

## Reactivity of a Trimethylstannyl Molybdenum Complex in Mesoporous MCM-41

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A highly thermostable tin–molybdenum complex is encapsulated into the hexagonal mesoporous channel host MCM-41 and thermally transformed into supported metal clusters.

The recent discovery of a new class of ordered mesoporous materials<sup>1</sup> with channel diameters between about 20 and 100 Å has opened up new opportunities for the design of hybrid catalysts. The immobilization of transition-metal catalysts on solid supports has been the focus of many research efforts.<sup>2–6</sup> Key challenges in the design of these catalysts include (i) control over the species that is actually immobilized, and (ii) sufficient stability against deactivation and leaching. The novel mesoporous MCM-41 hosts are prepared in liquid crystalline phases where combinations of amphiphile–metal-oxo systems order in channel or layer structures. In the case of aluminosilicate MCM-41, the pore system obtained after calcination presents well-defined hexagonal walls with terminal hydroxyl groups at 3745 cm<sup>-1</sup> (in vacuum). Surface reactions with organometallic compounds should therefore produce well-defined species, in contrast to the situation on some amorphous supports. The enormous pore sizes of the MCM-41 family offer new opportunities for the encapsulation of large catalyst species and for the catalytic conversion of substrates much larger than in common zeolites.

We have recently developed a concept for stabilizing low-valent transition-metal moieties [such as Cl<sub>2</sub>(THF)Ge-Mo(CO)<sub>5</sub><sup>7</sup> or Me<sub>3</sub>SnMn(CO)<sub>5</sub>]<sup>8</sup> in large-pore zeolites, by using bimetallic complexes where the second, oxophilic main-group element serves to attach the complex to the internal zeolite cage surface. This communication describes the attachment of the bimetallic complex Me<sub>3</sub>SnMo(CO)<sub>3</sub>(η-C<sub>5</sub>H<sub>5</sub>) into the hexagonal channels of MCM-41. This system also provides a convenient precursor for highly dispersed SnMo clusters made by thermolysis of the encapsulated complex.

All manipulations were carried out under nitrogen atmosphere, in thoroughly dried solvents, or high vacuum. The precursor Me<sub>3</sub>SnMo(CO)<sub>3</sub>(η-C<sub>5</sub>H<sub>5</sub>) (mp 97–99 °C) was synthesized from the reaction between Na[Mo(CO)<sub>3</sub>(η-C<sub>5</sub>H<sub>5</sub>)] and Me<sub>3</sub>SnCl following a modified reported method.<sup>9</sup> The hexagonal channel host MCM-41 (unit cell size, 4.0 nm; channel diameter, ca. 3.0 nm) was synthesized using C<sub>16</sub>H<sub>33</sub>NMe<sub>3</sub>OH according to published procedures.<sup>1</sup> MCM-41 was degassed by calcination in oxygen for 4 h at 100 °C and

for 8 h at 540 °C, followed by evacuation at 400 °C for 6 h (10<sup>-5</sup> Torr; heating rate 1 °C min<sup>-1</sup>). The host was loaded with 1.5 mmol of Me<sub>3</sub>SnMo(CO)<sub>3</sub>(η-C<sub>5</sub>H<sub>5</sub>) per g of host in 50 ml of dry hexane by stirring the slurry for 18 h, followed by washing and drying under vacuum. For thermal stability studies, 0.5 g batches of loaded host were heated in a tube furnace under 10<sup>-5</sup> Torr at the desired temperatures (heating rate 1 °C min<sup>-1</sup>, isothermal for 6 h). EXAFS measurements at the Mo K-edge (20 000 eV) and the Sn K-edge (29 200 eV) were carried out at NSLS (Brookhaven National Laboratories) at beamline X-11A with a stored energy of 2.5 GeV and ring currents between 100–200 mA, at about 100 K in transmission using a double-crystal Si(311) monochromator.

