

## Preparation of Porous Chromia-Pillared Molybdenum Trioxide

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A chromia-pillared layered molybdenum trioxide has been prepared by combining a  $\text{Cr}(\text{OAc})_3$  aqueous solution with a suspension of the molybdenum bronze for the first time; the resulting material after calcination at 350 °C is porous with a surface area of 82 m<sup>2</sup> g<sup>-1</sup>.

The successful insertion of pillaring species into the interlayer space of clay minerals<sup>1-3</sup> led to many attempts to prepare new classes of porous materials, which are of considerable interest as molecular sieves and catalysts. Recently, pillared derivatives of some layered phosphates,<sup>4</sup> double hydroxides,<sup>5</sup> titanates,<sup>6,7</sup> lanthanum-niobates<sup>8</sup> and titanium-niobates<sup>9</sup> have also been prepared.

Pillaring of lamellar transition metal oxides is also of interest.  $\text{MoO}_3$ , in particular, is a multifunctional material which has attracted considerable attention as a partial methane oxidation catalyst<sup>10</sup> and as a potential viable cathode in secondary batteries,<sup>11</sup> but molybdenum-based systems possess only a very low surface area.  $\alpha\text{-MoO}_3$ , a layered compound consisting of edge and vertex binding  $\text{MoO}_6$  octahedra which form corrugated sheets, is a potential host for intercalation<sup>12,13</sup> which may lead to new materials with high surface areas and catalytic properties. The intercalation of  $\text{Al}_{13}$ ,  $\text{Ga}_{13}$  and  $\text{Bi}_6$  polyoxycations into  $\text{MoO}_3$  via flocculation from colloidal solution of the bronze has been described.<sup>14,15</sup> We report here the first example of chromia-pillared layered molybdenum trioxide with high surface area and porosity prepared by a novel method, in which  $\text{Cr}(\text{OAc})_3$  solution is employed as a pillaring agent to react with a dispersion of the layered  $\text{Na}_x\text{MoO}_3$  bronze.

Sodium form of the molybdenum bronze was prepared according to Thomas and McCarron.<sup>13</sup> The X-ray diffraction (Shimadzu XD-3A, Cu-K $\alpha$  radiation) pattern of the as-prepared material is in accordance with that given in the original report, giving the interlayer distance in the fully hydrated state of 11.48 Å. An aqueous solution of  $\text{Cr}(\text{OAc})_3$  (0.1 mol dm<sup>-3</sup>) was treated with stirring at 95 °C for 36 h in a flow of nitrogen. Intercalation of the polyoxycations was carried out via ion exchange of sodium ions in freshly prepared  $\text{Na}_x\text{MoO}_3$  bronze. The solid was treated with an excess of the above-treated  $\text{Cr}(\text{OAc})_3$  solution at 75 °C for 24 h in a flow of nitrogen. The resultant product was centrifuged, washed and air-dried at room temperature, then calcined in a flow of mixed nitrogen and oxygen (4% O<sub>2</sub> V/V).

Figure 1 shows the X-ray diffraction pattern of the oriented thin film of the as-prepared sample. The full disappearance of the peaks attributable to the hydrated sodium bronze and the appearance of new peaks clearly indicate the insertion of polyoxycations and show complete ion exchange of the interlayer Na-cations. Fourteen ( $0k0$ ) reflections are evident, from which an average interlayer distance of 17.39 Å can be found. The net interlayer expansion in comparison with the unpillared

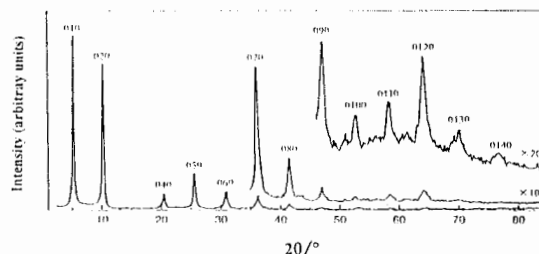


Figure 1 Cu-K $\alpha$  X-ray diffraction patterns of an oriented film of  $\text{Cr}^{3+}$  oligomers intercalated molybdenum trioxide. The intensity scale has been expanded by a factor of 10 and 20 in the right portion of the figure.

