Chromium substituted AlPO-11: synthesis, characterisation and its application in oxidation reactions

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Isomorphous substitution of Cr^{3+} for Al^{3+} in $AlPO_4$-11 framework followed by calcination converts Cr^{3+} to dioxochromium (VI) by incorporating extra framework O^{2-} ligands, generating Brønsted acidity. CrAPO-11 catalyses oxidation of phenol to dihydroxybenzenes to the extent of 28%.

Keywords: isomorphous substitution; $AlPO_4$-11 molecular sieve; phenol; dihydroxybenzene

1. Introduction

Isomorphous substitution of transition metal ions into the framework of $AlPO_4$s and their catalytic properties are being the subject of numerous studies [1–5]. The initial pH of $AlPO_4$-gel is weakly acidic, which promotes incorporation of a hydrolysable metal cations into the framework and inhibits the precipitation of spurious hydroxides and oxides [6]. However,the importance of Ti and Cr as redox metals has been realised only recently [7–9]. This work deals with the synthesis of CrAPO-11, its properties with respect to the oxidation state of chromium and its application in oxidation reactions.

2. Experimental

2.1. Synthesis of CrAPO-11

Aluminium isopropoxide, di-*n*-propylamine (DPA), phosphoric acid and chromium nitrate were used as the starting materials for the synthesis. Based on preliminary experiments, the following molar ratio of initial gel composition was chosen: $0.034Cr_2O_3 : Al_2O_3 : P_2O_5 : DPA : 40H_2O$.

In a typical synthesis, half of the required amount of water was added to aluminium isopropoxide and allowed to stand overnight, stirred vigorously for 2 h. Phosphoric acid mixed with the required amount of chromium nitrate was added to the above gel and stirred for a further 2 h. To this mixture DPA was added and again stirred for 2 h. The gel was transferred to a stainless steel autoclave and its pH was adjusted to 3.5 by adding HCl. The autoclave was closed and kept at 200°C for 24 h. The crystalline solid product was filtered, washed and dried at 110°C for 3 h.

2.2. Characterisation of CrAPO-11

The synthesised material was characterised by XRD (Philips X-ray diffractometer PW 1050 with microprocessor controller) using Cu K_α radiation, scanning electron microscopy (SEM) using a Hitachi S2400 scanning microscope, ^{27}Al and ^{31}P MAS NMR using a Bruker MSL 200 spectrometer at 8.3 kHz, diffuse reflectance spectroscopy (DRS) using a Cary-2390 UV–vis spectrophotometer, FTIR with a Bruker IFS 66V FTIR spectrometer using the KBr pellet technique and TGA using a Mettler-TA 2000 series. Elemental analysis was performed using inductively coupled plasma-emission spectrometry (ARL 3410 with minitorch). The acidity and the distribution of acid sites over oxidised and reduced CrAPO-11 were determined thermogravimetrically with pyridine as the base. The surface area and the pore volume were determined by conventional BET method. Reduction of the catalyst was performed by H_2 with a flow rate of 10 ml/min at 400°C.

3. Results and discussion

The XRD spectrum of as-synthesised CrAPO-11 given in fig. 1 does not differ much from that of as-synthesised $AlPO_4$-11, showing that it is highly crystalline. The SEM picture (fig. 2) shows large growth aggregates (10–15 μm) made up of small prisms. The individual prisms are 1.5–3 μm in length. The peaks at 35.11 and −29.80 ppm for the aluminium and phosphorus respectively, exhibited in the ^{27}Al and ^{31}P MAS NMR spectra (figs. 3 and 4), show that aluminium and phosphorus in CrAPO-11 are in tetrahedral coordination. The surface area of calcined CrAPO-11, determined by the BET method, was 272 m^2/g. The pore volumes obtained by O_2 (at $p/p_0 = 0.4$ at liquid N_2 temperature) and cyclohexane adsorptions (at $p/p_0 = 0.4$ at

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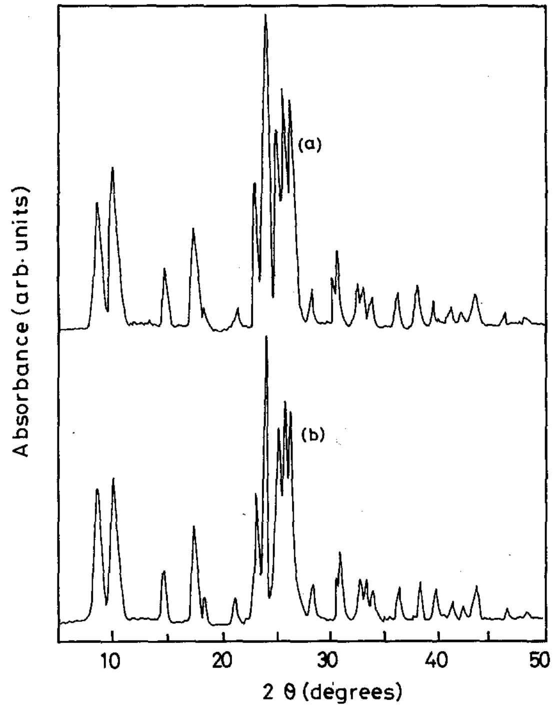

Fig. 1. XRD patterns of (a) $AlPO_4$-11 as synthesised, (b) CrAPO-11 as synthesised.

