Porous Chromia-Pillared \( \alpha \)-Tin Phosphate Materials

P. MAIRELES-TORRES, P. OLIVERA-PASTOR,* E. RODRÍGUEZ-CASTELLÓN, AND A. JIMÉNEZ-LÓPEZ

Departamento de Química Inorgánica, Cristalografía y Mineralogía, Facultad de Ciencias, Universidad de Málaga, 29071 Málaga, Spain

AND A. A. G. TOMLINSON*

I.T.S.E., Area della Ricerca di Roma, C.N.R., C.P. 10 Monterotondo Stazione 00016 Rome, Italy

Received January 8, 1991; in revised form May 14, 1991

The reactions of Cr(OAc)\(_3\) (OAc\(^-\) = CH\(_3\)OCONH\(_2\)\(^-\)) solutions with colloidal suspensions of tetramethylammonium \( \alpha \)-tin phosphate (\( \alpha \)-Sn\(\left[\text{Me}_4\text{N}\right]_{0.9-1.1} \cdot \text{H}_2\text{O} \cdot \text{PO}_4\text{O}_4 \cdot n\text{H}_2\text{O} = "\text{Me}_4\text{N-SnP}"\)) have been investigated over a wide range of [Cr(OAc)\(_3\)] : [Me\(_4\text{N-SnP}\)] ratios, Cr(OAc)\(_3\) concentrations, and heating conditions. On aging + reflux, Me\(_4\text{N-SnP}\) takes up oligomeric Cr\(^{3+}\) species to give crystalline, highly expanded materials having interlayer distances between 24 and 33 \( \AA \). Conversely, Cr(OAc)\(_3\) solutions treated in the same way, but separately, and then added to colloidal Me\(_4\text{N-SnP}\) gave composites with little expansion (interlayer distance, \( d_{002} = 15 \) \( \AA \)), collapsing to nonporous oxide-phosphates (\( d_{002} = 10 \) \( \AA \)) on calcination. Separately polymerized CrCl\(_3\)/NaOH or [Cr\(_3\)(OAc)\(_3\)(OH)\(_3\)]\(^+\) (standard precursors in clay-pillaring) also gave poorly defined delaminated materials. Chemical, TGA/DTA, and visible/near UV spectroscopic evidence shows the intercalates are polyhydroxyacetato-Cr\(^{3+}\) species, and some may be formulated as [Cr\(_3\)(OH)\(_4\)(OAc)]\(^{2+}\), [Cr\(_5\)(OH)\(_6\)(OAc)]\(^{3+}\), and [Cr\(_7\)(OH)\(_6\)(OAc)]\(^{5+}\). They are formed \textit{in situ} on the \( \alpha \)-tin phosphate surfaces; possible orientations within the layers (taking into account the presence of zeolite-type water) is discussed. Calcination under \( \text{N}_2 \) at 400°C gives chromium oxide-pillared materials with \( d_{002} \) in the ranges 12.5–14.0 \( \AA \) (from precursors prepared at higher Cr\(^{3+}\) concentrations) or 15–20 \( \AA \) (from precursors at lower Cr\(^{3+}\) concentrations). The surface areas (BET, \( \text{N}_2 \), 77K): 264–386 m\(^2\) g\(^{-1}\), compare well with analogues in clay chemistry (150–400 m\(^2\) g\(^{-1}\)). Pore-sized distributions (cylindrical pores model) are narrow, \( >70\% \) of pores having widths \(<40 \) \( \AA \). Calcination in air leads to segregation of Cr\(_2\)O\(_3\), which, after washing gives materials having wider pore-size distributions and lower surface areas. The ion-exchange properties of selected chromia-pillared materials with K\(^+\), Co\(^{2+}\), and Pr\(^{3+}\) have been investigated. The results are compared with models of porosity. © 1991 Academic Press, Inc.

