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| Experiment title: EXAFS studies of mesoporous silica-grafted dimolybdenum catalysts | Experiment number: CH883 | |
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Aims. Quadruply bonded dimolybdenum (II, II) complexes containing the $[\text{Mo-Mo}]^{4+}$ core and carrying labile acetonitrile ligands are efficient homogeneous and supported or unsupported heterogeneous catalysts for several polymerisation reactions. We immobilised the cations $[\text{Mo}_2(\text{CH}_3\text{CN})_8]^{4+}$ **1**, $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6]^{2+}$ **2** and $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_2(\text{dppa})_2]^{2+}$ **3** [dppa = bis(diphenylphosphine)amine] on the internal surface of the highly ordered mesoporous pure silica molecular sieve MCM-41 by solvent impregnation techniques (CH_3CN) [P. Ferreira *et al.*, *J. Mater. Chem.*, 2000, **10**, 1395]. The materials were characterised by FTIR spectroscopy, N_2 adsorption, and magic-angle-spinning (MAS) NMR studies. ^{29}Si and ^{13}C MAS NMR indicated that the initial anchoring of the $[\text{Mo-Mo}]^{4+}$ complexes to the surface occurs at the surface silanol (Si-OH) groups on removal of labile NCCH_3 ligands from the complexes. The aim of the proposed experiments on BM29 at the ESRF was to carry out Mo K-edge EXAFS studies of the supported catalysts to probe the exact nature of the final Mo species on the surface, that is, whether the Mo-Mo bond is retained or if it is broken to give mononuclear species.

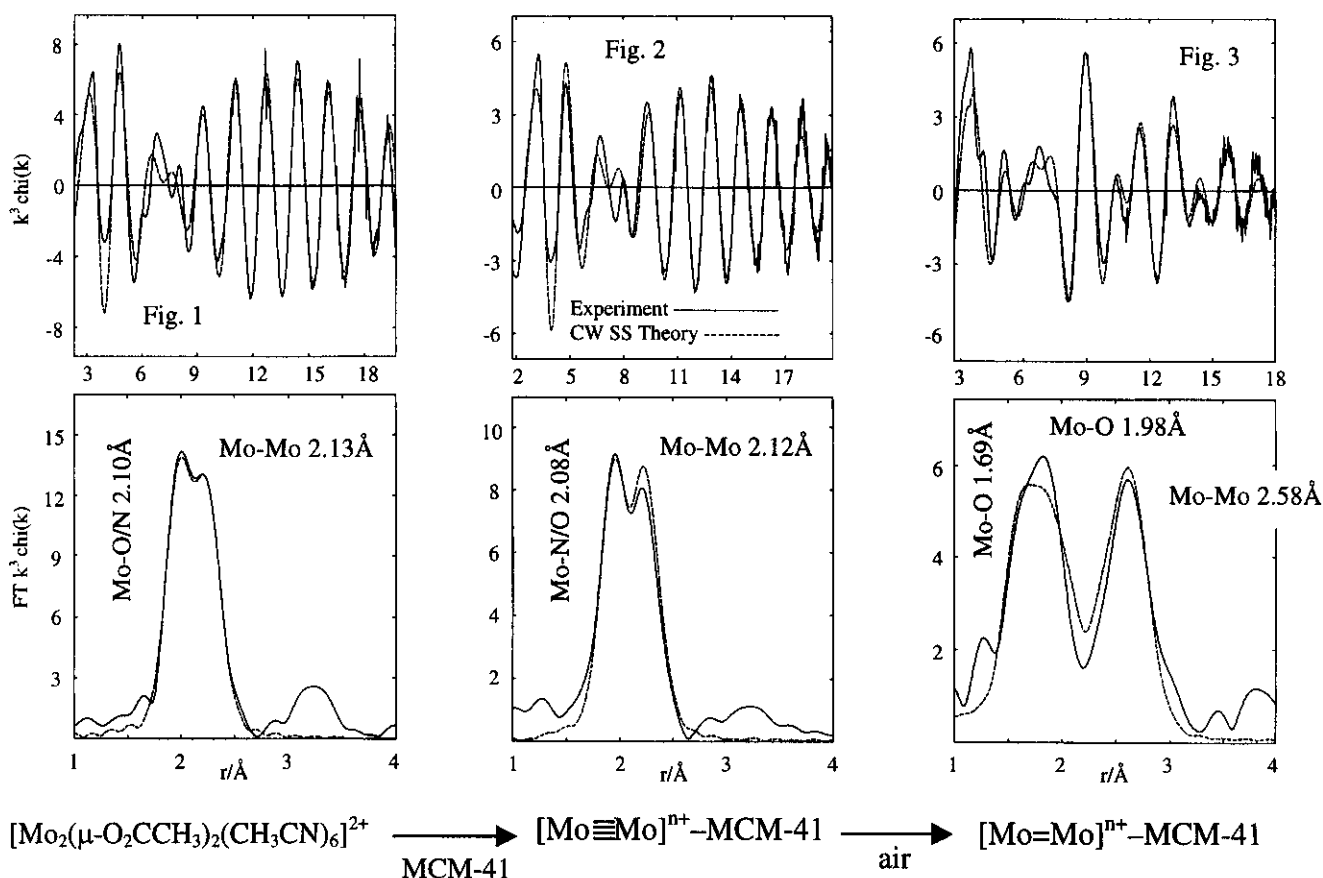
Experimental conditions. Mo K-edge XAS spectra were collected for samples in the solid state at room temperature in transmission mode with ion chamber detectors on BM29 [double crystal Si(311) monochromator], with the ESRF operating at 6 GeV in 2/3 filling mode and typical currents of 170–200 mA. Spectra were recorded in the range 19.8–21.5 KeV (40% harmonic rejection, EXAFS scan with optimised energy mesh, 2 s per scan point). Most samples were air-sensitive and 13mm pellet preparation (boron nitride matrix) was carried out using the glove box on BM29. A total of about 100 complete spectra were acquired for 20 different samples (3–9 scans per sample).

