

Catalytic oxidation of alkyl aromatics using a novel silica supported Schiff base complex

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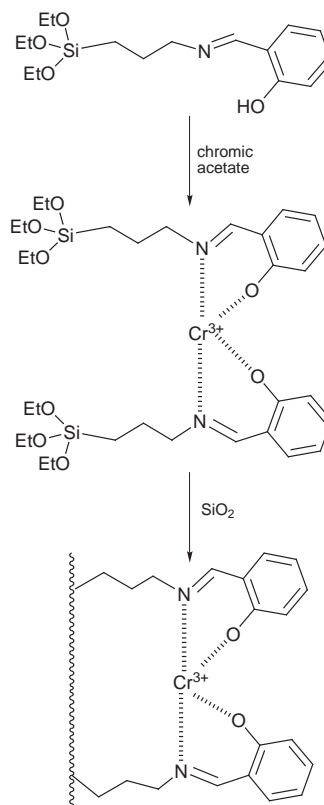
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A new heterogeneous catalyst based on a chemically modified mesoporous silica gel and possessing immobilised chromium ions has been prepared and successfully applied to the aerial oxidation of alkyl aromatics at atmospheric pressure and in the absence of solvent.

The oxidation of organic substrates provides routes to a wide range of functionalised molecules. Traditional methods involve the use of large quantities of poisonous high oxidation state Cr, Mn and Os reagents.¹ Lower oxidation state metals such as Co^{II}, Mn^{II} and Cu^{II} in AcOH may be used² with O₂ as the consumable oxidant. However, the conditions are often harsh, the reagent mixture is corrosive (bromide is used as a promoter), and the chemistry is rarely selective. Environmentally acceptable catalytic oxidations that operate under moderate conditions in the liquid phase with high selectivity are clearly desirable. A range of supported reagents has been used in the liquid phase oxidation of organic substrates. Advantages of supported reagents include ease of handling, use and recovery, low toxicity and the avoidance of solvents. However, in oxidations, supported reagents have generally acted as *stoichiometric* reagents, making their large scale use difficult and expensive. We have proven the possibility of developing genuinely *catalytic* supported reagents which are active in some oxidations.^{3,4} More recently, catalysts based on chemically modified silicas, which have higher catalytic site densities, have been prepared.^{5,6} We now report a novel heterogeneous catalyst for the liquid phase partial oxidation of alkyl aromatic substrates based on a chemically modified mesoporous silica gel which possesses significantly enhanced activity. The material strongly binds chromium ions and is robust, reusable and active in the oxidation of ethylbenzene and methyl aromatics.

The preparation of the chromium catalyst (CHRISS) is shown in Scheme 1. Salicylaldehyde (1 equiv.) was added to excess absolute EtOH, to which 3-aminopropyl(trimethoxy)silane (1 equiv.) was added. The solution instantly became yellow due to imine formation. Chromium(III) acetate (0.5 equiv.) was then added to the solution, and the mixture stirred for a further 30 min to allow the new ligands to complex the chromium. The silica (Kieselgel 100) was then added and the mixture stirred overnight. The final product was washed with water, EtOH and finally Et₂O until the washings were colourless. Further drying of the solid product was carried out on a rotary evaporator at 70 °C for 2 h. The loading achieved is *ca.* 0.10 mmol g⁻¹ [determined by atomic absorption spectroscopy (AAS)]. The catalyst has an average pore size of 100 Å and a particle size of 30–140 μm. The infrared spectrum of the free ligand (*i.e.* prior to complexation with the metal) shows a band at 1642 cm⁻¹ attributed to the C=N stretching vibration of the imine. This is reduced to 1593 cm⁻¹ upon complexation of Cr³⁺. Apart from bands in the 250–450 nm region, the diffuse reflectance UV spectrum of the catalyst shows a band at *ca.* 600 nm corresponding to d-d transition for the metal complex. The band is shifted to higher wavelength by about 30 nm from the corresponding band in pure Cr(OAc)₃ or Cr(OAc)₃ physisorbed on silica, consistent with a change in ligand environment.

The catalytic oxidation of ethylbenzene (used as a model substrate) was carried out in neat substrate using 1.5 g catalyst and air as the consumable source of oxygen. The reaction was performed in a baffled glass reactor with overhead stirring and fitted with a Dean–Stark trap to facilitate the removal of water from the reactor. After a short induction period the conversion rate in the first 5 h of operation was *ca.* 5% h⁻¹, corresponding to a frequency of 1225 turnovers h⁻¹ per catalytic site (assuming 0.10 mmol g⁻¹ loading of the active site). After the first 5 h, the rate of conversion dropped significantly; this is attributed to the inefficient removal of water from the reaction system, and poor adsorption of ethylbenzene onto the catalyst surface as the acetophenone concentration increases. In addition, catalyst reuse studies were performed by recycling 1.5 g of catalyst twice without any regeneration or conditioning by decanting the liquid from the reactor and adding fresh substrate and then repeating the experiment. The results shown in Fig. 1 demonstrate that the recycled catalyst retains its activity and the catalytic rate is equal to that of the fresh catalyst. Furthermore, the induction period observed with the use of fresh catalyst was eliminated when the catalyst was recycled. This suggests that poor product desorption when the catalyst is not saturated with the product was the cause of the induction periods observed.