Introduction

The formation of porous, thermally stable materials by calcining intercalated polyhydroxy-cation precursors in layered solids, known as “pillaring,” is an attractive means of obtaining acids with catalytic properties (\( f \)). Most work concerns smectite clays pillared by metal oxides, and chromia pillars have been particularly studied. In early work hydrolyzed Cr(III) solutions were used (2), but only recently have reproducible preparations of chromia-pillared smectites with high free heights (i.e., accessible height in the interlayer: interlayer distance–layer thickness) been re-
ported (3). Manipulating the cavity-acidity characteristics in layered phosphates provides an alternative to smectite clays, and should lead to different materials characteristics. However, unlike smectites, layered phosphates require preswelling or colloidalization for precursor intercalation reactions to be successful (4). [Me₄N]⁺ forms a stable colloid with α-Sn(HPO₄)₂·H₂O, of formula α-Sn[Me₄N]₀.₉·₁.₀H₁.₁·₀.₄(PO₄)₂·₇H₂O ("Me₄N-SnP"), which has recently been found to be useful for preparing intercalated Al₁₃–Keggin ion precursors (5). We here describe its use for obtaining chromia-pillared α-tin phosphates having porous structures with narrow pore-size distributions.

Experimental

**Materials**

Me₄N–SnP was freshly prepared as in Ref. (5). [Cr₃O(OH₂)₃(OAc)₆]Cl · 5H₂O was prepared by the method of Earnshaw et al. (6). Analysis: found C, 19.9; H, 5.2; Cl, 5.6; Cr, 21.1%; required for C₁₂H₃₁ClCr₃O₂₂: C, 19.9; H, 5.0; Cl, 4.9; Cr, 21.6%. Chromium(III) acetate was a Carlo Erba "pro analysi" product and was used as received. All other products were commercial products of the best available purity.

**Intercalation of Cr(III) Species into α-Tin Phosphate**

In preliminary experiments, aqueous Cr(OAc)₃ solutions were aged and/or refluxed separately and then added to Me₄N–SnP suspensions at 25°C. For all conditions, including very long reflux times, a material with d₀₀₂ = 15 Å, collapsing on calcination at 200°C to a nonporous one having d₀₀₂ = 10.3 Å, was obtained.

Direct reaction of aqueous Cr(OAc)₃ solutions with Me₄N–SnP suspensions under various conditions was then systematically explored using classical batch methods. Combining aging + reflux of the mixtures led to more ordered solids (high intensity d₀₀₂ reflection in XRD, characteristic of layered phosphates). The uptake curve for [Cr³⁺]: [Me₄N–SnP] mixtures varying between 11.6 and 276.9 meq Cr³⁺ added/g SnP₂O₇ submitted to reflux (1 day) is shown in Fig. 1. (Mixed "forcing" conditions, i.e., aging of the mixture at 25°C, followed by heating at 60°C, and then final reflux for 1 day, gave the same results.) Chromium concentrations in solution before and after uptake were monitored by colorimetry. After cooling the mixture, the solids corresponding to points 1–7 were filtered off (all were dirty green in color), washed well with water, air-dried, analyzed (C,H,N; TGA/DTA), calcined under air or nitrogen, and again analyzed. Analyses are listed in Table I.

The change in uptake with different chromium solution concentration was then followed in the region around points 4 and 5 of Fig. 1 (i.e., where lower [Cr(OAc)₃]: [Me₄N–SnP] ratios gave materials with higher chromium content and higher basal expansions). Samples 4a and 5a were separated and treated exactly as before. Subsequent work showed that refluxing for 4 days (to ensure complete polymerization) gave the same results.

![Fig. 1. Uptake of hydrolyzed Cr(OAc)₃ species by Me₄N–SnP. All points obtained under reflux for 1 day. Points 4a and 5a refer to Cr³⁺ solutions at lower concentrations (see text).](image-url)
TABLE I

