FARADAY

Synthesis, characterization and catalytic oxidation of alcohols with chromium-substituted aluminophosphates

Ji Dong Chen, Hans E. B. Lempers and Roger A. Sheldon*

Laboratory of Organic Chemistry and Catalysis, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

Chromium-substituted aluminophosphate-5 and aluminophosphate-11 (CrAPO-5 and CrAPO-11) have been hydrothermally synthesized and characterized by XRD, scanning electron microscopy, *n*-butane and N_2 absorption, IR spectroscopy of [$^2H_3$]acetonitrile adsorption and diffuse reflectance spectroscopy, showing that they are pure and possess high crystallinities and pore volumes. Calcined samples contain both strong Lewis-acid (Cr^{VI}) and weak Brønsted-acid (P—OH) sites, and the Cr^{VI} species is bonded to the internal $AlPO_4$-5 framework. CrAPO-5 and CrAPO-11 are selective and recyclable solid catalysts for the oxidation of benzylic and cyclic alcohols with O_2 or *tert*-butyl hydroperoxide (TBHP) as oxidant. It is proposed that the CrAPO-5-catalysed oxidation of alcohols with TBHP in the absence of O_2 proceeds *via* a heterolytic mechanism involving β-hydrogen elimination from an oxochromium(VI) alkoxide followed by reoxidation of the reduced Cr^{IV} by TBHP, giving high selectivities with respect both to substrate (>89%) and TBHP (>88%). The CrAPO-5-catalysed oxidation of alcohols with O_2 gives the corresponding ketones in selectivities of 72–97% at conversions of 26–78% when only 10 mol% of TBHP is added. The mechanism of the CrAPO-catalysed oxidations with O_2 and the changes in CrAPO-5 and CrAPO-11 structures after oxidation are discussed. Evidence is provided in support of the alcohol oxidation essentially taking place within the micropores of CrAPO-5.

The selective oxidation of primary and secondary alcohols to the corresponding carbonyl compounds is a key reaction in organic synthesis.[1] Traditionally such transformations have been performed with stoichiometric amounts of chromium(VI) reagents.[2–4] 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 more benign primary oxidants, such as *tert*-butyl hydroperoxide (TBHP),[5,6] peroxyacetic acid[7] or hydrogen peroxide derivatives.[8,9]

The use of heterogeneous catalysts in the liquid phase offers several advantages over homogeneous ones, *e.g.* ease of recovery, recycling and enhanced stability. For example, chromium(III)-impregnated Nafion K (a perfluorinated sulfonic acid resin) was shown to be an efficient catalyst for the chemoselective oxidation of a variety of unsaturated alcohols using TBHP as the oxidant.[10] Redox-pillared clays[11,12] constitute another type of attractive heterogeneous catalyst. Choudary and co-workers[13–16] reported that chromia-, vanadia- and titania-pillared montmorillonite catalysed the oxidation of various alcohols with either 30% aqueous H_2O_2 or TBHP, claiming unusually high regio-, shape- and enantioselectivities.

A problem associated with the chromium-catalysed oxidation of alcohols is low efficiency in the use of primary oxidants, because chromium is a good catalyst not only for the oxidation of alcohols *via* oxometal pathways but also for the homolytic decomposition of organic hydroperoxides. For example, to obtain high yields of carbonyl compounds from alcohols, a large excess of oxidant (*e.g.* four equivalents of TBHP) was needed with various homogeneous Cr-containing catalysts.[6]

On the other hand, the chromium-catalysed decomposition of organic hydroperoxides *via* a free-radical mechanism may be advantageous with regard to the use of O_2 as a co-oxidant, since the resulting alkoxy radicals are good initiators for rapidly generating other alkyl hydroperoxides in the presence of an active substrate and O_2. Furthermore, the alkyl hydroperoxides formed can reoxidize Cr^{IV} to Cr^{VI}, and the peroxides themselves are converted to the desired products and water.

Recently, we found that chromium-substituted aluminophosphate-5 (CrAPO-5) is an active and very selective catalyst for the oxidation of secondary alcohols and hydrocarbons, using either molecular oxygen or TBHP as the oxidant,[17a,b] and decomposition of alkyl hydroperoxides.[17c] We now report a detailed study of the synthesis, characterization and catalytic properties of CrAPO-5 and chromium-substituted aluminophosphate-11 (CrAPO-11) molecular sieves.

Experimental

Catalyst preparation

The details of synthesis and characterization of CrAPO-5 have been published previously.[18]

CrAPO-11 was synthesized as follows: typically, 5 g of pseudoböehmite was stirred with 10.5 g of water at room temperature for 2 h. A solution of 0.38 g $Cr_3(OH)_2\,(CH_3COO)_7$ in 10.6 g water was combined with another solution of 8.8 g H_3PO_4 (85%) in 10.6 g water, and the resulting solution was subsequently added to the alumina slurry at room temperature. After ageing at room temperature for 1 h, 3.9 g of dipropylamine was added dropwise followed by vigorous stirring at 0 °C for another 2 h. Finally, the gel was charged in a 50 ml Teflon-lined autoclave and allowed to crystallize at 175 °C for 24 h. The molar oxide composition in this example is $0.025Cr_2O_3 : 0.955Al_2O_3 : P_2O_5 : Pr_2NH : 50H_2O$. The yield of CrAPO-11 crystals was 43%.

A 2 g calcined CrAPO sample was shaken twice with 400 ml of 0.1 mol dm^{-3} NaCl aqueous solution (Na : Cr > 100) at room temperature for 24 h and subsequently washed three times with deionized water, to remove non-framework Cr species completely. The catalyst was subsequently recalcined at 500 °C for 24 h.