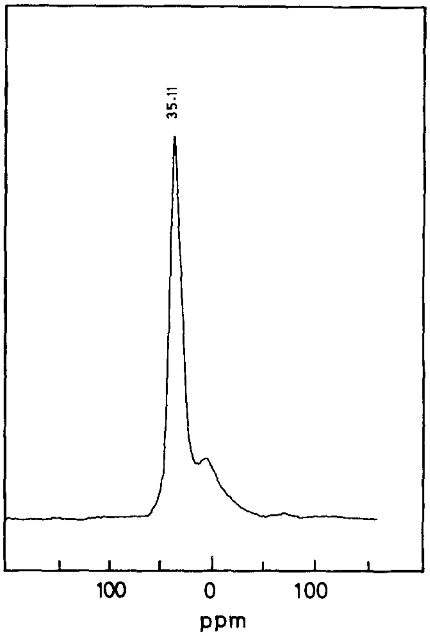

Fig. 3. ^{27}Al MAS NMR spectrum of as-synthesised CrAPO-11.

room temperature) were 0.087 and 0.068 cm^3/g respectively. The chemical composition by ICP analysis gives the following molar ratio: $0.03Cr_2O_3 : 0.97Al_2O_3 : P_2O_5$. The data obtained by chemical analysis gives good balance of (Cr + Al) to phosphorus indicating isomorphous substitution of aluminium by chromium and absence of chromium phosphate. Further, the absence of non-framework chromium as Cr_2O_3 in the as-synthesised and calcined samples is evident from the absence of the peaks around 700 cm^{-1} and at 951 and 906 cm^{-1} in FTIR. If Cr_2O_3 exists, it would be converted by calcination to CrO_3, which could be leached out by washing with water [10]. Analysis of the leachate by ICP and chemical

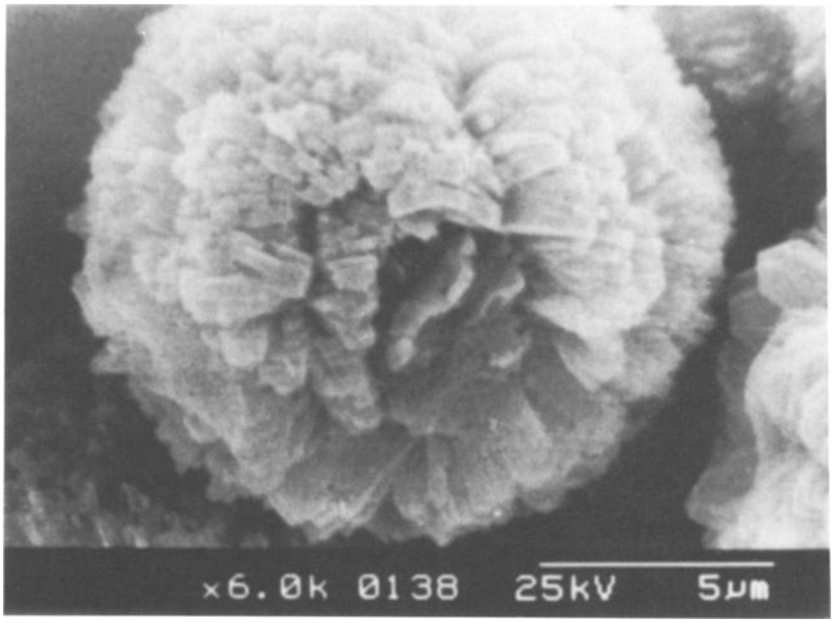

Fig. 2. SEM picture of as-synthesised CrAPO-11.

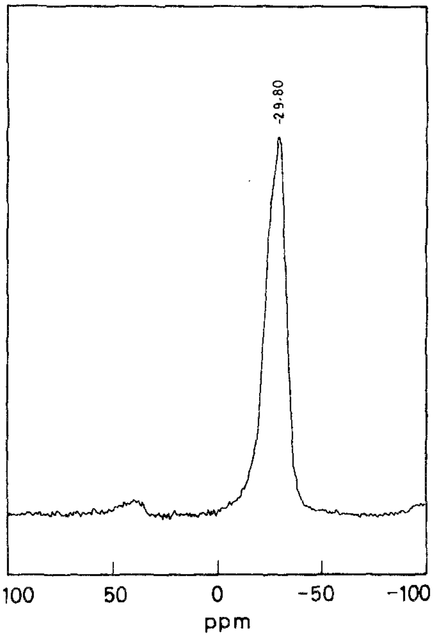

Fig. 4. ^{31}P MAS NMR spectrum of as-synthesised CrAPO-11.