<table>
<thead>
<tr>
<th>Sample</th>
<th>[Cr^{3+}] \textsuperscript{a} (mol dm\textsuperscript{-3})</th>
<th>meq Cr^{3+} added/g</th>
<th>meq Cr^{3+} taken up/g</th>
<th>d\textsubscript{002}\textsuperscript{b} (\textdegree)</th>
<th>OAc⁻/Cr^{3+}\textsuperscript{c}</th>
<th>Suggested oligomer species</th>
<th>(\lambda_{\text{max}}) (nm)</th>
<th>(d_{002}) after calcination \textsuperscript{d} (\textdegree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.02</td>
<td>11.6</td>
<td>11.5</td>
<td>0.25</td>
<td>—</td>
<td>[Cr\textsubscript{3}(OH)\textsubscript{4}(OAc)\textsubscript{3}]²⁺; (Cr\textsubscript{4})</td>
<td>593.424</td>
<td>14.0</td>
</tr>
<tr>
<td>2</td>
<td>0.03</td>
<td>23.1</td>
<td>22.8</td>
<td>0.35</td>
<td>—</td>
<td>(Cr\textsubscript{4}) + (Cr\textsubscript{3})</td>
<td>590.419</td>
<td>—</td>
</tr>
<tr>
<td>3</td>
<td>0.05</td>
<td>46.2</td>
<td>27.0</td>
<td>0.46</td>
<td>—</td>
<td>[Cr\textsubscript{3}(OH)\textsubscript{3}(OAc)\textsubscript{2}]²⁺; (Cr\textsubscript{4})</td>
<td>27.0 31.4 0.35</td>
<td>13.9</td>
</tr>
<tr>
<td>4</td>
<td>0.10</td>
<td>92.3</td>
<td>25.5</td>
<td>0.51</td>
<td>—</td>
<td>(Cr\textsubscript{4}) + (Cr\textsubscript{3})</td>
<td>589.414</td>
<td>13.9</td>
</tr>
<tr>
<td>5</td>
<td>0.17</td>
<td>153.2</td>
<td>24.6</td>
<td>0.55</td>
<td>—</td>
<td>—</td>
<td>588.420</td>
<td>13.8</td>
</tr>
<tr>
<td>6</td>
<td>0.20</td>
<td>184.6</td>
<td>24.1</td>
<td>0.57</td>
<td>—</td>
<td>[Cr\textsubscript{3}(OH)\textsubscript{3}(OAc)\textsubscript{2}]²⁺; (Cr\textsubscript{4})</td>
<td>24.6 27.9 0.51</td>
<td>12.5</td>
</tr>
<tr>
<td>7</td>
<td>0.30</td>
<td>276.9</td>
<td>21.7</td>
<td>0.61</td>
<td>—</td>
<td>—</td>
<td>588.423</td>
<td>12.5</td>
</tr>
</tbody>
</table>

\(a\) Determined from colorimetry (solutions) and flame photometry (solids).

\(b\) Determined from 3 orders of 002 basal spacing.

\(c\) C, H, N analyses and TGA (combustion to 950°C); no N present in all cases.

\(d\) Only \(d_{002}\), \(d_{004}\) observable in XRD.

Contacting NMe\textsubscript{4}–SnP suspensions with separately aged CrCl\textsubscript{3}/NaOH solutions for various times and [Cr\textsuperscript{3+}]:[NMe\textsubscript{4}–SnP] ratios (2), or contacting them freshly prepared [Cr\textsubscript{3}O(OH\textsubscript{2})\textsubscript{3}(OAc)\textsubscript{3}]Cl \cdot 5H\textsubscript{2}O (5–180 meq g\textsuperscript{-1} exchanger), both common methods in clay chemistry (7), gave amorphous blue-green solids (8).

Selective Ion-Exchange Experiments

The pillared Cr–SnP in the Li\textsuperscript{+} form (0.08 g) was suspended in mixed solutions of the metal acetate/lithium acetate of interest. Total concentration (2 \times c.e.c.) and volume (25 ml) were maintained constant. Equilibrium concentrations in solid and in solution were deduced from changes in M\textsuperscript{8+} compared with initial solution concentration. Concentrations of metal ions in solution were determined by colorimetry (Co\textsuperscript{2+}, Pr\textsuperscript{3+}) or flame photometry (Li\textsuperscript{+}, K\textsuperscript{+}).