Catalyst characterization

XRD powder patterns were recorded on a Philips PW 1877 automated powder diffractometer using Cu-Kα radiation.

Scanning electron microscopy (SEM) was performed using a JEOL JSM-35 scanning microscope, the sample to be measured was coated with an Au evaporated film. A Cahn 2000 microbalance was used for *n*-butane absorption and BET was performed with a Carlo Erba sorptomatic 1900 instrument. IR spectra were measured with a Bruker FTIR spectrometer (IFS 113v) equipped with a vacuum cell, using deuteriated acetonitrile as the probe molecule. Diffuse reflectance spectra (DRS) were measured using a Hitachi 150-20 UV–VIS spectrophotometer equipped with a diffuse reflectance unit and MgO as a reference. The UV–VIS adsorption data were converted to Kubelka–Munk units and the spectra were recorded in the wavelength range 190–900 nm.

Catalytic oxidations

An anhydrous solution of TBHP in chlorobenzene was prepared by a slightly modified literature procedure.[19,20] Oxidations of alcohols with TBHP were carried out in a 50 ml thermostated flask equipped with a condenser and a magnetic stirrer. Typically, to this flask 10 mmol of a substrate, 5 mmol of TBHP in 0.87 g of chlorobenzene, 10 ml of chlorobenzene (solvent) and 0.5 g of CrAPO-5 containing 0.14 mmol of Cr were added. The charged flask was flushed four times with dry nitrogen gas and kept in a nitrogen atmosphere. Subsequently the charged flask was heated to 85 °C and stirred with a speed of 1000 rev min^{-1} for 16 h in a nitrogen atmosphere. Some experiments were carried out in air, in this case the charged flask was not flushed with nitrogen.

Oxidations of secondary alcohols with O_2 were carried out in the flask described above. Typically, 50 mmol of a substrate, 5 ml of chlorobenzene (solvent), 1.0 g of *p*-dichlorobenzene (an internal standard) and 2.5 g of CrAPO-5 containing 0.73 mmol of Cr were charged and O_2 was bubbled at a rate of 15 ml min^{-1} through the reaction mixture. Subsequently the charged flask was put in an oil bath which had been heated to 110 °C. TBHP (5 mmol) in 0.87 g of chlorobenzene was added dropwise into the reaction mixture during the reaction with stirring at 1000 rev min^{-1}. The reaction was continued at 110 °C for 19 h.

Oxidations of some secondary alcohols with O_2 were carried out in a 300 ml autoclave (Parr Instrument, USA) equipped with a heating jacket, stirrer, water cooled condenser, liquid separator, outlet for gas with needle valve and sampling valve. Typically, 250 mmol of a substrate, 25 mmol of TBHP in 4.35 g of chlorobenzene, 12.5 g of CrAPO-5 containing 3.65 mmol Cr, 65 ml of chlorobenzene (solvent) and 6 g of 3 Å molecular sieve (drying agent) were introduced into the reactor with a Teflon insert inside. The reactor was charged with 20 atm† of air and 5 atm of O_2, heated to 110 °C within 15 min with stirring and kept at this temperature for 5 h, while O_2 was fed continuously to maintain a constant O_2 concentration.

The quantitative analyses were carried out by gas chromatography (GC) with a semi-capillary column (25 m × 0.53 mm, CP WAX 52 CB). For the oxidation of primary alcohols, samples were pretreated as follows: the reaction mixture was first diluted with twice its amount of acetone to dissolve all acids and silylated with a mixture of 200 μl of hexamethyldisilazane and 100 μl of trimethylchlorosilane for 30 min at room temperature before GC analysis using *p*-dichlorobenzene as an internal standard. The structures of products were also confirmed using GC–mass spectrometry. TBHP was determined by iodometric tritration according to a literature method.[19]

Results and Discussion

Synthesis and characterization of CrAPO-5 and CrAPO-11

In the syntheses of $AlPO_4$s and MeAPOs, the preferred sources of aluminium and phosphorus are pseudoböehmite (a reactive hydrated alumina) and phosphoric acid, respectively. To obtain a homogeneous gel mixture, the order of addition of the reactants is important. Instead of adding an aqueous solution of the Cr salt into an aluminophosphate precursor mixture, the Cr solution was combined with H_3PO_4 (85%) and the resulting mixture was subsequently added to a slurry of alumina in water. During addition of a template and the final ageing of a gel mixture, the temperature was maintained at 0 °C. In this way, a very homogeneous gel can be easily made and good reproducibility of the final crystalline product can be attained.

In the synthesis of CrAPOs, a Cr^{III} salt is generally used as the chromium source, because in an acidic aqueous medium Cr^{III} is a stable monomeric $Cr(H_2O)_6$. Table 1 shows the effect of template concentration on the synthesis of CrAPO-11. When increasing the ratio of $Pr_2NH : P_2O_5$ to 2 only amorphous materials were obtained. It was observed that the final pH of the gel mixture after crystallization was 8.7, which might cause the precipitation of $Cr(OH)_3$ and was possibly the cause of the failure of crystal formation. Rai *et al.*[21] concluded from a study of Cr^{III} hydrolysis that $Cr(OH)_3$ precipitates appeared at pH values between about 6.5 and 10.5. The effect of template concentration of Cr^{III} hydrolysis occurs not only in the course of ageing gel mixtures, but also during crystallization in which the pH normally increases with crystallization time. This effect suggests that there is a strong interaction between the Cr^{III} species and phosphorus in the gel phase and presumably the formation of the $Cr(OH)_3$ precipitates may strongly inhibit the growth of CrAPO-11 crystals. Furthermore, it was demonstrated by Kraushaar-Czarnetzki[22] that in the synthesis of $AlPO_4$-5 a slight excess of phosphoric acid led to a final Al : P ratio closer to unity. Accordingly, in the syntheses of the CrAPOs we controlled the pH of gel mixtures at a relatively low level (pH < 4), using one equivalent (based on P_2O_5) of a template and a slight excess of phosphoric acid to alumina in all syntheses.