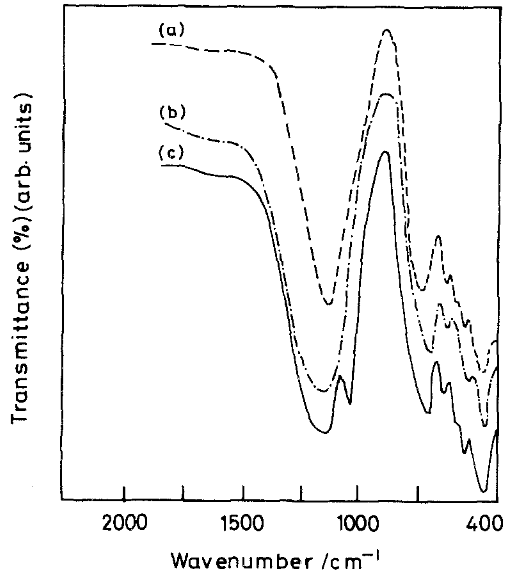

Fig. 6. FTIR spectra of (a) $AlPO_4$-11, (b) CrAPO-11 as synthesised, (c) CrAPO-11 calcined in air at 550°C for 12 h.

method showed the absence of chromium. The IR spectrum of the calcined and washed CrAPO-11 was not different from that of calcined CrAPO-11.

The diffuse reflectance spectrum (fig. 5) of the as-synthesised sample gives peaks at 410 nm and at 580 nm which were assigned to Cr^{3+} in the octahedral position [11], which is similar to that of Al^{3+} in VPI-5, AlPO-11 and SAPO-34 within the framework [12,13]. However, heating under vacuum at 400°C, gives a peak at 1200 nm in DRS, which is assigned to chromium in the tetrahedral sites [14]. This was further confirmed by the absence of a peak in ESR [15]. Upon calcination for 12 h, Cr^{3+} is oxidised to Cr^{6+} yielding a band at 370 nm in the DRS and no peak in the ESR spectrum.

The peak at 726 cm^{-1} in the FTIR (fig. 6) is due to a combination of Al–O and P–O vibrations [16] in AlPO-11 which is shifted to 736 cm^{-1} in CrAPO-11 indicating the

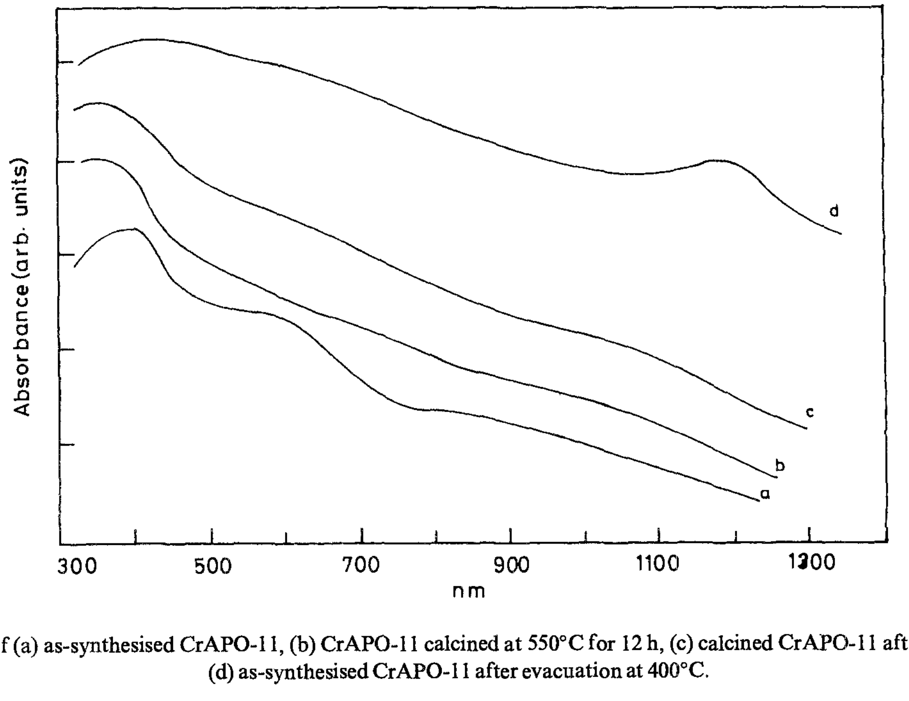

Fig. 5. DRS spectra of (a) as-synthesised CrAPO-11, (b) CrAPO-11 calcined at 550°C for 12 h, (c) calcined CrAPO-11 after washing with water, (d) as-synthesised CrAPO-11 after evacuation at 400°C.

