungstate (using molecular oxygen and a sacrificial aldehyde).⁷ Several supported reagents based on silica gels, clays and other high surface area supports have been used in

oxidations but are mostly stoichiometric oxidants or suffer from low activity⁴ although a clay-supported nickel complex has proven to be effective in high pressure catalytic epoxidations.⁸ Support materials that have been chemically modified to provide surface-bound metal complexes have been developed for some hydrocarbon oxidations although they require multiple components including acetic acid (reminiscent of commercial oxidation processes³), hydrogen peroxide and zinc.⁹ We now report a novel heterogeneous epoxidation catalyst based on a chemically modified mesoporous silica gel which can strongly bind cobalt ions and is active using molecular oxygen with a sacrificial aldehyde. The catalyst is robust, reusable and gives excellent selectivity to the epoxide.

The most active cobalt-catalyst was prepared as outlined in Scheme 1. Mesoporous silica gel (average pore diameter 60 Å) was activated by refluxing in concentrated hydrochloric acid and then washed and dried before undergoing chemical surface modification. Refluxing the activated silica gel with 2-cyanoethyltriethoxysilane in dry toluene under nitrogen gave the surface bound nitrile at a loading of *ca.* 0.3 mmol g⁻¹ (by elemental analysis) which on refluxing with 50% sulfuric acid gave the surface-bound carboxylic acid at approximately the



Scheme 1 Preparation of silica-supported cobalt acetate

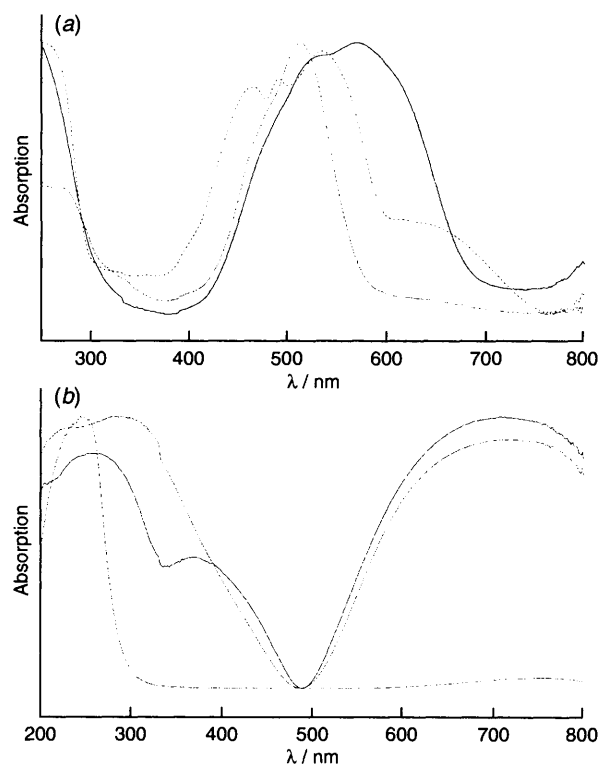


Fig. 1 UV-VS spectra of (a) solid cobalt acetate (---), silica-supported cobalt acetate (—) and aqueous cobalt acetate (···); (b) solid copper(II) acetate (—), silica-supported copper acetate (···) and aqueous copper acetate (---).

same loading. This material shows a characteristic band in the diffuse reflectance FTIR ('DRIFTS') spectrum at *ca.* 1720 cm^{-1} due to the acid carbonyl stretch and a pronounced exotherm in the differential scanning calorimetry (DSC) at *ca.* 280 °C due to decarboxylation. This material was then treated with aqueous $\text{Co}(\text{OAc})_2$ at 0.3 mmol g^{-1} and the water slowly removed to give the supported cobalt catalyst which was finally dried at 90 °C under vacuum. Acetic acid is released in the final cobalt-loading stage of the process and we believe that the active centres in the catalyst are made up of cobalt(II) ions partly complexed by surface carboxylate groups. This is supported by the DRIFTS spectrum in which the free acid carbonyl stretch band is absent and a strong broad band is present at *ca.* 1600 cm^{-1} presumably due to both surface-bound and 'free' acetate carbonyl groups. There is no exotherm in the DSC at or near 280 °C and the thermogravimetric analysis (TGA) reveals a broad weight loss ranging from *ca.* 300 to >400 °C due to loss of the chemisorbed groups. We have also recorded the diffuse reflectance UV-VIS spectra for this and related supported materials (Fig. 1). The diffuse reflectance UV-VIS spectra of cobalt(II) acetate and the supported reagent are shown in Fig. 1(a). The appearance of the spectra are very similar although the bands in the supported reagent spectrum are shifted by *ca.* 50 nm. It is also worth noting at this stage that the analogous Cu^{II} material does not show the band (at *ca.* 380 nm) characteristic of the dimeric copper(II) acetate structure. We believe that this is evidence for isolated metal ion sites in the supported reagent.

The strong metal ion-surface binding is nicely illustrated by simple washing studies which show that dichloromethane, acetone, and acetonitrile [all of which dissolve free cobalt(II) acetate to some extent] do not remove any cobalt from the supported reagent. Interestingly even after stirring vigorously

Table 1 Catalytic epoxidation of organic substrates using supported cobalt^a

Alkene	Reaction time/h	Epoxide yield (GC, %) ^b
Cyclohexene	5	85
Oct-1-ene	5	45
Octa-1,7-diene	24	48 ^c
2,4,4-trimethylpent-2-ene	5	95
Hex-1-ene	24	30
Styrene	3	32 ^d

^a All reactions were carried out at 19 °C in CH_2Cl_2 (120 cm^3) with isobutyraldehyde (60 mmol), substrate (20 mmol) and catalyst (0.6 g). ^b Along with unreacted starting material and isobutyric acid (see text); no other alkene-derived products were observed other than those noted here. The isolated yields are 5–10% less than the GC yields. In the absence of catalyst, there is a low level of oxidation (<0.5% h^{-1}). ^c Along with 7% of the diepoxide. ^d Along with 5% benzaldehyde and 21% of a polymeric product.

with water for 2 h only 50% of the cobalt was washed off the catalyst.

Initial screening of the catalytic activity of the supported cobalt was carried out by varying the solvent and the aldehyde in the epoxidation of cyclohexene at 19 °C with an oxygen atmosphere. The best conditions proved to be dichloromethane (120 cm^3) and isobutyraldehyde (60 mmol), with 20 mmol of cyclohexene and 0.6 g of the catalyst. This system gave >85% conversion by GC to the cyclohexene oxide only in <5 h corresponding to a turnover number of 94 moles of cyclohexene oxidised per equivalent of cobalt(II). Work-up of the reaction mixture gave an isolated yield of cyclohexene oxide of 15 mmol (75%) along with unreacted cyclohexene, isobutyric acid (*ca.* 40 mmol) and isobutyraldehyde (including aldehyde oligomers). Other aldehydes were less effective although propionaldehyde was also reasonably effective. A number of other substrates have been reacted under the same conditions and of those tested only styrene gave more than one oxidation product (Table 1). Product yields could be increased by longer reaction periods or by adding more sacrificial aldehyde to the reaction system after the rate of epoxidation had slowed. There was no cobalt detected in any of the solution phases during reaction.

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Footnote

† 'Envirocats' is a tradename belonging to Contract Chemicals, Knowsley Industrial Park, Prescot, Merseyside.

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