The basic properties of CrAPO-5 and CrAPO-11 are given in Table 2. In agreement with the literature,[18] Cr molecular sieves of the $AlPO_4$-5 type have the AFI structure and those

Table 1 Effect of template concentration on the synthesis of CrAPO-11[a]

P : Al	$Pr_2NH : P_2O_5$	initial pH[b]	final pH[c]	XRD
1.05[d]	1.0	3.9	6.6	AEL
1.05	1.5	4.7	7.1	AEL
1.05	2.0	6.3	8.7	amorphous

[a] Gel compositions: $0.025Cr_2O_3 : 0.955Al_2O_3 : P_2O_5 : xPr_2NH : 50 H_2O$; crystallization temperature, 175 °C; crystallization time, 24 h. [b] Measured before crystallization. [c] Measured after crystallization. [d] Compositions of the calcined CrAPO-11 : $0.019Cr_2O_3 : 0.994 Al_2O_3 : P_2O_5$.

Table 2 Basic properties of (Cr)APO-5 and (Cr)APO-11

sample	structure XRD	pore volume /ml g^{-1} *n*-butane	BET	morphology (size/μm)[a]	Cr (wt.%)[b]
$AlPO_4$-5	AFI	0.110	0.138	—	0
CrAPO-5	AFI	0.115	0.139	spheres (50)	1.5
$AlPO_4$-11	AEL	0.080	0.90	—	0
CrAPO-11	AEL	0.071	—	spheres (5)	0.9

[a] From SEM. [b] Cr : (Cr + Al + P)O_2 (wt.%); from ICP (accuracy ±3%).

---

† 1 atm = 101 325 Pa

of the $AlPO_4$-11 type have the AEL structure. Because CrAPOs possess unidimensional channels, if the channels are partially blocked by some impurities, such as Cr clusters or Cr oxides, the accessible internal space will be considerably reduced. As can be seen in the table, the pore volume of CrAPO-5 is 0.139 ml g^{-1} (determined by the BET method), comparable to that (0.138 ml g^{-1}) of $AlPO_4$-5 and close to the theoretical value of 0.140 ml g^{-1} confirming that no impurities block the micropores of catalysts. Similar results were obtained with CrAPO-11.

It has been reported that non-framework Cr^{VI} species can be easily or almost quantitatively extracted from a calcined CrS-1 sample[23] or a calcined Cr-exchanged zeolite[24] by washing it with cold water. However, repeated ion-exchange treatments of our calcined CrAPO-5 with NaCl aqueous solution caused no apparent loss of Cr^{VI} from the calcined CrAPO-5, as presented in Table 3. Sodium can exchange two types of site, *i.e.* the cation sites which might be occupied by non-framework Cr or Al, and acidic sites. During synthesis of CrAPOs, Cr^{III} replaces Al^{III}, which results in a neutral framework with very little Cr present as non-framework, *i.e.* ion-exchangeable, species at the cation sites. However, during calcination Cr^{III} is oxidized to Cr^{VI}, which generates acidic P—OH groups while Cr^{VI} remains bonded to the internal $AlPO_4$ framework. Therefore, after sodium exchange, only some sodium ions replace protons at the acidic sites and there is no other element proportion change.

Recently, IR using acetonitrile as a probe molecule was reported to be[25,26] a very useful characterization technique for investigation of acidity changes in the molecular sieves after metal incorporation. For instance, incorporation of transition metals, such as Mn, Co, Cu and Zn, into $AlPO_4$-5 and $AlPO_4$-11 frameworks created both strong Lewis-acid sites and other weaker acidic centres.[25,26] A Cr^{VI} species bonded to the $AlPO_4$ framework is coordinatively unsaturated and should exhibit the characteristics of strong Lewis acid.[27]

Fig. 1 shows IR difference spectra of CrAPO-11 loaded with [$^2H_3$]acetonitrile. The bands at 2114 and at 2265 cm^{-1} are due to the symmetric vibration of the CD_3 group and C≡N stretching vibration of physisorbed acetonitrile, respectively; and the band at 2282 cm^{-1} is assigned to C≡N stretching after interaction with P—OH groups. The strong band at 2319 cm^{-1} is ascribed to Lewis-bonded acetonitrile on framework Cr, because only the P—OH can be detected in the ν(OH) region. On the other hand, all acetonitrile interacting with non-framework aluminium (Lewis acids) can be desorbed by degassing the sample at room temperature for 15 min while the Lewis-bonded acetonitrile on framework Cr is still present after degassing the sample even at 80 °C for 60 min [see Fig. 1(d)]. The broad band observed at *ca.* 3070 cm^{-1} is due to the stretching vibration of the P—OH group (at 3677 cm^{-1}) after interaction with acetonitrile. When the P—OH stretching vibration shifts from 3677 to 3070 cm^{-1} the band at 2282 cm^{-1} mentioned above appears, indicating a correlation between the P—OH stretching vibration and the C≡N stretching vibration. As reported for CrAPO-5[18] the calcined CrAPO-11 also contains both strong Lewis-acid (Cr^{VI}) and weak Brønsted-acid (P—OH) sites, and the Cr^{VI} species is presumably bonded to the internal $AlPO_4$-11 framework.