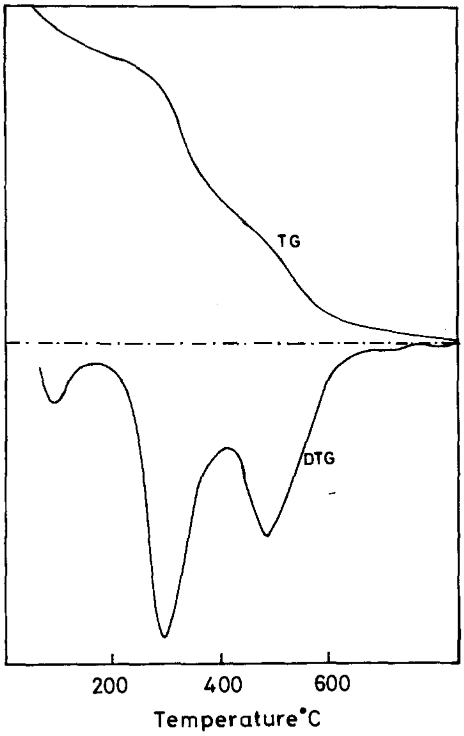

Fig. 7. TG curve of as-synthesised CrAPO-11.

possibility of incorporation of chromium into the AlPO-11 framework. The appearance of the peak at 1010 cm^{-1} for calcined CrAPO-11 and its absence in as-synthesised CrAPO-11 confirms the formation of oxochromium (VI) during calcination by incorporation of O^{2-} ligands. This peak at 1010 cm^{-1} is assigned to the Cr=O vibration [17]. To balance the negative charge created by the formation of oxochromium, Brønsted acid sites are generated.

TG studies of neutral $AlPO_4$-11 show weight losses only at two temperatures [9,18], one due to desorption of physisorbed water molecules and the other due to removal of physically adsorbed template molecules. In the case of divalent metal substituted $AlPO_4$-11, the loss occurs in more than two stages and the weight losses at higher temperatures (> 400°C) are attributed to the degradation of protonated or metal complexed amines [19,20]. The observed weight loss in this investigation (fig. 7) at a relatively higher temperature (470°C) is similar to the weight loss suffered by MeAPO-11 (Me = divalent metals) which may be attributed to removal of protonated amine from CrAPO-11. This lends support to the creation of Brønsted acid sites during calcination [21].

Moreover, the oxidised form of CrAPO-11 possesses stronger acid sites determined by pyridine adsorption, while the acidity of the reduced form is almost the same as that of neutral AlPO-11 (table 1), which further confirms the above observation.

Liquid phase oxidation of phenol, toluene and benzene by H_2O_2 over oxidised and reduced CrAPO-11 (reduced with H_2 at 400°C for 4 h, and showing a peak for Cr^{5+} in the ESR spectrum) was carried out and the results are presented in table 2. Compared to oxidised

Table 1
Distribution of acid sites over CrAPO-11 and AlPO-11

Catalyst	< 200°C weak (mmol/g)	200–400°C medium (mmol/g)	> 400°C strong (mmol/g)	Total acidity (mmol/g)
oxidised CrAPO-11	0.14	0.08	0.05	0.27
reduced CrAPO-11 [a]	0.12	0.02	–	0.14
AlPO-11	0.11	–	–	0.11

[a] Reduced with H_2 (flow rate 10 ml/min) at 400°C for 8 h.

Table 2
Liquid phase oxidation with H_2O_2 catalysed by CrAPO-11 [a]

Catalyst	Reactant	Conversion (mol%)	Product	Yield (mol%)
oxidised CrAPO-11	phenol	19.0	hydroquinone	9.5
			catechol	8.7
reduced CrAPO-11	phenol	28.7	hydroquinone	17.0
			catechol	10.8
oxidised CrAPO-11	toluene	6.4	*o*-cresol	3.0
			p-cresol	3.2
reduced CrAPO-11	toluene	7.7	*o*-cresol	3.4
			p-cresol	3.8
oxidised CrAPO-11	benzene	5.0	phenol	4.9
reduced CrAPO-11	benzene	7.8	phenol	7.6

[a] Conditions: catalyst 200 mg; H_2O_2/reactant mole ratio = 3; T = 80°C for phenol, 55°C for toluene and benzene oxidation. Products were analysed by HP-5890 GC (OV.17 column). Solvent: water (5 ml) for phenol, acetonitrile (12 ml) for toluene, acetone (12 ml) for benzene. Reaction time: 5 h for phenol, 12 h for toluene and benzene.

CrAPO-11, reduced CrAPO-11 gives a comparatively higher amount of hydroxy compounds.

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