Chemical Analyses and Physical Measurements

Manipulations of solids were monitored by XRD (Siemens D501 diffractometer; graphite monochromator, CuK\(\alpha\) radiation) on powders and cast films. TGA and DTA were measured on a Rigaku Thermoflex (calcined Al\textsubscript{2}O\textsubscript{3} as reference, 10°C min\textsuperscript{-1} heating rate) and Cr\textsuperscript{3+} was colorimetrically analyzed by the chromate method on alkaline solutions of samples (Kontron-Uvicon 810 spectrophotometer). Diffuse reflectance spectra were registered on a Shimadzu MPC 3100 spectrophotometer (BaSO\textsubscript{4} as reference). Adsorption–desorption of N\textsubscript{2} at 77 K was measured on a conventional volumetric apparatus. Samples were first degassed at 200°C overnight and adsorption–desorption of N\textsubscript{2} followed at 77.4 K.

Results

Heating and/or aging Cr(OAc)\textsubscript{3} and Me\textsubscript{4}N–SnP together leads to expanded ordered intercalated precursors, not obtained if the Cr(OAc)\textsubscript{3} is first heated or aged. Under reflux conditions, Cr\textsuperscript{3+} uptake is rapid (up to 46.2 meq Cr\textsuperscript{3+} added/g SnP\textsubscript{2}O\textsubscript{7}) after which the amount of Cr\textsuperscript{3+} exchanged decreases smoothly (Fig. 1). This behavior is typical of an ion-exchange process oc-
ring simultaneously with a solution equilibrium, as described by Giles et al. (9). As the ion-exchange reaction proceeds, large oligomeric Cr\(^{3+}\) species are formed in solution which are too large to diffuse into the SnP matrix, but hinder exchange by smaller Cr\(^{3+}\) oligomers which become available. This model suggests that the species adsorbed are in a narrow range and well-defined, in agreement with variations in Cr\(^{3+}\) concentration in the contact solution. It also agrees with the chemical analyses and TGA/DTA of the materials separated at points 2–7, and in particular points 2, 4, and 7.

Further evidence that the species intercalated are well-defined species is the fact that the materials separated at points 1–7 of the uptake curve are phase pure; there is no evidence for more than one basal (\(d_{002}\)) XRD peak. All have XRD still characteristic of crystalline layered structures with narrow \(d_{002}\) peaks (although 00l progressions are visible only to \(l = 3\)). Low-loaded species (point 1 in Table I) are an exception, giving amorphous products on calcination, even at temperatures as low as 200°C, and will not be discussed further.

Instead, the precursor-intercalation methods used for smectites indicate that more than one species intercalates. The uptake of [Cr\(_3\)(OH\(_2\))\(_2\)(OAc)\(_4\)]\(^+\) by Me\(_4\)N–SnP is non-Langmuir in type, presumably because partial hydrolysis of the Cr\(^{3+}\) cluster in solution leads to a range of oligomers, in turn providing only amorphous particles consisting of short-range order intercalated “packets” (still considered as “pillared” by some authors (10)). Brindley and Yamanaka’s method (7) also fails, because at equilibrium the Cr\(^{3+}\) solution pH of 2.5 is too acidic for exchange kinetics conditions required by layered phosphates (11).

The Cr\(^{3+}\) content in materials 4 and 5 increases as solution Cr\(^{3+}\) concentration decreases. For example, when Cr(OAc)\(_3\) corresponding to 92.3 meq Cr\(^{3+}\)/g SnP\(_2\)O\(_7\) is diluted twice, the Cr\(^{3+}\) taken up increases from 25.5 to 29.7 meq Cr\(^{3+}\)/g SnP\(_2\)O\(_7\) (see Table I). Figure 2 also shows the XRD for these materials. The following points are of importance:

(i) \(d_{002}\) values are very similar for precursor solutions aged at 25°C or 60°C alone (B);

(ii) \(d_{002}\) are much higher for reflux conditions (24–25 Å) than for aging at 25 and/or 60°C (19–21 Å) alone (A);

(iii) for more forcing reflux conditions, higher dilutions lead to materials with higher interlayer distances (\(d_{002} = 27–32\) Å) (C,D);

(iv) calcination—in either air or N\(_2)—leads to varying decrease of the interlayer
(v) the calcined materials retain layered structures.

The crystallinity of these precursor materials is high (see Fig. 3 for a typical example). However, calcination in air leads to formation of an impurity phase (probably α-SnP) and also—as expected—to formation of considerable amounts of dichromate ion (from optical spectrum, after washing well with deionized water). This presumably derives from segregated Cr₂O₃ (characteristic XRD reflexions observed at \( T > 500^\circ C \)); its presence led to higher apparent surface areas when materials were not washed first. Calcination under \( N_2 \) gave practically no detectable dichromate washings. All porosity and ion-exchange results refer to calcined samples first washed well with water.