$\text{MoO}_3$  ( $d_{020} = 6.92 \text{ \AA}$ <sup>15</sup>) is 10.47 Å. The large number of reflections, together with the small variation ( $\pm 0.03 \text{ \AA}$ ) in the d-spacing of the higher order reflections indicates that there is a high degree of order along the axis perpendicular to the layer.<sup>14</sup> The XRD patterns after calcination at different temperature is shown in Figure 2. The interlayer distance of the product calcined at 250 °C is 16.67 Å [ $2\theta = 5.3^\circ$ , Figure 2(b)], a bit smaller than 17.39 Å. As a result of decomposition of organic matter, this value decreases remarkably to 10.92 Å [ $2\theta = 8.1^\circ$ , Figure 2(c)] at 350 °C. There appear weak peaks of  $\text{MoO}_3$  after calcination at 400 °C, indicating that the interlayer begins

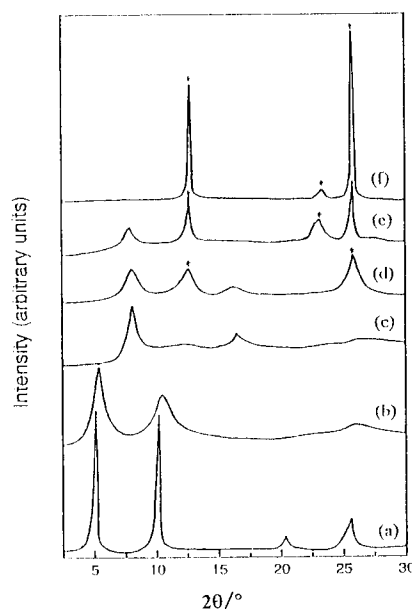
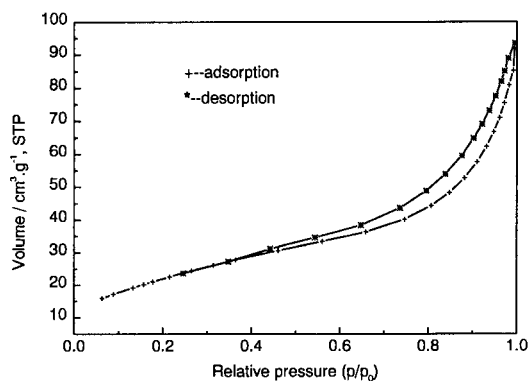


Figure 2 Cu-K $\alpha$  X-ray diffraction patterns of an oriented film of: (a)  $\text{Cr}^{3+}$  oligomers intercalated molybdenum trioxide, dried at room temperature; (b) calcined in a flow of mixed nitrogen and oxygen (4% O<sub>2</sub> V/V) for 2 h at 250 °C; (c) 350 °C, 2 h; (d) 400 °C, 2 h; (e) 450 °C, 2 h; (f) 550 °C, 2 h; and reflections arising from  $\text{MoO}_3$  are marked (\*).



**Figure 3** Adsorption-desorption isotherm of  $N_2$  on the chromia-pillared layered molybdenum trioxide (350 °C, 2 h).

to collapse at this time, although the interlayer distance of the product remains unchanged [ $2\theta = 8.1^\circ$ , Figure 2(d)]. The peak characteristic of layer structure is still retained upon heat treatment at 450 °C and fully disappeared at 550 °C [Figure 2(e) and (f)]. TG-DTA and XPS analysis results imply that after calcination of resultant product at 350 °C, Cr-oligomers have decomposed and converted to chromia (binding energy,  $E_b$  of Cr  $2p_{3/2} = 577.5$  eV). The apparent layered structure of chromia-pillared molybdenum trioxide can also be observed from the image of transmission electron microscopy. It is in agreement with the result obtained from XRD.

The  $N_2$  adsorption-desorption isotherm of the chromia-pillared molybdenum trioxide calcined at 350 °C is shown in Figure 3. The apparent hysteresis loop indicates that this type of material is porous. The un-pillared material is non-porous and the surface area [BET ( $N_2$ )] is very low ( $<2$   $m^2 g^{-1}$ ), whereas, the pillared material has a relatively high specific surface area of  $82$   $m^2 g^{-1}$ .

Since its special component containing Mo and Cr, the new material with porosity and high specific surface area is expected to show attractive catalytic activity for hydrocarbon oxidation reactions and to show certain catalytic properties through sulfurization in hydrodesulfurization and related

hydrotreating processes. Further investigation on systematic characterization and catalytic properties is underway.

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