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Sol-gel entrapped chromium(VI): a new selective, efficient and recyclable oxidizing system

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Abstract—The sol-gel entrapment of chromium(VI) within a silica matrix, obtained by oxidation with ozone of the corresponding entrapped chromium(III), was found to be an efficient and recyclable oxidizing system (at least up to 16 times) for benzylic alcohols. No leaching of chromium in solution was observed, which prevented any environmental pollution.

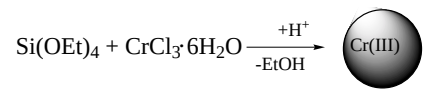
The oxidation of primary and secondary alcohols to aldehydes and ketones is one of the most widely employed reaction in organic synthesis laboratories. A huge amount of different methods have been developed,[1] often using chromium(VI) reagents, such as, in addition to the Jones' reagent,[2] other dipyridine Cr(VI) oxide (Collins' reagent),[3] pyridinium chlorochromate (Corey's reagent)[4] and pyridinium dichromate.[5] The concept of using reagents adsorbed on inert inorganic supports has been applied in organic synthesis. Such efficiency resulting from inorganic material-supported reagents may come from the combination of three factors: (i) an increase in the effective surface area for reactions; (ii) the presence of pores which constrain both substrate and catalyst and thus lowers the activation entropy of reactions; (iii) the acceleration of the reaction resulting from bringing substrate and reagent into proximity.[6]

Chromium oxidants adsorbed on solid supports, such as chromic acid on silica,[7] chromyl chloride on silica/alumina,[8] pyridinium chlorochromate on alumina,[9] *N*-methyl piperidinium chlorochromate on alumina,[10] chromium trioxide on Celite[11] have been reported to give high yields under mild conditions.

The sol-gel technology provides a new approach to the preparation of heterogeneous catalysts. Purity, homogeneity and controlled porosity combined with the ability to form large surface area materials are the potential advantages of sol-gel processing.[12] Since the chromium residues are environmentally hazardous it would be advantageous to develop oxidizing methods in which there is no trouble in carrying out the work-up and the chromium reagent can be easily recycled. Polymeric reagents, such as poly(vinylpyridinium dichromate),[13] poly(vinylpyridinium chlorochromate),[14] chromic acid on anion exchange resins[15] or imidazolium chlorochromate,[16] have been reported as recyclable oxidizing agents. However, the resins were regenerated after complete removal of the spent chromium salts. To the best of our knowledge, the most suitable recyclable oxidant is, in our opinion, Magtrieve™, based on chromium dioxide.[17]

Continuing our studies on new materials,[18] we report preliminary results about the sol-gel entrapment of chromium(VI) within a silica matrix. Our efforts have been devoted to the realization of an efficient and recyclable oxidizing system for selective oxidation of alcohols.

A new sol-gel, double step method, has been followed in order to minimize the gelation and aging times by working in an aqueous sol and to avoid the presence of residual -OR groups not hydrolyzed.



Scheme 1. Sol-gel entrapment of Cr(III).

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In a typical preparation procedure 0.1 mol of tetraethoxysilane was added to 10 mL of an aqueous solution of 0.01N HCl and mixed with 5 mL of ethanol as co-solvent. The mixture was stirred for 30 min to obtain a sol containing principally hydrolyzed tetraethoxysilane. In order to complete the hydrolysis step, the ethanol was removed by distillation under vacuum at 35°C. Next, the sol solution was cooled at 0°C to avoid gelation that would be promoted at room temperature. Chromium(III) chloride hexahydrate (2.66 g, 0.01 mol) was dissolved in 10 mL of bi-distilled water and cooled at 0°C. Finally, the solution containing chromium chloride was added slowly to the sol and the pH was raised from 2 to 4 (Scheme 1).

The gelation occurred in about 20 h. The resulting oxide ground in granules (<425 μ) was washed with water and sonicated for 30 min in the same solvent in order to remove any chromium compound that adhered onto the outer surface of the silica matrix. The resulting material was heated to 343 K until a constant weight was achieved (24 h). The Cr(III) in the washing solution was determined spectrophotometrically as CrO_4^{2-}. The calculated content of the silica entrapped chromium was 4% wt. Before use the resulting oxide was dried at 25°C at 1 mmHg for 12 h.