A typical TG/DTA analysis (material 4a) is shown in Fig. 4 (2–7 gave analogous results). Water is lost up to ca 230°C (in two steps, the first from hydration-shell and

![Fig. 3. Typical XRD; material 4 of Fig. 1 (film). (A) before and after calcination in \( N_2 \); (B) before and after calcination in air.](image)

![Fig. 4. Typical TGA/DTA analysis; material 4, with decomposition pathway.](image)
pseudozeolitic water and the second probably from condensation reactions occurring in the oligomer intercalate. Combustion of organic residues (acetate groups, from chemical analysis and IR spectra) occurs between 230 and 350°C (i.e., the precursors themselves are relatively thermally stable). The exotherm for acetate combustion lies at 341−342°C in materials prepared at 25°C and 60°C, whereas in refluxed samples it lies at 300°C, clear evidence that the interlayer precursor species is different in the two cases. There was no clear evidence for the characteristic endotherm—expected at 430−460°C—due to the phosphate → pyrophosphate condensation, nor was there an exotherm expected at 800−900°C for a layered SnP₂O₇ → cubic SnP₂O₇ transition (12).

Several chemical tests were carried out on the materials:

(i) All precursor materials gave only partial exchange-elution of oligomer on suspension in 0.2 mol dm⁻³ HCl (Al–Keggin ion analogues are completely eluted from naturally occurring silicates under these conditions (13)). This indicates that the polyhydroxyacetato-Cr³⁺ moieties interact more strongly with the phosphate layers.

(ii) A sample containing 25.5 meq Cr³⁺/g SnP₂O₇ was calcined under different conditions and contacted with hot water (60°C) for 1 day and the washings were analyzed for Cr³⁺. The extractable Cr³⁺ was: 1.35% (as prepared), 45.0% (calcined in air at 400°C), 25.7% (calcined in air at 500°C), and 7.7% (calcined under N₂ at 400°C).

(iii) After calcination and thorough washing, no remaining Cr³⁺ species could be extracted with either 0.2 mol dm⁻³ HCl or transition metal ion-containing solutions. This provides indirect evidence that there is bonding between chromia moieties and phosphate layers, further corroborated by the fact that no calcined products could be swelled with ethyleneglycol (commonly used in past clay studies (14) as a criterion for swellability).

Figures 5 and 6 show the results of ion-exchange selectivity experiments using calcined materials 2 and 4. The ion exchange of Li⁺ with M⁺⁺ ions may be expressed as

\[ n \text{Li(PLP)} + M^{n⁺} \rightarrow M(\text{PLP})_n + n\text{Li}^+ \]

where (PLP) is the formula weight of the "pillared layered phosphate" containing 1.6 eq of exchange. The reaction is described by a selectivity coefficient \( K_{	ext{Li}⁺}^{M^{n⁺}} \):

\[ K_{	ext{Li}⁺}^{M^{n⁺}} = \frac{[M^{n⁺}](\text{Li}^+)^n}{[\text{Li}^+]^n(M^{n⁺})} \]

\[ 2.01 \leq \frac{\text{mg M}^{n⁺}\text{added/g}}{0.2} \leq 3.5 \]

\[ 1.0 \leq \frac{\text{mg M}^{n⁺}\text{added/g}}{0.6} \leq 1.0 \]

\[ \log \frac{\text{mg M}^{n⁺}\text{added/g}}{0.2} \leq 2 \]

\[ \log \frac{\text{mg M}^{n⁺}\text{added/g}}{0.6} \leq 3 \]

\[ \frac{\text{mg M}^{n⁺}\text{added/g}}{0.2} \leq 1 \]

\[ \frac{\text{mg M}^{n⁺}\text{added/g}}{0.6} \leq 0 \]

\[ \log (\theta/\theta - 1) \leq -7 \]

\[ \log (\theta/\theta - 1) \leq -3 \]