Table 3 Comparison between the CrAPO-5 with and without the ion-exchange treatment

sample	Cr (wt.%)	Na (wt.%)	Na : Cr (molar ratio)
CrAPO-5	1.64	—	—
Na-CrAPO-5[a]	1.62	0.64	0.90

[a] Sodium-exchanged CrAPO-5.

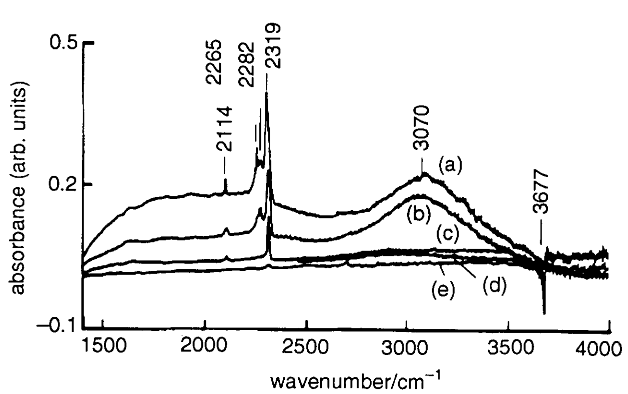
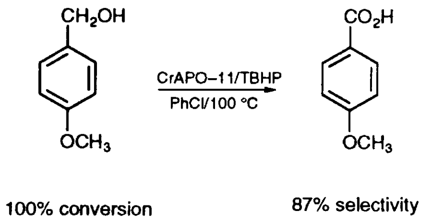


Fig. 1 IR difference spectra of CrAPO-11 loaded with [$^2H_3$]acetonitrile: (a) adsorption at 22 °C for 30 min with a pressure of 1.3 mbar and (b) with 0.05 mbar; (c) desorption at 22 °C for 15 min, (d) at 80 °C for 60 min and (e) at 300 °C for 60 min

Oxidation of primary benzylic alcohols with TBHP

Benzyl alcohol is an interesting substrate because the primary product benzaldehyde is susceptible to further oxidation to benzoic acid, especially when O_2 is the oxidant owing to the facile free-radical autooxidation of aldehydes. Table 4 indicates that CrAPO-5 and CrAPO-11 are both active and fairly selective catalysts for the oxidation of benzyl alcohol to benzaldehyde when TBHP is used as the oxidant. Substantial amounts of benzoic acid were also formed, which may arise from the chromium-catalysed autoxidation of the benzaldehyde, the O_2 being derived from competing decomposition of TBHP during the oxidation.

To obtain a high yield, a higher temperature (100 °C) and a TBHP : reactant ratio of 5 were employed. Under these conditions, CrAPO-11-catalysed oxidation of *p*-methoxybenzyl alcohol with TBHP gives *p*-methoxybenzoic acid in an 87% yield based on the reactant, but a lower selectivity on TBHP of 42%, indicating significant competing (homolytic) decomposition of the TBHP:



(1)

Oxidation of secondary alcohols with O_2

We reported previously that CrAPO-5-catalysed oxidations of secondary alcohols with TBHP at 85 °C gave the corresponding ketones in good to excellent selectivities with respect both to substrate and to TBHP.[17a] When the oxidation of α-methylbenzyl alcohol with TBHP was carried out in either air or an N_2 atmosphere, as shown in Fig. 2, no difference in the conversion or selectivity on the alcohol substrate was

Table 4 CrAPO-catalysed oxidation of benzyl alcohol with TBHP[a]

catalyst	turn-over frequency[b]	conversion (%)	selectivity (%) benz-aldehyde	selectivity (%) benzoic acid
CrAPO-5	15	43	62	38
CrAPO-11	13	47	63	37

[a] Conditions: benzyl alcohol, 2 mmol; TBHP, 4 mmol; catalyst, 0.02 mmol Cr; chlorobenzene (solvent), 10 ml; *T*, 60 °C; stirring, 1000 rev min^{-1}; reaction time, 5 h; in N_2. [b] Converted mol substrate mol^{-1} Cr in 1 h at 30% conversion.

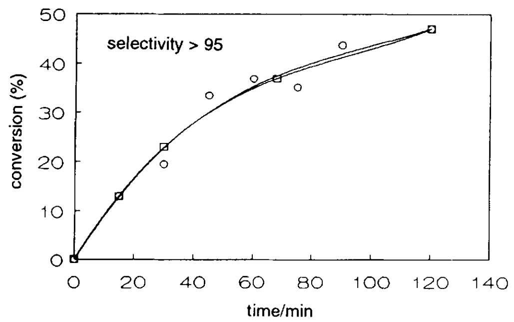
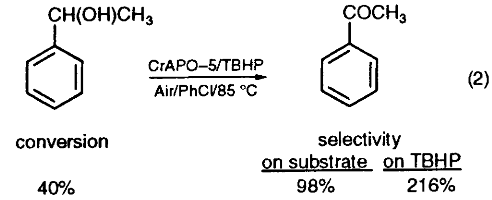


Fig. 2 Effect of reaction atmosphere on the oxidation of α-methylbenzyl alcohol with TBHP. Reaction atmosphere: ○, N_2 ; □, air. Conditions: α-methylbenzyl alcohol, 10 mmol; TBHP 10 mmol; CrAPO-5, 0.14 mmol Cr; chlorobenzene (solvent), 10 ml; *T*, 85 °C; stirring, 1000 rev min^{-1}, reaction time, 2 h.

observed. However, significant differences in selectivities on TBHP were observed. The selectivity on TBHP refers to the product obtained (mol), divided by TBHP consumed (mol). When the experiment was carried out in air, the selectivity on TBHP was 216% indicating that O_2 is also acting as an oxidant:

Reaction 2



Indeed, subsequent experiments showed (Table 5) that this was the case. Good to excellent selectivities on substrates were obtained at conversions of 26 to 78%. 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 pressure (9×10^5 Pa) 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.

