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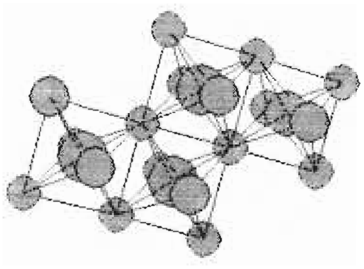
EXAFS Studies of the Formation of Chromia Pillared Clay Catalysts

Pillared clays have attracted considerable interest as microporous catalysts.[1] Generally though it has proven to be extremely difficult to characterize the polynuclear metal unit that comprises the pillars, with MAS NMR spectroscopy being the most informative technique, as demonstrated for Al-based pillars.[2] However, for other pillars, this technique is not applicable. One such case is illustrated by chromia pillared clays for which ion exchange of partially hydrolyzed aqueous Cr^{III} is used en route to cyclohexane dehydrogenation catalysts.[3] The identity of the solution species is not clear beyond being oligomeric hydroxy aquo units, nor is the chemistry during the ion exchange calcination, and hydrogenation steps of the catalyst activation.[4,5] We now report use of Cr K-edge X-ray absorption spectroscopy to provide some structural detail of these processes.

A dark green pillaring solution was formed by heating a 0.1 M solution of chromium nitrate with Na_2CO_3 (Cr^{III}:CO_3^{2-} = 1:1) at 95 °C for 36 h.[5] EXAFS data for this solution[6] indicated CrO_6 coordination sites (Cr–O = 1.97 Å), with two additional shells due to Cr back-scatterers at 2.97 and 3.89 Å, each due to ca. two Cr centers. Unlike the report on Cr^{III} solutions in perchlorate media, albeit at lower concentrations,[12] clear evidence was found for polynuclear species in the pillaring solution. The Cr–O distance may be compared with those obtained for the $[Cr_2(OH)_2(OH_2)_8]^{4+}$ ion in the crystal.[13] For that ion, the bridging Cr–O distance is 1.936 Å, with the terminal Cr–OH_2 bonds being rather longer (ca. 1.98 Å), so the mean Cr–O distance obtained from EXAFS is in accord with this type of coordination site. Indeed comparison of the shorter EXAFS-derived Cr⋯Cr distance with that reported for the chromium dimer (2.97 Å cf. 3.01 Å), and also of the O–Cr–O (82° cf. 78°) and Cr–O–Cr angles (98° cf. 102°) support a solution model involving edge-bridged octahedral units. These oligomeric chromium species in the pillaring solution can be rationalized on the basis of cis-linked edge-bridged octahedral centers. The absence of any other than the two Cr⋯Cr shells is consistent with sheet structures, shown as **1**. This tetranuclear species has mean coordination numbers of 1.5 and 1 for the first and second Cr–Cr distances, respectively, with these values rising to 1.8 and 1.6, respectively, for a decanuclear unit and each limiting to 2 for infinite zigzag chains based on the geometry of **1**.



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After addition of a 2-μm fractionated (by sedimentation) montmorillonite clay bentonite sample (ex Potclays, Stoke-on-Trent, U.K.) to the hot pillaring solution and stirring for 1.5 h,[5] a dark green sample was obtained with a d_{001} spacing of 18 Å (increased from 12 Å in the original clay). These results are similar to those previously reported for this Cr^{III}:CO_3^{2-} ratio.[4,5] The Cr K-edge EXAFS of this material can be analyzed with essentially the same structural parameters as the pillaring solution, consistent with a retention of the original chromium centres (Figure 1). The gallery spacing is about 8 Å in this material, consistent with a sheet of the octahedra one layer deep (ca. 7 Å in depth).