**Fig. 5.** (A) Exchange isotherms for K⁺(○), Co²⁺ (▲), and Pr³⁺ (■) on the material 2 exchanged with Li⁺ after calcination at 400°C under N₂. (B) Relationship between surface ion composition of the M⁺⁺/Li–Cr–SnP and the selectivity coefficient \( K_{	ext{Li}⁺}^{M^{n⁺}} \). (C) Relationship between the M⁺⁺ adsorption function, \( \theta/\theta - 1 \), and the solution activity of M⁺⁺ for Li⁺/M⁺⁺.
where the bar represents ions in the adsorbed phase, square brackets the equivalent fractions in the solid, and parentheses the ion activities in solution phase. The c.e.c. of both Li+-exchanged forms is 1.6 meq/g exchanger. The McBride and Bloom Langmuir-type equation for describing adsorption of $M^{n+}$ ions on clays (15) has been utilized, in which the activity of $M^{n+}$ in solution is a function of the coverage, $\theta$, of the phosphate surface by $M^{n+}$:

$$ (M^{n+}) = K(\theta/1 - \theta)x, $$

where $K$ and $x$ are constants and $\theta$ the equivalent fraction in the solid. In this model of ion exchange, the strong adsorption of high-charge ions is a result of the entropy gain connected with water disorder or with an increase in ion disorder at the exchange sites (16). Fits of the log $(M^{n+})$ vs log $(\theta/1 - \theta)$ plots to the McBride–Bloom equation gave the parameters

<table>
<thead>
<tr>
<th>Material 2</th>
<th>Material 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K$</td>
<td>$x$</td>
</tr>
<tr>
<td>Li$^+$/K$^+$</td>
<td>$1.8 \times 10^{-2}$</td>
</tr>
<tr>
<td>Li$^+$/Co$^{2+}$</td>
<td>$1.7 \times 10^{-4}$</td>
</tr>
<tr>
<td>Li$^+$/Pr$^{3+}$</td>
<td>$3.2 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

The adsorption–desorption isotherms for N$_2$ are all of type IV in the BDDT classification (Fig. 8); i.e., they are characteristic of mesoporous materials with microporous contributions (17), as inferred from the adsorption values in the low relative pressure region. Micropore volumes were calculated from $\alpha_s$ methods (17).

**Discussion**

**Intercalate Precursor Species**

Whether or not pillared materials find uses in the future, identification of precursor intercalates remains a major unsolved issue. The large Keggin-type polyhydroxyaluminum ("chlorhydröl") (1) and polyhydroxy chromium(III) (2, 7) used to date are formed $ex$ $situ$. Problems arise due to the presence of solution equilibria (18), and to large variations in local concentrations of base (with metal hydroxide precipitation) and parallel exchange reactions with surface groups (e.g., the Na$^+$ ions from NaOH used for polymerizing CrCl$_3$). These may lead to both lateral disordering effects during intercalation and irreproducible stuffing of interlayers. By contrast, the hydrolysis of Cr(OAc)$_3$ $in$ $situ$ on the colloidal surfaces of Me$_4$N–SnP, which exploits the kinetic robustness of Cr$^{3+}$ with no complications by redox processes during intercalation and...

Fig. 6. As for Fig. 5; Calcined, Li$^+$-exchanged material 4.
buffering by OAc\(^-\) ions, provides an apparently cleaner route to porous solids.

Chemical identification is straightforward: the precursors are polyhydroxyacetate-Cr\(^{3+}\) species, having chain lengths which differ depending on aging–heating regime and concentration. The more promising ones, in terms of interlayer expansion are those at points 2, 4, and 7 of the uptake curve, formulated as

material 2:
\[
\alpha\text{-Sn}[\text{Cr}_3(\text{OH})_6(\text{OAc})(\text{OH}_2)_6]_{0.8}{\text{H}_2}\text{O}(\text{PO}_4)_{2}\]

material 4:
\[
\alpha\text{-Sn}[\text{Cr}_4(\text{OH})_7(\text{OAc})_2(\text{OH}_2)_7]_{0.6}{\text{H}_2}\text{O}(\text{PO}_4)_{3}\]

material 7:
\[
\alpha\text{-Sn}[\text{Cr}_5(\text{OH})_7(\text{OAc})_3(\text{OH}_2)_8]_{0.8}{\text{H}_2}\text{O}(\text{PO}_4)_{2}\]

(water molecules included for analytical balance and to give six-coordinate Cr\(^{3+}\)).