Scheme 1

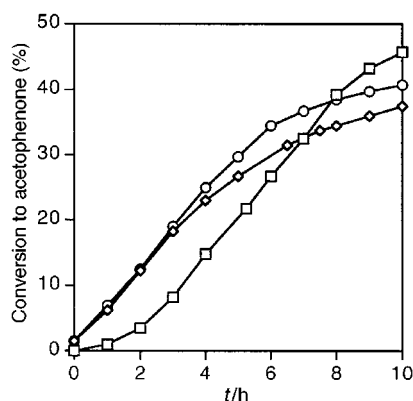


Fig. 1 Production of acetophenone in the oxidation of ethylbenzene using 5 g of the immobilised chromium on silica catalyst: (□) fresh catalyst, (○) first recycle and (◇) second recycle

After 5 h the activity of the recycled catalyst begins to decrease; the effect is more pronounced on the second recycle. The reason for this deactivation is not fully understood. Further reuse studies are in progress, including regeneration and conditioning of spent catalyst.

It is believed that the imprinted method of synthesis allows the chromium to become very tightly bound to the support. To verify that oxidation is occurring due to heterogeneous catalysis, several test reactions were carried out which were designed to encourage the formation of leached chromium. In one test reaction, an unimprinted version of the catalyst was made. Unlike the original catalyst, where the ligands are complexed with the metal and then grafted onto the silica support, the unimprinted version involves the grafting of the ligands before the complexation with the metal ions. This method of production gave a lower loading (0.05 mmol g^{-1} by AAS) and it is likely that the metal–ligand binding is significantly reduced in strength due to the less favourable spatial orientation of the ligands on the surface, leading to a less robust catalyst. In the second experiment, a catalyst based on physisorbed chromium(III) on the silica surface was made. The catalyst was formed by dissolving chromium(III) in EtOH, and stirring with the silica gel. The solvent was then removed by rotary evaporation, leaving a grey solid. The results shown in Fig. 2 indicate that the imprinted version of the CHRISS catalyst is the most active of the species studied. Both the

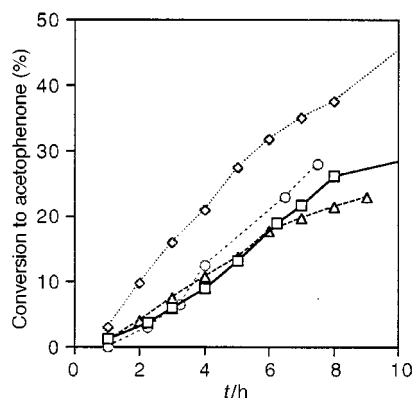


Fig. 2 Production of acetophenone in the oxidation of ethylbenzene using (□) an unimprinted catalyst, (○) a physisorbed chromium(III) catalyst, (◇) the imprinted catalyst and (△) no catalyst

unimprinted and the physisorbed materials show little activity above that of a control reaction, containing no catalyst.

We have successfully extended catalytic chemistry to the commercially important oxidation of methyl aromatics. *p*-Chlorotoluene, *p*-xylene and *o*-xylene all undergo aerial oxidation at atmospheric pressure in neat substrate with the supported chromium catalyst (Table 1). Again it was necessary to prove that the catalysis was not due to leached chromium. Following the method described by Lempers and Sheldon,⁷ a *p*-xylene reaction was hot filtered after 1 h (*i.e.* at an early stage of the reaction) to remove the catalyst. The reaction was then restarted without the catalyst, and the product isolated after 24 h. The reaction yielded 15 g of *p*-toluic acid (compared to 166 g from the reaction with CHRISS) which corresponds to the amount formed during an oxidation without the catalyst, *i.e.* the formed product is due to autoxidation. Analysis of the reaction mixture after hot filtration of the catalyst showed <0.5 ppm of chromium.‡

Table 1 Oxidation reactions using CHRISS^a

Substrate	<i>T</i> /°C	Product(s)	Isolated yield (%)
Ethylbenzene	130	acetophenone	50
<i>p</i> -Xylene	138	<i>p</i> -toluic acid	29
		terephthalic acid	5
<i>o</i> -Xylene	145	<i>o</i> -toluic acid	7
<i>p</i> -Chlorotoluene	130	<i>p</i> -chlorobenzoic acid	12

^a Reactions were carried out using the supported chromium catalyst (1.5 g) in neat substrate (4.1 mol) with an air feed rate of 800 ml min^{-1} and an agitation rate of 1500 rpm, for a period of 24 h.

The activity of the catalyst is significantly greater than the commercial supported chromium catalyst and other supported reagents based on chemically modified surfaces.^{3–6} The fact that we were not able to detect Cr, that experiments with less-robustly held catalysts proceeded at the background rate, and that the reaction after filtration failed to exceed the background rate leads us to believe that the active species is the surface bound Cr complex. The efficiency of the catalytic systems, the use of air as the only consumable source of oxygen and the avoidance of solvent makes them excellent examples of environmentally friendly processes.

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Notes and References

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‡ Metal analysis was undertaken by AAS, with a detection limit of 0.5 ppm.

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