Calcination of this sample in vacuo at 250 °C effected a color change to black, while retaining the ca. 18-Å d_{001} spacing. The Cr XAS spectrum now showed a sharp preedge feature (Figure 2) typical of the dipole-allowed $1a_1(1s)$–$t_2(3d/4p)$ transition in a tetrahedral site.[14] Indeed the EXAFS data (Figure 3) now required an extra Cr–O shell at the distances expected for a $Cr^{VI}O_4$ center (1.65 Å); the other Cr–O shell showed a reduced occupancy (ca. 5). This data suggests the chromium is more akin to the mixed-valence material $Cr^{III}_2Cr^{VI}_3O_{12}$[15] than the rutile structure of CrO_2.[16] The evidence for partial oxidation is clear, and over

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[6] X-ray absorption spectra were recorded on Station 7.1 of the Synchrotron Radiation Source at the Daresbury Laboratory using a Si(111) order-sorting monochromator. Data was acquired in transmission mode. Data reduction was carried out by using PAXAS,[7] with the spherical wave analysis performed by using EXCURVE.[8] The statistical validity of shells was assessed by published means.[9,10] Error estimates on bond distances are likely to be about 1.5%.[11]

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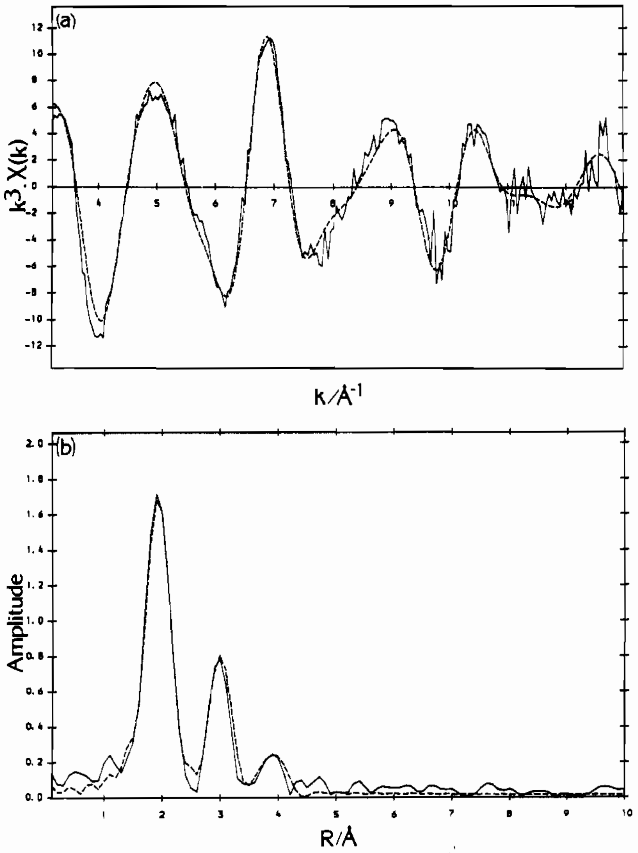

Figure 1. Cr K-edge EXAFS data of the chromium ion exchanged bentonite at room temperature: (a) k^3-weighted EXAFS and (b) the Fourier transform, phase-shift corrected for oxygen. Key: (—) experiment and (--) spherical wave theory for six O at 1.97 Å, two Cr at 2.97 Å, and two Cr at 3.90 Å gives a fit with R = 20%.

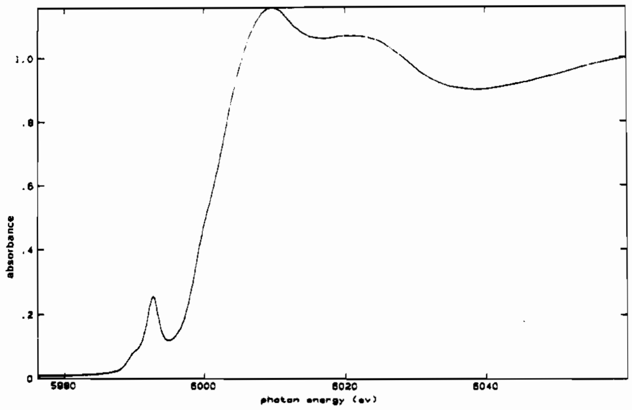

Figure 2. Cr K-edge XAS near-edge structure of the chromium ion exchanged bentonite recorded at room temperature after being calcined at 250 °C.

a series of samples there was a good correlation between the intensity of the preedge peak and the coordination number of the 1.64-Å shell. For this calcined sample, the proportion of Cr^{VI} is ca. 20% of the total chromium.

