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Modified mesoporous silicate MCM-41 materials: immobilised perruthenate—a new highly active heterogeneous oxidation catalyst for clean organic synthesis using molecular oxygen

Andrew Bleloch,[a] Brian F. G. Johnson,[b] Steven V. Ley,[b] Adam J. Price,[b] Douglas S. Shephard[b] and Andrew W. Thomas[b]

[a] *Cavendish Laboratory, Madingley Road, Cambridge, UK CB3 OHE*
[b] *Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW. E-mail: svl1000@cam.ac.uk*

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A new oxidation catalyst containing perruthenate immobilised within MCM-41 has been prepared and used in the clean oxidation of alcohols to carbonyl compounds with molecular oxygen.

Previously, we[1] and others[2] demonstrated that tetrapropylammonium perruthenate (TPAP)[3] may serve as a convenient catalyst for the oxidation of alcohols to carbonyl derivatives by molecular oxygen. Furthermore, we discovered that when bound to a polystyrene bead the same catalytic species (RuO_4^-–polymer supported perruthenate) provided a cleaner synthetic alternative.[4] However, because of difficulties in the recycling of the PSP reagent (that may be attributed to oxidative degradation of the polystyrene support), we decided to investigate other materials as suitable supports. Here we report that on tethering this same perruthenate catalytic species within the mesoporous solid MCM-41, a remarkably clean and more efficient catalyst is produced.[5]

The mesoporous solid MCM-41 has both internal and external surfaces supporting silanol groups (SiOH) which may be suitably derivatised to immobilise a known catalytically active species (Fig. 1).[6] Treatment of this material with the appropriate amount of Ph_2SiCl_2 (using a proven methodology) effectively caps the external surface inhibiting any further reaction and yielding material **1**.[7] Further treatment of **1** with [3-(trimethoxysilyl)propylamine] yields a material with the internal $Si(CH_2)_3NH_2$ tether. After treatment with HBF_4 to give the tethered primary ammonium system $Si(CH_2)_3NH_3^+$ **2**, the required perruthenate catalyst **3** may be prepared by ion exchange with potassium perruthenate in aqueous solution.

Material **3** has been found to serve as a highly effective and clean catalyst for the oxidation of primary alcohols to aldehydes with a superior performance over that of the previously reported polymer based system (PSP). The oxidations, using our previously published protocol, produced the corresponding aldehydes in less than 3 h using 10 wt% of solid catalyst;[8] significantly, the aldehydes were free of contaminants.

Material **1** was also treated with 3-bromopropyltrichlorosilane to yield material **4** containing a propyl tether with a bromohead group. Substitution with either Me_3N or Et_3N to form the corresponding quaternary ammonium species, followed by ion exchange with potassium perruthenate, afforded the catalytic species **5** and **6** respectively. The black solid **5** was found to be an equally efficient catalyst for the oxidation reactions (Scheme 1) and **6** was found to be a more highly active recoverable and reusable catalyst for the preparation of a wide range of aldehydes (see Table 1). Optimum results were obtained when 10 wt% of the solid catalyst **6**[9] in a solution of the alcohol in toluene was employed. Maximum yields were found on heating the mixture at 80 °C for between 30 min and 3 h, in an oxygen atmosphere. The reactions were faster if a suspension of the catalyst in dry toluene was pre-saturated with oxygen. Alternatively, the reactions may be run in MeCN, CH_2Cl_2 or toluene, but in these cases a reaction time of 12 h was required for completion. Addition of up to 50 wt% of the catalyst led to complete formation of the aldehyde without any over-oxidation to the acid. Recovery and re-use of the catalyst has been investigated (3 mg of the catalyst **6**, and 30 mg of the

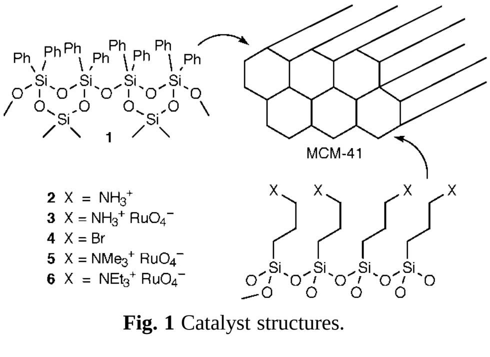
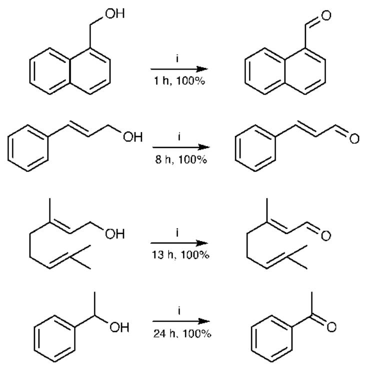
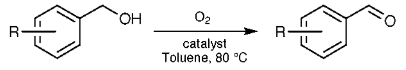


Fig. 1 Catalyst structures.



Scheme 1 *Reagents and conditions*: i, O_2, **5** (10 wt%), toluene, 80 °C, for time shown.