Mechanism of alcohol oxidations in the absence of O_2

Evidence for a liquid-phase oxidation involving a free-radical chain mechanism is usually obtained by performing an experiment in the presence of a radical scavenger such as a substituted phenol.[28] As can be seen from Table 6, addition of 3% *p*-*tert*-butylphenol does not inhibit the CrAPO-11-catalysed selective oxidation of benzyl alcohol to benzaldehyde with TBHP, but improves both the selectivity to benzaldehyde and the efficiency of TBHP used. Therefore we conclude that the CrAPO-catalysed oxidation of alcohols mainly follows an oxygen-transfer mechanism.

Table 5 CrAPO-5-catalysed oxidation of secondary alcohols with O_2[a]

reactant	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; TBHP, 25 mmol; CrAPO-5, 3.65 mmol Cr; chlorobenzene (solvent), 65 ml; 3 Å molecular sieve (drying agent), 6 g; *T*, 110 °C; O_2 pressure, 5 atm; air, 20 atm; 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 rev min^{-1}; reaction time, 19 h.

Table 6 Effect of a radical scavenger on the selective oxidation of benzyl alcohol to benzyldehyde with TBHP[a]

catalyst	conversion (%)	selectivity (%) benz-aldehyde	benzoic acid	selectivity (%) (on TBHP[b])
none	4	79	21	—
CrAPO-11	60	62	38	63
CrAPO-11[c]	63	75	21	71

[a] Conditions: benzyl alcohol, 2 mmol; TBHP, 4 mmol; CrAPO-5, 0.06 mmol Cr; chlorobenzene (solvent), 10 ml; *T*, 60 °C; stirring, 1000 rev min^{-1}; reaction time, 16 h; in N_2. [b] Based on both benzaldehyde and benzoic acid. [c] 0.06 mmol of *p*-*tert*-butylphenol added.

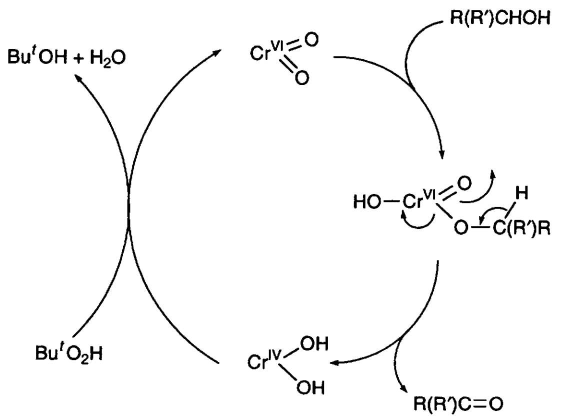
In addition, an appreciable amount of ketone was formed when using a relatively large amount of CrAPO-5 for a liquid-phase adsorption measurement with a secondary alcohol at the reaction temperature in the absence of any other oxidant. This indicates that the active oxidant in these oxidations is an oxochromium(VI) species.

An oxometal mechanism is generally accepted for the oxidation of alcohols when using Cr^{VI} as stoichiometric oxidant.[3] On the other hand, Muzart[29] has suggested a peroxometal mechanism for the oxidation of secondary alcohols with TBHP catalysed by CrO_3. According to this mechanism, a *tert*-butylperoxochromium species interacts with an alcohol to form an alkoxy-*tert*-butylperoxychromium intermediate which finally produces the ketone and *tert*-butyl alcohol. In this catalytic cycle the formal oxidation state of Cr^{VI} is maintained.

We propose that the CrAPO-catalysed oxidation of alcohols with TBHP in the absence of O_2 proceeds *via* a heterolytic mechanism involving β-hydrogen elimination from an oxochromium(VI) alkoxide followed by reoxidation of the reduced chromium(IV) by TBHP. The catalytic cycle is shown in Scheme 1.

Mechanism of alcohol oxidations in the presence of O_2

In the oxidation of alcohols catalysed by a microporous solid catalyst, the effect of products and byproducts on the oxidation rates may be important. We performed a CrAPO-5-catalysed oxidation of α-methylbenzyl alcohol by adding one equivalent (based on the reactant) of acetophenone, *tert*-



Scheme 1 Mechanism of alcohol oxidations in the absence of O_2

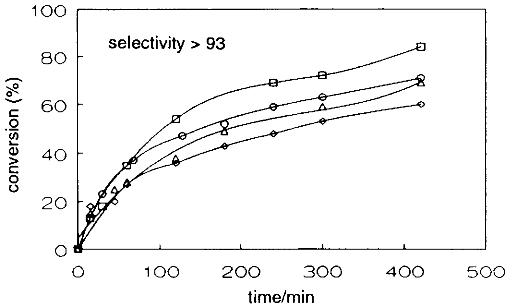


Fig. 3 Effect of additives on the oxidation of α-methylbenzyl alcohol with TBHP. Additives (10 mmol): □, H_2O; ○, none; △, *tert*-butyl alcohol; ◇, acetophenone. Conditions: α-methylbenzyl alcohol, 10 mmol; TBHP, 10 mmol; CrAPO-5, 0.14 mmol Cr; chlorobenzene (solvent), 10 ml; *T*, 85 °C; stirring, rev min^{-1}; reaction time, 7 h; in air.

butanol and water into the reaction mixture. The oxidation was carried out at 85 °C for 7 h in air. As can be seen in Fig. 3, the addition of acetophenone or *tert*-butyl alcohol somewhat decreases the oxidation rate, indicating a slight inhibition of the oxidation by the acetophenone or *tert*-butanol. Surprisingly, the addition of water slightly increases the oxidation rate. No leaching of chromium from CrAPO-5 was found after treatment of the catalyst with NaCl aqueous solution (see Table 3). Moreover, there is no difference in acetophenone selectivities between the oxidation with and without the addition of water. Recently Csányi and Jáky[30] reported that small quantities of water alone could promote liquid-phase autoxidations of hydrocarbons probably owing to molecule-induced homolysis of traces of hydroperoxide initiators.

