Liquid phase oxidations using novel surface functionalised silica supported metal catalysts

Janet Chisem (neé Bovey), Ian C. Chisem, John S. Rafelt, Duncan J. Macquarrie and James H. Clark*

Department of Chemistry, University of York, Heslington, York, UK YO1 5DD

Metal species supported on a surface functionalised silica gel are active heterogeneous catalysts for the liquid phase, room temperature epoxidation of cyclohexene and the aerobic oxidation of ethylbenzene.

The oxidation of organic substrates leads to the production of many functionalised molecules which are of great commercial and synthetic importance. The oxidation of alkyl aromatic substrates is one such example, enabling the production of key groups such as ketones, aldehydes and esters. Epoxides are useful synthetic intermediates because they readily undergo ring-opening reactions to form bifunctional molecules. Alkene oxidation is a common method of epoxide synthesis. Use of a so-called sacrificial aldehyde as an oxygen transfer agent is a convenient and effective way of facilitating the epoxidation reaction.[1–5] However, in general, direct oxidation using organic oxygen donors such as peroxyacids and peroxides is the most important method of oxidation in industry.[6] The formation of by-products and decomposition of the desired product are often problems in these systems. The heterogenisation of reagents and catalysts and the use of molecular oxygen or air in place of homogenous oxidants is clearly desirable in economic and environmental terms.[6–7] However, air and oxygen are weak, non-selective oxidation reagents and suitable heterogeneous catalysts therefore need to be developed that work effectively in conjunction with these oxidants. Heterogeneous catalysts which have been used for liquid phase oxidations are often based on active species (notably transition metals, metal ions or metal complexes) adsorbed on supports (such as carbon, aluminas, silicas, zeolites, clays and ion exchange resins).[8] Chemically modified support materials offer great scope for the development of new catalysts.[5,9–11] Here we report on a new range of active oxidation catalysts based on chemically modified mesoporous silica with metal ions immobilised on a hydrophobic chain which, unusually, are capable of facilitating both alkene epoxidation and alkylaromatic oxidation reactions.

The preparation of the catalysts is illustrated in Scheme 1 and was carried out at room temperature. Silica with an average pore diameter of 100 Å (Kieselgel 100) was suspended in ethanol. Trimethyl-3-aminopropylsilane was added such that a ratio of 1.0 mmol silane (g silica)$^{-1}$ was obtained and the mixture was stirred for 24 h. The solid was then separated by filtration and washed thoroughly with diethyl ether to yield aminopropylsilica (AMPS). The AMPS was suspended in excess ethanol and terephthaldialdehyde added at a ratio of 1 mmol (g silica)$^{-1}$. The mixture was stirred for 2 h before being filtered and washed with diethyl ether. The resulting solid was then suspended in ethanol and *p*-aminobenzoic acid was added at a ratio of 1 mmol (g silica)$^{-1}$. The mixture was stirred for *ca.* 24 h. The solid was again separated by filtration and washed with diethyl ether. The product was resuspended in ethanol and the metal acetate (Cr, Mn, Co, Ni or Cu) was added at a ratio of 1.0 mmol metal (g silica)$^{-1}$ and the mixture stirred for 3 h. The excess solvent was removed using a rotary evaporator and the catalyst thoroughly washed with ethanol until the washings were colourless. Finally, the catalyst was dried under vacuum at *ca.* 95 °C for 16 h.

The epoxidation of cyclohexene to cyclohexene oxide was carried out as follows. A reaction flask under an O_2 atmosphere was charged with 17.5 mmol of cyclohexene, 60 mmol of isobutyraldehyde and 0.6 g of catalyst. Dichloromethane was used as the solvent and *tert*-butylbenzene as an internal standard. The reaction was run for 6 h at room temperature with constant stirring using a magnetic stirrer. The oxidation of ethylbenzene to acetophenone was carried out in a baffled flask with overhead stirring (1500 rpm). Air was used as the oxidant at a rate of 800 ml min^{-1}. 1.5 g of the Cr catalyst was added to 500 ml of neat substrate and the reactions carried out at reflux (130 °C) for 24 h. Water produced during the reaction was collected in twin Dean Stark traps. Both reactions were analysed by gas chromatography (GC) and the amount of product (mmol) thus determined.