Hydrogenation at 250 °C for 2 h caused a further color change to gray-green, and the Cr K-edge EXAFS data showed that the $Cr^{VI}O_4$ centers had been lost with regeneration of a mean chromium environment similar to that of the pillared bentonite sample. This sample catalyzed the conversion of methanol to hydrocarbons and some oxygenates.

These results demonstrate that the cis-linked octahedral units formed in aqueous solution on hydrolysis of Cr^{III} solutions are retained on incorporation into a clay and are partially oxidized to a mixed-valence $Cr^{VI}Cr^{III}$ material on calcination, with hydrogenation regenerating the octahedral CrO_6 units in the "chromia pillared clay" catalysts. This last material may have differing OH_2/OH^- ligand sets as compared to the original ion-exchanged clay.

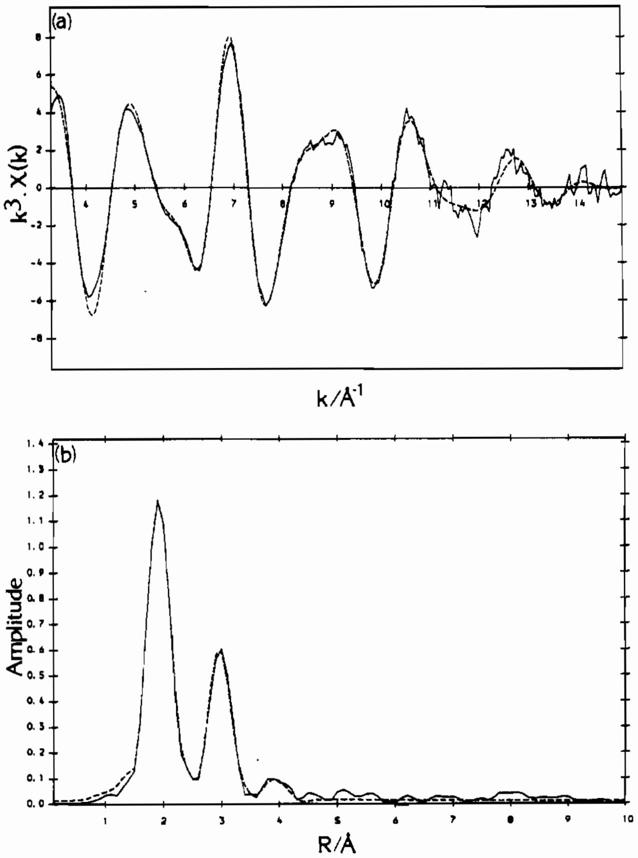

Figure 3. Cr K-edge EXAFS data of the chromium ion exchanged bentonite at room temperature and calcined at 250 °C: (a) k^3-weighted EXAFS and (b) the Fourier transform, phase-shift corrected for oxygen. Key: (—) experiment and (--) spherical wave theory for one O at 1.64 Å, five O at 1.95 Å, two Cr at 2.93 Å, and one Cr at 3.87 Å gives a fit with R = 15%.

We are continuing our work to correlate the structural and catalytic properties of these materials.

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Crystal and Molecular Structures and Spectroscopic Properties of $Au_2(tmb)Cl_2$ (tmb = 2,5-Dimethyl-2,5-diisocyanohexane). Evidence for Quasi-One-Dimensional Linear Chains with Weak Au(I)···Au(I) Interactions in the Solid State

Quasi-one-dimensional (1D) metal complexes have been investigated extensively, as they exhibit a variety of low-dimensional phenomena. The square-planar transition-metal complexes of Rh(I), Ir(I), Pd(II), Pt(II), and Au(III)[1] and halogen-bridged