In TBHP alcohol oxidations in the presence of O_2 both the CrAPO-5 catalyst and the TBHP are necessary to achieve an efficient oxidation as shown for α-ethylbenzyl alcohol in Table 7.

A possible reaction mechanism[31] consistent with the experimental observations is as follows:

$$Cr^{VI}{=}O + R^1R^2(OH)CH \rightarrow Cr^{IV} + R^1R^2C{=}O + H_2O$$

$$Cr^{IV} + Bu^tO_2H \rightarrow Cr^{VI}{=}O + Bu^tOH$$

$$Cr^{IV} + Bu^tO_2H \rightarrow Cr^{V}OH + Bu^tO^{\bullet}$$

$$Bu^tO^{\bullet} + R^1R^2(OH)CH \rightarrow R^1R^2(OH)C^{\bullet} + Bu^tOH$$

$$R^1R^2(OH)C^{\bullet} + O_2 + R^1R^2(OH)CH \rightarrow R^1R^2(OH)CO_2H + R^1R^2(OH)C^{\bullet}$$

$$R^1R^2(OH)CO_2H + Cr^{IV} \rightarrow Cr^{VI}{=}O + R^1R^2C{=}O + H_2O$$

We assume that the reactions involve oxidation of the alcohols by oxochromium(VI) followed by reoxidation of the reduced chromium(IV) by TBHP or the hydroxyalkyl hydroperoxide[32] derived by the chromium-catalysed autoxidation of the alcohol. TBHP functions as both an oxidant and an initiator.

Accessibility of active sites and stability of catalysts

Oxidation of α-methylbenzyl alcohol catalysed by the homogeneous catalyst $Cr(acac)_3$ in the presence of a triphenylmethyl hydroperoxide oxidant give a conversion of 40% in a selectivity of 43% to acetophenone. In contrast, CrAPO-5 under the same conditions gave virtually no oxidation (Fig. 4), which is consistent with the reaction taking place within the micropores of CrAPO-5.

Table 7 Oxidation of α-ethylbenzyl alcohol to propiophenone with O_2 [a]

catalyst	TBHP (mol%)[b]	conversion (%)	selectivity (%)
CrAPO-5	10	38	90
CrAPO-5	0	11	93
none	0	5	85

[a] Conditions as given in Table 5; footnote b. [b] Based on the α-ethylbenzyl alcohol introduced initial.

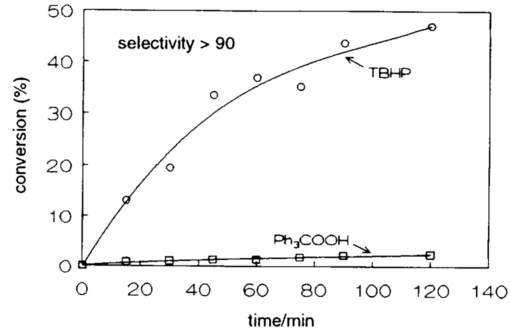


Fig. 4 Accessibility of Cr^{VI} in CrAPO-5

In one experiment with α-methylbenzyl alcohol as reactant and TBHP as oxidant, the CrAPO-5 catalyst was filtered, washed three times with chlorobenzene and recalcined at 500 °C for 5 h before reuse. During the recycles the amount of reused catalyst was gradually reduced owing to mechanical losses, and all chemicals used were proportionally reduced based on the exact amount of the reused catalyst for the next cycle. Under the conditions given in the experimental section, the CrAPO-5 was recycled four times without apparent loss of activity or selectivity (see Table 8).

The Brønsted acidity of CrAPO-5 had little effect on the selectivity of α-methylbenzyl alcohol oxidation in the liquid phase. However, on recycling the CrAPO-5 without recalcination, it became more active but less selective (Table 9). This may be due to acid-catalysed side reactions, *e.g.*, the dehydration of α-methylbenzyl alcohol to styrene.

Fig. 5 shows XRD spectra of CrAPO-5 before and after the oxidation of α-methylbenzyl alcohol. Both spectra are essentially the same.

Fig. 6 shows DRS spectra of CrAPO-5 before and after the oxidation of α-methylbenzyl alcohol. In the latter case, the catalyst was not recalcined before measurement. The strong absorption bands around 270 and 340 nm represent the two charge-transfer transitions of Cr^{VI}. The spectra showed that most of the chromium remained in the hexavalent state within

Table 8 Recycles of CrAPO-5 in the oxidation of α-methylbenzyl alcohol to acetophenone with TBHP in N_2 [a]

	conversion (%)		selectivity (%)	
recycles[b]	substrate[c]	TBHP	substrate	TBHP
1	77	83	96	89
2	79	86	95	92
3	75	77	90	89
4	74	80	93	91

[a] Conditions as given in the experimental section. [b] Catalyst was recalcined at 500 °C for 5 h before reuse. [c] Conversion of substrate based on the amount of TBHP employed.

