A novel immobilised cobalt(III) oxidation catalyst†

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Received (in Liverpool, UK) 19th January 2000, Accepted 25th February 2000

A complex form of cobalt(III) has been successfully immobilised on a chemically modified silica and proven to be an active catalyst for the selective oxidation of alkylaromatics using air as the source of oxygen and in the absence of solvent.

Cobalt salts are widely used as catalysts in the liquid phase oxidation of alkylaromatics.[1] Reactions are normally carried out in acetic acid as solvent and in the presence of a promoter such as a bromide. It has been reported that under such reaction conditions, the aerial oxidation of Co(II) to Co(III) is a slow process[2] although this can be accelerated by the addition of bases such as pyridine which stabilises the higher oxidation state of the metal.[3] The heterogenisation of catalysts and their use in the oxidation of neat substrates are subjects of considerable interest especially in these environmentally conscious days when solvent losses and catalyst losses on separation can lead to unacceptable levels of waste.[4] Several heterogeneous metal catalysts have been designed for aerial oxidation reactions[5] but limited activities and questionable stabilities[6] have delayed their commercial exploitation. It seemed to us that if we could design a heterogeneous system that favours and stabilises Co(III), this should enhance rates of reaction where the Co(II) to Co(III) step was rate limiting and should increase catalyst stability owing to the relative substitutional inertness of Co(III). Here, we report our preliminary results from designing such a catalyst that can indeed be successfully used to catalyse the aerial oxidation of alkylaromatics in the absence of solvents.

The novel catalyst is based on a chemically modified porous silica.[7,8] Cyanoethyl-silica was prepared from the sol–gel reaction of tetraethylorthosilicate (196 mmol) and cyanoethyltriethoxysilane (98 mmol) in aqueous ethanol in the presence of *N*-dodecylamine as the templating agent. The resulting precipitate was washed with boiling ethanol to remove the template and then treated with hot aqueous H_2SO_4 so as to hydrolyse the CN group to CO_2H.[9] The resulting silica-$(CH_2)_2CO_2H$ material was washed with water and ethanol and then dried at 110 °C before use as a support for the Co(III) complex. Pyridine (40 mmol) was added dropwise to a mixture of the silica material (5g), $Co(NO_3)_2{\cdot}6H_2O$ (20 mmol), and sodium acetate (40 mmol) in water (100 ml). Complexation of the cobalt to the support only occurs on addition of the pyridine as witnessed by the purple colour of the solid particles. After adding more water (50 ml), the mixture was heated to boiling and dilute hydrogen peroxide (80 mmol) was slowly added over 8 h. This resulted in the apparent oxidation of the immobilised cobalt with a change in colour of the solid particles from purple to olive green. It is necessary to treat the supported metal complex with peroxide so as to form the immobilised Co(III). This solid was separated by filtration, thoroughly washed with water and acetone and then dried at 110 °C.

While the precise structure of the surface-bound cobalt complex is as yet unknown we have carried out a number of analytical studies to gain information on the cobalt loading and distribution, the material structure and the surface species (Table 1). Atomic absorption analysis of the digested material gives a cobalt loading of 0.68 mmol g^{-1}. Optical and scanning electron microscopic studies on the material reveal a homogeneous mass with elemental analysis (EDAX) carried out at randomly selected spots showing a consistent Co : Si ratio of *ca.* 1 : 7. This suggests an evenly distributed cobalt complex rather than a simple mixture of a cobalt complex with the silica. The BET isotherms for the supported Co(III) complex and the intermediate silica-$(CH_2)_2CO_2H$ material have almost identical appearances and suggest a mixture of micropores and mesopores. The BJH pore size distributions of these materials show *ca.* 65 and 80%, respectively, of the pore volumes are due to pores with diameters of < 6 nm. The surface area is also reduced on going from the intermediate supported carboxylic acid to the final supported metal complex (from 1041 to 528 m^2 g^{-1}) although it is still very high compared to more traditional supported reagents.[10,11] These results are consistent with a reasonably homogeneous build-up in the surface species as the metal complex is formed. The powder X-ray diffraction pattern of the supported Co(III) material shows a weak peak at $< 2°$ with the strongest peak at 2θ *ca.* 22.5° consistent with a lack of long range order as expected for materials of this type.[8,10] Diffuse reflectance FTIR (DRIFTS) of the final material reveals bands characteristic of surface bound CO_2^-, pyridine and acetate. The difference in the wavenumbers of the symmetric and asymmetric stretching vibrations of the acetato ligand carboxyl group (125 cm^{-1}) is consistent with these ligands bonding in a bridging fashion. The diffuse reflectance UV–VIS spectrum of the final material shows an ill-defined absorption maximum at *ca.* 580 nm in contrast to the strong band at 545 nm for the material before treatment with hydrogen peroxide. This is consistent with a change from Co(II) to Co(III) on peroxide treatment. Furthermore, by carrying out a similar complex preparation but in the absence of the support material, the final cobalt complex, believed to contain the cation $[Co_3(\mu_3\text{-}O)(\mu\text{-}O_2CR)_6(py)_3]^+$ [12] (ClO_4^- as counter anion) gives an olive green complex with a very similar UV–VIS spectrum. The measured C : N ratio of 12 : 1 in the final material is consistent with the presence of a similar complex rather than a simple species containing two pyridines and two carboxylato ligands per cobalt atom (for which the C : N ratio would be 7 : 1)