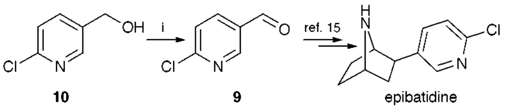
Table 1 Oxidation of **7** to **8**, using catalyst **6**



7 **8**

R	Catalyst **6** (wt%)	*t*/h	Yield (%)
H	10	0.5	quant.
4-Cl	10	1.0	quant.
4-OMe	10	2.0	quant.
3-OMe	10	3.0	quant.
2-OMe	10	2.0	quant.
4-NO_2	10	2.0	quant.
2-NO_2	10	3.0	quant.
4-F	10	1.0	quant.
3-CF_3	10	2.0	quant.
4-OBn	10	2.0	quant.

alcohol **7**). In each case, the pure aldehyde product **8** was obtained in quantitative yield, after 1 h, using oxygen in toluene as the oxidant at 80 °C, even after 12 recycle runs.[10] The catalyst **6** was efficiently used for the oxidation of allylic alcohols to the corresponding enals, and acetophenone was obtained from 1-phenylethanol. However, neither cyclohexanol nor cyclohexenol were converted to the corresponding ketones using this method. Finally, catalyst **6** was used in the preparation of aldehyde **9** from alcohol **10** on a 1 g scale, using only 25 mg of the triethylammonium catalyst **6** following the previously mentioned toluene/oxygen protocol (Scheme 2). A quantitative yield of the pure aldehyde **9** was obtained. This aldehyde was used in a ten-step linear synthesis of the potent analgesic natural product epibatidine, which employed only solid supported reagents.[11]



Scheme 2 *Reagents and conditions*: i, O_2, **6** (2.5 wt%), toluene, 80 °C, 12 h.

Instead of oxygen, NMO or trimethylamine *N*-oxide (TMAO) may be used as oxidant, and although this protocol was efficient in generating the desired aldehydes in high yield, a noticeable contamination by both ruthenium and an organic impurity was found. These were probably unreduced, involatile NMO or TMAO, and a product formed by β-elimination (Hofmann elimination) of the ammonium species. Only in this experiment was the catalyst found not to be reusable.

Leaching was shown not to take place with **6** under the conditions employed. Thus, oxidation was allowed to proceed to 50% completion, and the solid catalyst was removed by filtration and stored under argon; the filtrate was then heated at 80 °C under an oxygen atmosphere and no further oxidation was observed by HPLC after 12 h. The catalyst was then re-added to the reaction mixture, the reaction was re-established and complete oxidation was observed in less than 1 h under the usual conditions.

In separate experiments designed to help elucidate the catalytically active species we have established that: (i) MCM-41 alone shows no activity; (ii) diphenylsilyl capped MCM-41 treated with potassium perruthenate (lacking the supporting tether) shows little activity and complete leaching; (iii) uncapped MCM-41 treated with potassium perruthenate (lacking the supporting tether) shows little activity and complete leaching; (iv) colloidal RuO_2 absorbed within the MCM-41 mesopores[12] shows no activity. These experiments demonstrate that a perruthenate derived species is responsible for the catalysis and not RuO_2.[13] Scanning transmission electron microscopy (STEM) revealed that coverage of the MCM-41 internal surface was uniform (also the external surface of Carbosil *vide infra*). There was no evidence for the formation of colloidal RuO_2.[14] It is worth noting that X-ray diffraction studies of the catalysts **5** and **6** indicate that long range order in the MCM-41 structure is reduced, whilst STEM showed that there are residual 'domains' of parallel mesopores. An alternative synthetic route was used to reproduce **6** without the loss of long range order by eliminating the water solvated ion exchange. However no superior performance was observed under the same reaction conditions. X-Ray diffraction also revealed that no large inorganic crystallites were formed in the catalyst preparation. We have also demonstrated that an aerogel silica tethered triethylammonium perruthenate species (preparation akin to **6**) is a good oxidation catalyst although significantly longer reaction times are needed (5 h on a 0.1 mmol scale).

In summary, we have developed a new, highly active, recoverable and re-usable heterogeneous catalytic oxidant **6** for the oxidation of alcohols to carbonyl derivatives by molecular oxygen. It may be prepared from the siliceous MCM-41 material following a reliable tethering method and ion exchange with potassium perruthenate. The immobilisation of other reagents using the improved MCM-41 support should allow us to incorporate these new solid supported reagents in our future clean chemistry programmes.[15]

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8 10 wt% of the solid catalyst **3** corresponds to 0.3 wt% Ru by ICP analysis.

9 10 wt% of the solid catalyst **6** corresponds to 1.1 wt% Ru by ICP analysis.

10 *General procedure* for the oxidation of alcohols: To a solution of the alcohol (30.0 mg) in dry toluene (5 cm^3) was added MCMSP **6** (3.0 mg) and the resulting mixture heated at 80 °C, for 30 min to 3 h in an oxygen atmosphere. After cooling, filtration of the mixture followed by evaporation of the solution afforded the pure aldehyde in quantitative yield (Table 1). The solid catalytic oxidant reagent can be re-used many times (up to 12 times without loss of activity). It can be easily filtered through a polypropylene filter or through a bond elut cartridge and then washed off the surface with toluene. In addition, recovery by centrifugation was also found to be quantitative.

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13 In experiments (i) and (iv), no oxidation was observed after 50 h, in toluene/oxygen at 80 °C, implying that a perruthenate derived species was responsible for the catalysis and not RuO_2. In experiments (i) and (iii), approximately 10 and 70% oxidation, respectively, to the aldehyde was observed after 3 days under the same conditions and complete leaching of potassium perruthenate was observed in both cases. The used solid material from experiments (ii) and (iii) showed no catalytic oxidative activity when reused.

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