Table 9 Effect of recalcination during CrAPO-5 recycles in the oxidation of α-methylbenzyl alcohol with TBHP in air[a]

recycles[b]	conversion (%)	selectivity (%)	Cr (wt.%)[c]
1	65	95	2.08
2	79	93	—
3	83	86	2.00

[a] Conditions as given in Fig. 3. [b] Catalyst was not recalcined before reuse. [c] Fresh catalyst, 2.08 Cr(wt.%); ICP accuracy is ±3%.

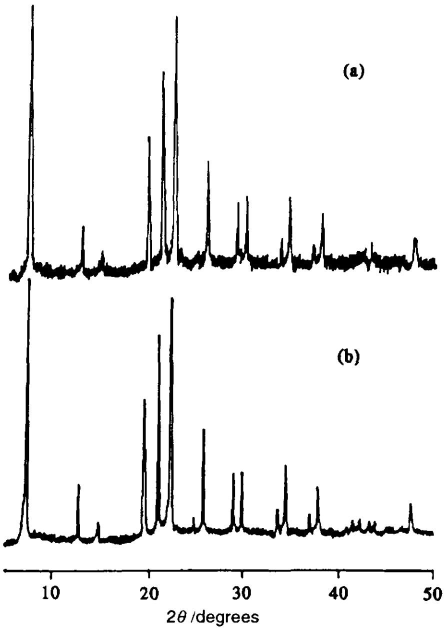


Fig. 5 XRD spectra of CrAPO-5 before (a) and after (b) the oxidation of α-methylbenzyl alcohol. (The CrAPO-5 samples measured are the fresh one, and the same catalyst after the first cycle with recalcination before the measurement; those shown in Table 8.)

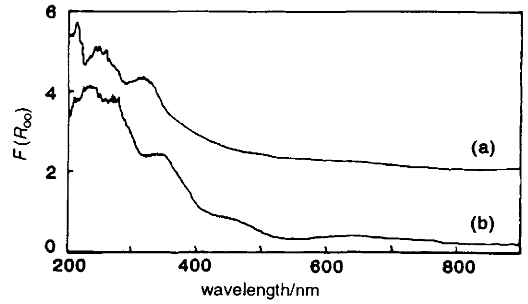


Fig. 6 DR spectra of CrAPO-5 before (b) and after (a) the oxidation of α-methylbenzyl alcohol. (The CrAPO-5 samples measured are the fresh one and the same catalyst after the first cycle without recalcination before the measurement; those shown in Table 8.)

the $AlPO_4$ framework after the oxidation. The green–yellow of the used catalyst, compared with yellow for the freshly prepared CrAPO-5, suggested the possible presence of small amounts of Cr^{III}. However, we note that the colour change from yellow to green–yellow was also observed on adding a small amount of water to a (yellow) sample of calcined CrAPO.

Fig. 7 shows DRS spectra of CrAPO-11 before and after the oxidation of benzyl alcohol under different conditions. The CrAPO-11 used was not recalcined before the measurements. Interestingly, when the oxidation was carried out in the absence of a radical scavenger one (*ca.* 340 nm) of the two absorption bands of Cr^{VI} was greatly reduced. In contrast the intensity of the absorption bands remained almost unchanged when the catalyst was used in the oxidation with TBHP, in the absence of O_2, using *p-tert*-butylphenol as the radical scavenger. Presumably the inhibition of a competing free-radical reaction makes it easier to reoxidize Cr^{IV} to Cr^{VI} by TBHP.

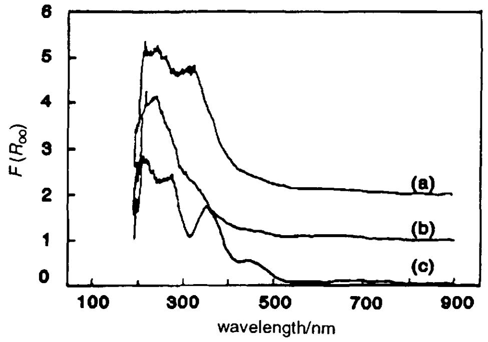


Fig. 7 DR spectra of CrAPO-11 before and after the oxidation of benzyl alcohol. (a) After the oxidation in the presence of a radical scavenger; (b) after the oxidation in the absence of a radical scavenger and (c) before the oxidation. (The CrAPO-11 samples measured are the fresh one and the same catalyst after the oxidation without recalcination before the measurement, those shown in Table 6.)

Conclusion

CrAPO-5 and CrAPO-11 were hydrothermally synthesized. Characterization by XRD, SEM, *n*-butane and N_2 absorption. IR spectroscopy of [$^2H_3$]acetonitrile adsorption and DRS showed that these samples are pure and possess high crystallinities and pore volumes. Calcination of the samples leads to significant increase of weak Brønsted-acid (P—OH) sites, and the formation of strong Lewis-acid sites which are probably $AlPO_4$ framework-bonded Cr^{VI}.

The CrAPO-catalysed oxidation of alcohols with TBHP in the absence of O_2 proceeds *via* a heterolytic mechanism involving β-hydrogen elimination from an oxochromium(VI) alkoxide followed by reoxidation of the reduced chromium(IV) by TBHP, giving high selectivities with respect both to substrate (>89%) and to TBHP (>88%). Evidence is provided in support of the alcohol oxidation taking place essentially within the micropores of CrAPO-5.