In order to have an oxidizing material, the sol-gel entrapped chromium(III) was oxidized to Cr(VI) by reaction with ozone. The Cr(VI)–SiO_2 reagent was obtained by packing the sol-gel Cr(III) in a column, letting the substrate stand in contact with a continuous ozone flow (10 Nl/h, ca. 50 mg O_3/h) for several hours. At the end of the process the starting green silica turned to a red-brown material. Oxidation by heating in air at 550°C for 5 h was inefficient.

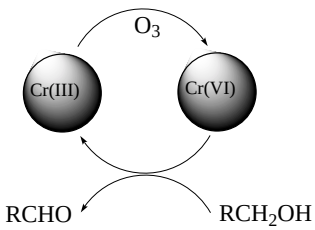
The sample showed a very high surface area (650 m^2/g) with a pore size distribution centered at 10–20 Å as determined by nitrogen adsorption/desorption measurements at 77 K. This pore size should be suitable for the reaction with the entrapped Cr(VI). The X-ray diffraction pattern showed only the background of the silica amorphous glass. No reflections due to any chromium oxide phase were detected. This could be an indication that the chromium species are highly dispersed.

Oxidation of primary alcohols was carried out using a molar ratio Cr/alcohol of 2.5/1. The reactions were performed in dichloromethane/diethyl ether 3/1 at room temperature in a Pyrex-glass reactor, equipped with magnetic stirring, working in batch conditions.[19] The solvent mixture was chosen in order to minimize leaching of chromium in solution, stressing the incompatibility between solvent and Cr-species, as chromium trioxide is insoluble in dichloromethane.[11] The reactions were monitored by GC–MS; all the products were identified and quantified by comparison with known samples. The Cr(VI)–SiO_2 reagent was found to lead to a very easy work-up, which became reduced to a mere filtration. No leaching of chromium in solution was observed (spectrophotometric measurements). The spent Cr(VI)–SiO_2 reagent was washed with more dichloromethane, then dried in the oven for a few minutes. Chromium(VI) was regenerated by packing the reagent in a column and again letting the substrate stand in contact with a continuous ozone flow as before [usually 50 mg/h within 48 h, ca. 1.3 g of spent Cr(VI)–SiO_2]. After several cycles, the Cr(VI)–SiO_2 showed no change in the pore size distribution (Scheme 2).

Several benzylic alcohols were oxidized to the corresponding aldehydes in >99% selectivity and in 84 to >99% conversion in 5–24 h (Table 1).

In the first three cycles, the reaction time was longer, probably because the entrapped reduced chromium was oxidized with ozone for a shorter time (30 h). After these cycles the entrapped reduced chromium was oxidized for 48 h. Both benzylic alcohols with electron-withdrawing or electron-donating groups were promptly oxidized. It has been proposed that the role of the silica is to adsorb the lower valent chromium species produced during the oxidation.[11] At this stage we have made no attempt to characterize fully both the oxidized and reduced species bound to the silica. The poor conversion (38%) of in the oxidation of *p*-chloro-benzyl alcohol, using a molar ratio Cr/alcohol of 2/3 (entry 8), could be an indication that the reduced species is Cr(IV).

In summary the most interesting feature of this material is the recyclability (at least up to 16 times) without loss in activity; moreover, we believe that the fact that the chromium remains firmly entrapped before and



Scheme 2. Oxidation cycles.

Table 1. Oxidation reactions of benzylic alcohols with Cr(VI)–SiO_2

Entry	Alcohol	*t* (h)	Aldehyde (%)	Cycles
1	$PhCH_2OH$	48	98	1–3
2	$PhCH_2OH$	23	>99	4–5
3	*p*-Cl-$C_6H_4CH_2OH$	7	96	6–7
4	*o*-Br-$C_6H_4CH_2OH$	22	84	8–10
5	*p*-MeO-$C_6H_4CH_2OH$	5	>98	11–12
6	*o*-Me-$C_6H_4CH_2OH$	17	>98	13–14
7	*o*-OEt-$C_6H_4CH_2OH$	24	97	15–16
8[a]	*p*-Cl-$C_6H_4CH_2OH$	24	38	17

[a] Molar ratio Cr/alcohol 2/3.

after each reaction cycle may be valuable in preventing environmental pollution. Further studies are in progress in order to develop this methodology and characterize fully the silica entrapped chromium species.

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19. Typical oxidation reaction: a Cr(VI)–SiO_2 (1.57 g) suspension in dichloromethane/diethyl ether 3/1 (7 mL) containing benzyl alcohol (51 mg) was magnetically stirred at room temperature.