Points 3, 5, and 6 represent materials containing mixtures of oligomers.

Structural conclusions are more uncertain, although comparison with studies of the early stages of aquochromium\(^{3+}\) polymerization in solution (19–22) seems reasonable (there are no comparable studies with acetate-containing species). Dimers to tetramers have been most clearly identified (19, 20), both being major species at pH 4 (21). They have edge-shared "closed" structures (Scheme 1), although the dimer also gives an open form (22), and the tetramer has an even more closed form (formed after deprotonation (23), which is unlikely in the present pH conditions). Further, Stünzi and Marty (23) used an empirical spectral criterion \(\varepsilon_1 / \varepsilon_2\) (1.17-monomer; 1.18 = dimer; 1.6-trimer; 1.95 = tetramer, and 1.5–1.6 = pentamer and hexamer) to distinguish between these structures. This criterion appears to be related to the connectivity between octahedra; the higher the connectivity, the higher is \(\varepsilon_1\) with respect to \(\varepsilon_2\) (\(\varepsilon_1, \varepsilon_2\) are the molar absorbances of bands \(\nu_1 (4T_{2g} \leftrightarrow 4A_{2g})\) and \(\nu_2 (4T_{1g} \leftrightarrow 4A_{2g})\)).

In materials 2–7 and 5a, \(\varepsilon_1 / \varepsilon_2\) = ca 1.18–1.2, from which we conclude that linear edge-shared oligomers are present, rather than the closed ones of Scheme 1. (The electronic spectra of 3 and 5 show evidence for broadening of both bands compared with those for 2, 4, and 7). IR spectra confirm that acetate ions are present, and they are characteristic of bidentate MeCO\(^-\) groups rather than ionic ones, as expected. This is also supported by the fact that \(\nu_2\) in the electronic spectra increases in wavelength compared with the spectra of both Cr(OAc)\(_3\) itself (\(\nu_2\) 446, \(\nu_1\) 590) and [Cr\(_3\)O(OH)\(_2\)\(_3\)(OAc)\(_6\)]\(^+\) (\(\nu_2\) 448, \(\nu_1\) 611 nm) (Fig. 7).

It is not possible to construct a suitable stereomodel and fit it into the interlayer space, as often done in intercalation chemistry (24), because large amounts of struc-
Fig. 7. Diffuse reflectance spectra. (A) [Cr₃(OH)&(OAc)₃]Cl·5H₂O; (B) Cr(OAc)₃; (C) 4 (25°C aged); (D) 4 (25°C/60°C, aged, then refluxed).

Table II

| Material | Calcination temp. | S_BET | C_BET | Σ|d| | ΣV|d| | d|p| | V|micro|
|----------|-------------------|-------|-------|---|---|---|---|---|---|---|---|
| 2        | 400 (N₂)          | 267   | 98.8  | 287 | 0.247 | 37 | 0.088 |
| 4        | 400 (N₂)          | 386   | 132.6 | 416 | 0.324 | 34 | 0.115 |
| 4a       | 400 (air)         | 236   | 84.5  | 272.4 | 0.284 | 84 | 0.040 |
| 4        | 400 (N₂)          | 288   | 237.9 | 263.6 | 0.222 | 30.8 | 0.107 |
| 5a       | 400 (air)         | 242   | 242.9 | 233.3 | 0.212 | 35.0 | 0.101 |
| 5a       | 400 (N₂)          | 264   | 437.9 | 188.2 | 0.145 | 21.9 | 0.107 |

* Parameters as defined and calculated in Cranston and Inkley (28).
* Using τα plot (27).

