Chromium-substituted Aluminophosphate-5: a Recyclable Catalyst for the Selective Oxidation of Secondary Alcohols

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Isomorphous substitution of aluminium by chromium in the aluminophosphate-5 framework by hydrothermal synthesis leads to an active, selective and recyclable catalyst for the liquid phase oxidation of secondary alcohols, to the corresponding ketones, using molecular oxygen or *tert*-butyl hydroperoxide as the terminal oxidant.

The oxidation of primary and secondary alcohols to the corresponding carbonyl compounds is a key reaction in organic synthesis.[1] Traditionally such transformations were performed with stoichiometric amounts of chromium(VI) reagents.[2] However, because of the serious environmental problems associated with chromium-containing effluent attention has been focused on the use of catalytic amounts of soluble chromium compounds in conjunction with, *e.g.* *tert*-butyl hydroperoxide (TBHP) as the stoichiometric oxidant.[3] The use of heterogeneous catalysts in the liquid phase, on the other hand, offers several advantages compared with their homogeneous counterparts, *e.g.* ease of recovery and recycling and enhanced stability.

One approach to creating solid catalysts with novel activities is to incorporate redox metals, by isomorphous substitution, into the lattice framework of zeolites and related molecular sieves. The resulting redox molecular sieves[4,5] may be regarded as 'mineral enzymes'. Since the discovery of aluminophosphate ($AlPO_4$) molecular sieves[6] in 1982 much attention has been focused on the incorporation of various elements into the framework of these molecular sieves.[7] However, redox metal substituted aluminophosphates have not yet found wide application as oxidation catalysts.[8] Recently, we showed that chromium- and cobalt-substituted aluminophosphates (CrAPO and CoAPO) catalysed the autoxidation of *p*-cresol, in alkaline methanolic solution, to *p*-hydroxybenzaldehyde.[9] We now report the use of chromium substituted $AlPO_4$-5 (CrAPO-5) as a recyclable solid catalyst for the selective oxidation of secondary alcohols with O_2 or TBHP.

CrAPO-5 was hydrothermally synthesized in a 300-ml Teflon-lined autoclave by essentially following the reported procedure,[10] using the following molar ratios: 0.05 Cr_2O_3 : 0.9 Al_2O_3 : P_2O_5 : Pr_3N : 50 H_2O. Crystallization was performed at 175 °C for 24 h. The crystalline material was subsequently calcined by heating from room temp. to 500 °C at a rate of 60 °C h^{-1} and maintaining at 500 °C for 10 h. The synthesized and calcined CrAPO-5 were characterized by powder X-ray diffraction (XRD) which gave well-defined, reproducible patterns. Scanning electron microscopy (SEM) showed that the particle sizes (from 5 to 70 μm) and morphologies of CrAPO-5 were dependent on the synthesis conditions. Dif-

Table 1 CrAPO-5 catalysed oxidations in the liquid phase with TBHP[a]

Substrate	Product	Conversion (%)[b]	Selectivity (%)	
			Substrate	TBHP
α-Ethylbenzyl alcohol[c]	Propiophenone	77	100	91
α-Methylbenzyl alcohol	Acetophenone	77	96	89
Cyclohexanol[d]	Cyclohexanone	72	85	73
Carveol	Carvone	62	94	66

[a] *Conditions*: substrate (10 mmol); TBHP (5 mmol); CrAPO-5 (0.14 mmol Cr); chlorobenzene(solvent) (10 ml); *T*, 85 °C; stirring, 1000 rpm; reaction time, 16 h; under N_2. [b] The conversion of substrate based on the amount of TBHP employed. [c] Reaction time, 7 h. [d] Reaction time, 12 h.

Table 2 CrAPO-5 catalysed oxidations in the liquid phase with O_2[a]

Substrate	Product	Conversion (%)	Selectivity (%)
Cyclohexanol	Cyclohexanone	30	97
α-Methylbenzyl alcohol	Acetophenone	31	96
α-Ethylbenzyl alcohol[b]	Propiophenone	38	90
α-Tetralol[b]	α-Tetralone	26	73
1-Indanol[b]	1-Indanone	78	72

[a] *Conditions*: substrate (250 mmol); O_2 pressure, 5 atm; TBHP (25 mmol); CrAPO-5 (3.65 mmol Cr); chlorobenzene(solvent) (65 ml); 3 Å molecular sieve (drying agent) (6 g); *T*, 110 °C; reaction time, 5 h. [b] *Conditions*: substrate, 50 mmol; O_2, 15 ml min^{-1}; TBHP, 5 mmol; CrAPO-5 (0.73 mmol Cr); chlorobenzene(solvent), 5 ml; *T*, 110 °C; stirring, 1000 rpm; reaction time, 19 h.

fuse reflectance electronic absorption spectroscopy (DREAS) showed that most of the chromium was present as Cr^{VI} after calcination at 500 °C. Inductively coupled plasma-atomic emission spectrometric (ICP-AES) analysis showed that a Cr content of up to 1.5% could be achieved. These results are essentially in agreement with published data.[10,11]

The results of CrAPO-5 catalysed oxidations of secondary alcohols with TBHP at 85 °C in chlorobenzene solvent are shown in Table 1. Good to excellent selectivities to the corresponding carbonyl compounds were observed with respect to both substrate and TBHP. Carveol underwent chemoselective oxidation of its alcohol group, to give carvone, without any attack at its double bonds. Moreover, one of the two isomers (*cis/trans*) of carveol appeared to react much faster than the other, suggesting that the catalyst exhibited some (shape) selectivity.

Interestingly, when the oxidations with TBHP were carried out under an atmosphere of air, instead of N_2, yields on TBHP of greater than 100% were observed, suggesting that O_2 could also act as the terminal oxidant. Indeed, subsequent experiments showed (Table 2) that this was the case. The best results were obtained when a small amount (10 mol%) of TBHP was added, presumably to initiate these reactions. The oxidations of α-methylbenzyl alcohol and cyclohexanol were carried out under O_2 with pressure in a stirred 300 ml autoclave with a Teflon insert. The other alcohols were oxidized at atmospheric pressure by bubbling O_2 through the reaction mixture at a rate of 15 ml min^{-1}. The TBHP was slowly added during the reaction.

Reaction mixtures were separated from the catalyst and analysed by gas chromatography using a semi-capillary column (CP WAX 52 CB) and *p*-dichlorobenzene as internal standard. The structures of products were also confirmed using GC-MS.

In one experiment with α-methylbenzyl alcohol as substrate (at 85 °C) and TBHP as terminal oxidant, the CrAPO-5 catalyst was filtered, washed 3 times with chlorobenzene and recalcined at 500 °C for 5 h before reuse. Under the conditions, as shown in Table 1, the CrAPO-5 could be recycled four times without any loss of activity or selectivity. DREAS spectra showed that most of the chromium remained in the hexavalent state within the $AlPO_4$ framework after recycling. however, the greenish-yellow colour of the used catalyst, compared to yellow for the freshly prepared CrAPO-5, suggested the presence of small amounts of Cr^{III}.

In conclusion, CrAPO-5 is a stable, recyclable solid catalyst for the selective, liquid phase oxidation of secondary alcohols, to the corresponding ketones, using O_2 or TBHP as the terminal oxidant.

Further research on the mechanism of this reaction and the scope of CrAPO-5 and related redox molecular sieves as solid catalysts for various liquid phase oxidations is in progress.

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