Table 1 Physical data for the supported Co(III) complex

	HMS–Co(III) complex	HMS–CO_2H
BET surface area/m^2 g^{-1}	528	1041
Pore volume/cm^3 g^{-1}	0.315	0.688
Co : Si ratio (EDAX)	1 : 7	—
Co loading (AAS)/mmol g^{-1}	0.68	0
λ_{max}(UV–VIS)/nm	580	—

The supported cobalt(III) reagent was tested as a catalyst in the aerial oxidation of neat ethylbenzene, chlorotoluene and toluene as representative alkylbenzenes (Table 2). Reactions were carried out at atmospheric pressure with 400 ml of substrate and 0.8 g of the catalyst in a baffled glass reactor with a overhead stirrer operating at 700 rpm, an air feed at 400 ml min^{-1}, chilled water condensers and twin Dean–Stark separators to remove the water produced during the reactions. Reactions could be monitored both by the amount of water

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† UK Patent application, 1999.

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DOI: 10.1039/b000535p

Table 2 Catalytic oxidations of alkylaromatics using the supported Co(III) complex (0.8 g) in neat substrate (400 ml) at atmospheric pressure for 22 h

Substrate	T/°C	Product (isolated yield%)[a]
PhEt	130	PhCOMe (70)
4-ClC_6H_4Me	130	4-$ClC_6H_4CO_2H$ (25)
PhMe[b]	100	$PhCO_2H$ (6)

[a] Purified (> 99%) product. [b] 1% added PhCHO which remains constant.

produced and by GC/GC–MS. Ethylbenzene was converted to acetophenone at a rate of *ca*. 4% h^{-1} at 130 °C, and with no induction period (in contrast to other reports of heterogeneously catalysed aerial oxidations[13]). The absence of an induction period may be due to the metal existing in its higher oxidation state at the beginning of the reaction. After 22 h a remarkable 76% of the ethylbenzene had been oxidised with selectivity to acetophenone of 94%, the remainder being benzoic acid. An isolated yield of 70% acetophenone can be obtained. We believe that this is the highest reported yield of acetophenone obtained from a heterogeneous oxidation of ethylbenzene.[5,14] Previous reports have shown that conversions of > 60% are very difficult to achieve with neat substrate and this has been linked to the rate limiting adsorption of the relatively non-polar ethylbenzene from an increasingly acetophenone-rich mixture.[5,13] Here the rate of oxidation is almost linear up to *ca*. 70% conversion and this may be a result of the relatively organophilic surface of the new catalyst facilitating the adsorption–desorption processes. Under the same conditions a 25% isolated yield of pure 4-chlorobenzoic acid was obtained from the oxidation of neat 4-chlorotoluene after 22 h simply by filtering the solid product from the cooled final reaction mixture and washing it with light petroleum. No other products were observed. This oxidation occurred at over twice the rate of comparable reactions reported elsewhere.[5,13] We were also able to achieve a small but significant rate of oxidation for toluene itself. At 100 °C and in the presence of a small amount of benzaldehyde (1% by volume) as a promoter,[5] we obtained an isolated yield of recrystallised benzoic acid of 6% after 22 h reaction (the 1% benzaldehyde remains almost constant throughout the reaction). This is again a marked improvement in reaction rate compared to similar systems.[5] In none of these reactions was leached cobalt detectable by atomic absorption spectroscopy in the organic liquors and the amount of cobalt measured in the catalyst (after digestion) was always unchanged. However, our first attempts to reuse the catalysts failed. Closer analysis of the used catalysts showed that there had been a complete loss of pyridine during reaction although the cobalt was still present. By adding a small amount of pyridine (0.48 g) to any of the substrate–used catalyst reaction systems, or by treatment of recovered catalyst with pyridine, the rate of reaction returned to close to the original value and very similar levels of substrate oxidation and conversions to product were achieved. The facile loss of pyridine from the catalyst at elevated temperatures was confirmed from thermal analysis on the material under nitrogen which shows loss of pyridine at *ca*. 150–200 °C with decomposition of the remaining catalyst structure starting at > 300 °C. We are now investigating methods for stabilising the catalyst notably the replacement of pyridine by a less volatile nitrogen base.

We gratefully acknowledge the support of the Commonwealth Institute for a Fellowship to B. K. D. and the RAEng.-EPSRC for a Clean Technology Fellowship to J. H. C., as well as the support and advice of the York Green Chemistry group.

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Communication b000535p