Chromia Pillars

Calcination of materials 2–7 subsequently occurs with less precipitous collapse in interlayer distance, and all remain crystalline up to 400°C. More importantly, surface areas are quite high, ranging between 200 and 380 m² g⁻¹ (Table II). (The theoretical surface area for a pillared α-tin phosphate is expected to be 850 m² g⁻¹, assuming the basal structure is similar to that in α-zirconium phosphate (5)). This again argues for the presence in the precursors of
relatively ordered interlayer oligomer organization, as in Scheme 2. The surface areas compare well with those obtained to date for pillared clays (26) and are much higher than those reported in a study of Cr(OAc)₃ intercalated in α-(Zr PO₄)₂HNa · 5H₂O, in which surface areas of ca 40 m² g⁻¹ for calcined materials were imputed to "stuffing" of the interlayer by fragments (27). As shown in Table II, the decrease in surface area on calcining in air (rather than N₂) may also be due to some blocking of the cavities formed, but this was never sufficient to cause complete porosity removal.

The textural parameters were derived from the cylindrical pore model (28), and applying "t" plots (29) and the αₜ method (17), as before (5), for assessing microporosity. The pore-radius distributions obtained lie in a relatively narrow range for all four materials examined: 8–15 Å (see Fig. 9); this is as narrow as that found for porosity induced by derivatization of phosphate groups with phosphonates (30).

Note that, although the increase in average pore diameter with increase in the amount an size of chromium oligomer precursor agrees with the increase in pillar height, there does not appear to be a simple relation between the latter and surface area.

An objection is that the pore distributions represent mesoporosity induced by cavities formed by "packets" of layers (i.e., limiting small particles) becoming associated in an end-side fashion to give almost triangular pores, rather than by pillaring (6, 31). (The literature on porous solids is replete with examples of materials giving pores classified as "mesopores" in the width range 2rₚ = 15–40 Å (32); others classify these as micropores (1)). A typical SEM micrograph (Fig. 10) shows considerable
macroporosity and the presence of mesopor- 
pores. However, the latter appear always 
to be restricted to within the packets of lay-
er. Further, we note from Fig. 9 that air-
treated materials have broader, more inho-
mogeneous, pore-size distributions, which 
is as expected for a "thinning out" of chro-
mium oxide pillars, but is not easily ration-
alized on the interpacket pore model. We 
conclude that the porosity is indeed in-
duced by pillaring (and it seems highly un-
likely that aggregation of packets would oc-
cur in so homogeneous and reproducible a 
fashion as to give rise to such narrow pore-
size distributions).

The ion-exchange results support this 
view: c.e.c.s are too high to be due to sur-
face exchange alone. There is, however, no 
obvious relationship between surface area 
and c.e.c. (Note that these materials 
present cation-exchange properties alone, 
differently than pillared clays, which show 
both anion and cation exchange (33). In a 
rigid system, as expected to occur in a pil-
lared material with high available internal 
space (recall pores with radii of 8.5 and 11.2 
Å) accommodation of highly mobile ions 
and hydrated cations is to be expected, i.e., 
exchange effectiveness is directly related to 
the charge/radius ratio of the $M^{n+}$ cations. 
There is nonlinearity in the log ($M^{n+}$) vs log 
($\theta/1 - \theta$) plots (especially for Co$^{2+}$) (16), 
and thus, heterogeneity of the internal ex-
change sites may account for the composi-
tion-dependent selectivities. We conclude 
that there are different accessibilities of the 
internal surface of these materials to N$_2$ 
molecules (possibly reflected in the high 
$C_{BET}$ parameters) and hydrated cations.

Clearly, considerations of pore geometry
should also take into account other factors, such as the volume of the exchanged cation, the size and shape of the pores, structural rigidity, and accessibility of layer or pillar to N$_2$, which must await further structural information.

Conclusions

Colloidally dispersed, buffered $\alpha$-tin phosphate surfaces provide a good medium for obtaining well-ordered Cr$^{3+}$-oligomers as precursors for preparing chromia-pillared layered phosphates. The accessible colloidal surface permits growth of polyhydroxyacetate-Cr$^{3+}$ oligomers in an ordered way, which on calcination give rise to porous oxide-pillared materials of narrow pore range. Further work is under way to assess how general the method is, and to resolve ambiguities in interpretation of pore radii.

Acknowledgments

We thank the EEC (Euram Project I-0027) and C.I.C.Y.T. (Project No. MAT90-298) for financial support.

References


32. K. S. W. Sing, Pure Applied Chem. 54, 201 (1982).