In the presence of O_2, the reactions involve oxidation of the alcohols by dioxochromium(VI) followed by reoxidation of the reduced chromium(IV) by TBHP or the hydroxyalkyl hydroperoxide derived from chromium-catalysed autoxidation of the alcohol. In this case, TBHP functions as both an oxidant and an initiator. The CrAPO-5-catalysed oxidation of alcohols with O_2 gives the corresponding ketones in selectivities of 72–97% at conversions of 26–78% when only 10 mol% of TBHP is added.

When the reactions are complete, the crystal structure of CrAPO-5 is unchanged and most of the chromium in either CrAPO-5 or CrAPO-11 remains in the hexavalent state within their frameworks, especially when a free-radical type of oxidation is circumvented by employing TBHP as the oxidant in the presence of a radical scavenger. CrAPO-5 is a stable and recyclable solid catalyst for the selective liquid-phase oxidation of alcohols to the corresponding ketones.

References

1 R. A. Sheldon and J. K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981.
2 K. B. Wiberg, in *Oxidation in Organic Chemistry, Part A*, ed. K. B. Wiberg, Academic Press, New York, 1965, p. 69.
3 G. Cainelli and G. Cardillo, *Chromium Oxidations in Organic Chemistry*, Springer Verlag, Berlin, 1984.
4 G. Cainelli, G. Cardillo, M. Orena and S. Sandri, *J. Am. Chem. Soc.*, 1976, **98**, 6737.
5 S. Kanemoto, H. Saimoto, K. Oshima and H. Nozaki, *Tetrahedron Lett.*, 1984, **25**, 3317.
6 J. Muzart, *Chem. Rev.*, 1992, **92**, 113.
7 E. J. Corey, E. P. Barrette and P. A. Magriotis, *Tetrahedron Lett.*, 1985, **26**(48), 5855.
8 S. Kanemoto, K. Oshima, S. Matsubara, K. Takai and H. Nozaki, *Tetrahedron Lett.*, 1983, **24**, 2185.
9 S. Kanemoto, S. Matsubara, K. Takai, K. Oshima, K. Utimoto and H. Nozaki, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 3607.
10 S. Kanemoto, H. Saimoto, K. Oshima and H. Nozaki, *Tetrahedron Lett.*, 1984, **25**, 3317.
11 F. Figueras, *Catal. Rev., Sci. Eng.*, 1988, **30**, 457.
12 R. A. Sheldon and J. Dakka, *Catal. Today*, 1994, **19**, 215.
13 B. M. Choudary, A. Durga Prasad and V. L. K. Valli, *Tetrahedron Lett.*, 1990, **31**(40), 5785.

14 B. M. Choudary, V. L. K. Valli and A. Durga Prasad, *J. Chem. Soc., Chem. Commun.*, 1990, 721.

15 B. M. Choudary and V. L. K. Valli, *J. Chem. Soc., Chem. Commun.*, 1990, 1115.

16 B. M. Choudary, V. L. K. Valli and A. Durga Prasad, *J. Chem. Soc., Chem. Commun.*, 1990, 1186.

17 (*a*) J. D. Chen, J. Dakka, E. Neeleman and R. A. Sheldon, *J. Chem. Soc., Chem. Commun.*, 1993, 1379; (*b*) R. A. Sheldon, J. D. Chen and J. Dakka, International Patents PCT/NL94/06319, 1994 and (*c*) PCT/NL93/00199, 1993.

18 J. D. Chen and R. A. Sheldon, *J. Catal.*, 1995, **153**, 1; and references cited therein.

19 K. B. Sharpless and T. R. Verhoeven, *Aldrichimica Acta*, 1979, **12**, 63.

20 J. G. Hill, B. E. Rossiter and K. B. Sharpless. *J. Org. Chem.*, 1983, **48**, 3607.

21 D. Rai, B. M. Sass and D. A. Moore, *Inorg. Chem.*, 1987, **26**, 345.

22 B. Kraushaar-Czarnetzki, Ph.D. Thesis, Eindhoven University of Technology, Eindhoven, The Netherlands, 1989.

23 J. S. T. Mambrim, E. J. S. Vichi, H. O. Pastore, C. U. Davanzo, H. Vargas, E. Silva and O. Nakamura, *J. Chem. Soc., Chem. Commun.*, 1991, 922.

24 J. F. Hemidy and D. Cornet, *J. Chim. Phys.*, 1974, **71**, 739.

25 J. Jänchen, M. J. Haanepen, M. P. J. Peeters, J. H. M. C. van Wolput, J. P. Wolthuizen and J. H. C. van Hooff, in *Studies in Surface Science and Catalysis* ed. J. Weitkamp, H. G. Karge, H. Pfeifer and W. Hölderich, Elsevier, Amsterdam, 1994, vol. 84, p. 373.

26 J. Jänchen, M. P. J. Peeters, J. H. M. C. van Wolput, J. P. Wolthuizen, J. H. C. van Hooff and U. Lohse, *J. Chem. Soc., Faraday Trans.*, 1994, **90**(7), 1033.

27 U. Cornaro, P. Jiru, Z. Tvaruzkova and K. Habersberger, in *Zeolite Chemistry and Catalysis*, ed. P. A. Jacobs, N. I. Jaeger and L. Kubelkova, Elsevier, Amsterdam, 1991, p. 165.

28 J. A. Howard, *Adv. Free Radical Chem.*, 1972, **4**, 126.

29 J. Muzart, *Tetrahedron Lett.*, 1987, **28**, 2133.

30 L. J. Csányi and K. Jáky, *J. Catal.*, 1993, **141**, 721.

31 R. S. Drago, *Coord. Chem. Rev.*, 1992, **117**, 185.

32 J. A. Howard and S. Koreck, *Can. J. Chem.*, 1970, **48**, 2165.

Paper 5/06434A; *Received* 29*th September*, 1995