Analysis. The program JESF (BM29) was used for background subtraction and EXAFS curve-fitting analyses have been carried out within the program EXCURVE (version EXCURV98, Daresbury Laboratory, U.K.).

Sample characteristics. EXAFS spectra were measured for supported and unsupported dimolybdenum complexes **1–3** (BF_4^- counterion), and also $\{\text{Mo}_2[\text{CH}_3\text{COCH}=\text{C}(\text{O}-)\text{CH}_3]_2(\text{CH}_3\text{CN})_6\}[\text{BF}_4]_2$. The content of Mo in the functionalised materials was between 2 and 4 wt%. For each of the supported catalysts, there were several different samples: 1. Materials prepared

2 weeks before the EXAFS experiments. 2. Materials prepared 4 months before the EXAFS experiments. 3. Materials from 1 that were subsequently exposed to air for 1–2 hours prior to further EXAFS measurements. 4. Materials that were prepared more than 6 months before the EXAFS measurements. Reference samples of $\text{Mo}(\mu\text{-O}_2\text{CCH}_3)_4$ and Na_2MoO_4 were also measured.

Results. Summed EXAFS spectra were of high quality up to 20 \AA^{-1} for the free complexes and up to $16\text{-}18 \text{ \AA}^{-1}$ for the supported complexes. Detailed analysis of the results is still ongoing but some preliminary results can be outlined. EXAFS-derived structural information for the free complexes was in agreement with single crystal X-ray diffraction data. For example, the Mo-Mo bond distance for **2** was determined as 2.133 \AA from the EXAFS data, compared with 2.134 \AA from single crystal data (Fig. 1). For the freshly prepared MCM-supported complex, analysis of the EXAFS strongly indicates that the structure of the cationic fragment was largely unchanged on the silica surface (Fig. 2). This is in agreement with other structural studies which have indicated that the complexes initially undergo a weak interaction with the surface. The mechanism of surface attachment probably involves the displacement of labile acetonitrile ligands in the axially coordinated position by reaction with isolated nucleophilic silanol groups at the silica surface. All of the supported complexes are however extremely sensitive to air and moisture. When supported **2** was exposed to air there was clear evidence from the EXAFS data for a disruption in the Mo-Mo quadruple bond – the metal-metal distance increased from 2.12 \AA to 2.58 \AA , and Mo=O units were formed (Fig. 3). The new Mo-Mo distance is in the range found for double bonded edge-sharing molybdenum compounds. We conclude the formation of edge-sharing bioctahedral structures on the silica surface. Comparable results were obtained with the other supported complexes.



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