The loading of metal on the catalysts was determined by atomic absorption spectroscopy (AAS). The solids were first dissolved in concentrated sulfuric acid and the resulting solution diluted with deionised water. Loadings were found to be in the
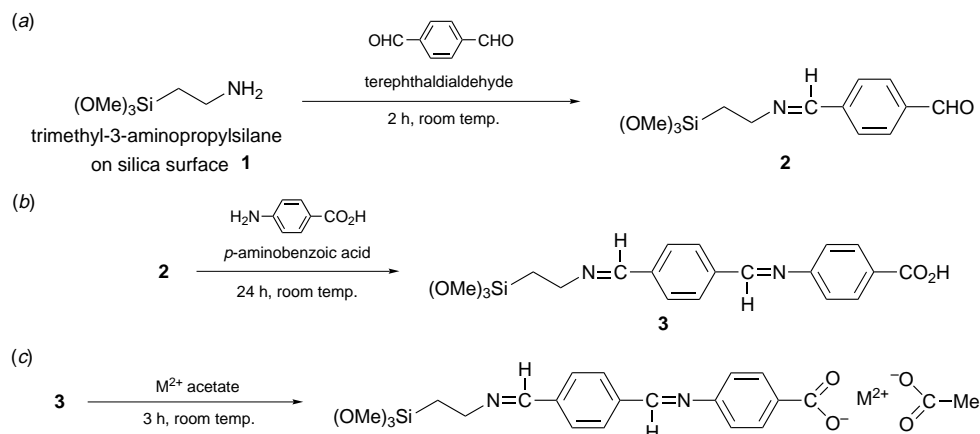
Scheme 1 Diagrammatic representation of the functionalisation of the silica support (*a,b*) and the addition of the active metal species (*c*)
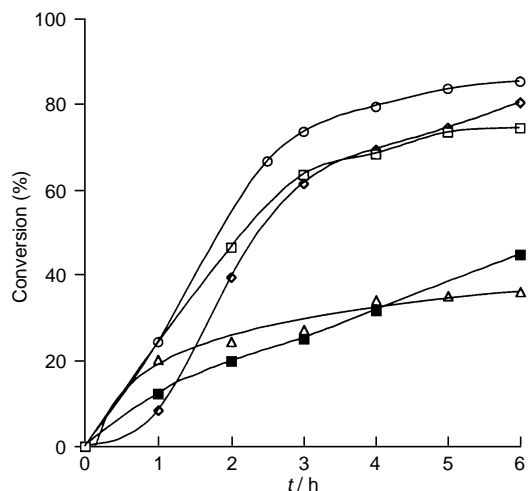
Fig. 1 Percentage conversion of cyclohexene to cyclohexene oxide by various supported metals: Cr ($\square$), Mn ($\triangle$), Co ($\blacksquare$), Ni ($\bigcirc$) and Cu ($\Diamond$)
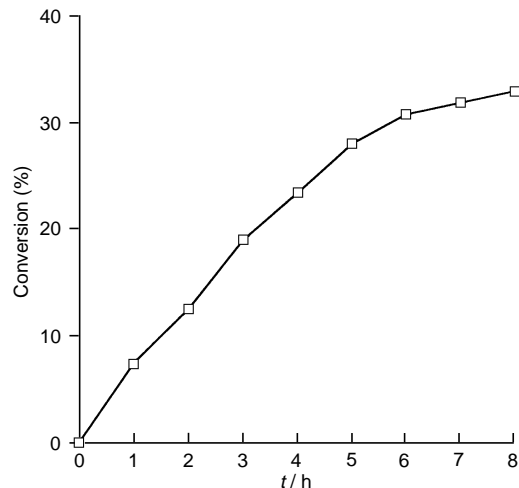
Fig. 2 Percentage conversion of ethylbenzene to acetophenone by supported Cr catalyst

range 0.36–0.46 mmol g^{-1}, depending on the metal, which is typical of supported metal catalysts.[8] The loadings of metal are lower than the initial aminopropyl groups which may be due to incomplete metal binding during synthesis. Furthermore, the stoichiometry of the binding of the metal complexes has not yet been confirmed. Fourier-transform infrared spectroscopy revealed a band at 1684 cm^{-1} which is indicative of the imine group, as shown in the proposed structure of the catalyst (see Scheme 1). Bands at 1584 and 1456 cm^{-1} were attributed to the antisymmetric and symmetric stretching modes of the carboxylate group respectively. Preliminary leaching studies were carried out by performing AAS on the Ni catalyst following reaction. The loading of Ni was 0.36 mmol g^{-1} for both the spent and fresh catalysts. This suggests that metal leaching is not occurring, which in turn is indicative of chemical bonding between the metal and the support of the catalyst.

In the cyclohexene epoxidations, all the catalysts showed excellent selectivity for the epoxide with only trace amounts (in total $< 1.0\%$) of by-products being detected by GC. Under homogeneous conditions, Murahashi *et al.*[1] obtained cyclohexenone as a by-product in the epoxidation of cyclohexene, in accordance with a peracid mechanism. Whilst we see only trace quantities of by-products in the heterogeneous reaction, we cannot rule out the possibility of cyclohexenone production. Fig. 1 shows the conversions (epoxide yields) achieved by each catalyst plotted *vs.* time. It should be noted that these activities have not been corrected for metal loadings but the range of loadings is narrow. It can be seen that the activity of the catalyst is dependent upon the identity of the supported cation, with high conversions being achieved for the Cr, Ni and Cu catalysts. The most active catalyst is the supported Ni variant which gives a conversion of 85% epoxide yield after 6 h. 80 and 74% epoxide yields are obtained with the Cu and Cr catalysts respectively. The fastest rates achieved are by the Ni and Cu catalysts and are 28 and 26.5% h^{-1} respectively, over the first 3 h. These rates correspond to a frequency of 12 and 11 turnovers h^{-1} per catalytic site (at an average loading of 0.41 mmol g^{-1}), respectively. Fig. 2 shows the conversion of ethylbenzene to acetophenone by the Cr catalyst *vs.* time. It can be seen that the catalyst showed excellent activity for the reaction, reaching 33% conversion after 8 h. A rate of *ca.* 5.5% h^{-1} was reached

over 5 h which is equivalent to > 370 turnovers h^{-1} per catalytic site (assuming a loading of 0.41 mmol g^{-1}). After 5 h the rate decreased significantly which may be attributed to the inefficient removal of water from the system which leads to poisoning of the catalyst. The catalyst was highly selective to the ketone and no induction period was observed.

These new catalysts show remarkable and unusual versatility as they are capable of selectively catalysing reactions which proceed *via* very different mechanisms.[6] Further work is being directed at the use of other alkylaromatic and alkene substrates as well as Baeyer–Villiger systems. Catalyst re-use studies and the activities of other metal variants including Ti, V and Fe are also being investigated.

Footnote and References

* E-mail: jhc1@york.ac.uk

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