If the carbonyl stretching region of the precursor (in hexane: 2001, 1927, and 1904 cm<sup>-1</sup>) is compared with that of

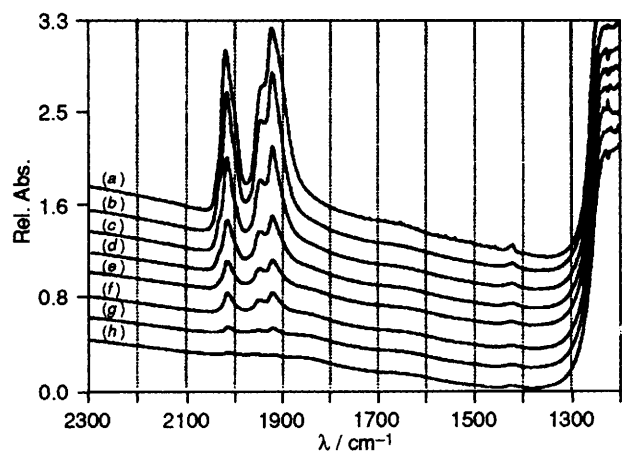


Fig. 1 *In situ* FTIR spectra of Me<sub>3</sub>SnMo(CO)<sub>3</sub>(η-C<sub>5</sub>H<sub>5</sub>) in the MCM-41 host under vacuum: (a) 30, (b) 290, (c) 320, (d) 340, (e) 360, (f) 370, (g) 390, (h) 400 °C. Heating rate 2 °C min<sup>-1</sup>. Peaks observed at 2019, 1948, 1921 and 1422 cm<sup>-1</sup>.

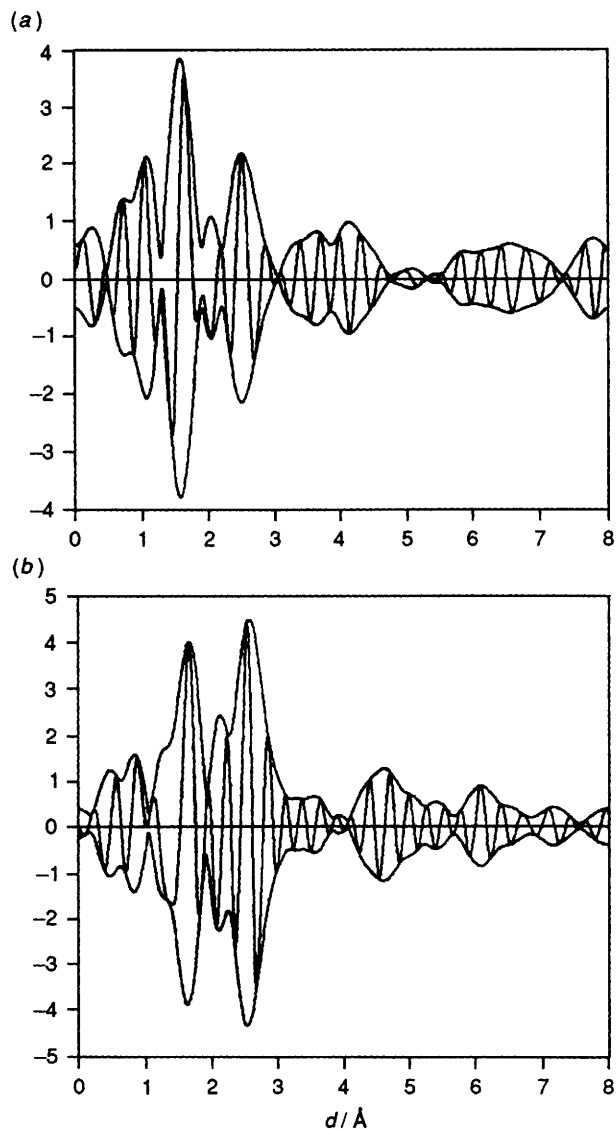


Fig. 2 Fourier-transformed EXAFS data of Me<sub>3</sub>SnMo(CO)<sub>3</sub>(η-C<sub>5</sub>H<sub>5</sub>) in MCM-41 at different treatment temperatures: (a) Sn-edge, 30 °C; (b) Sn-edge, 300 °C

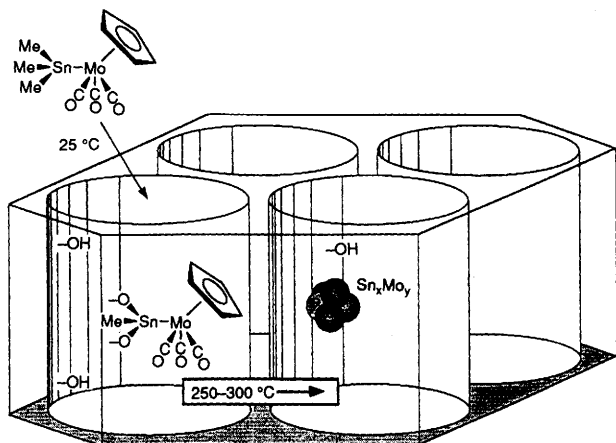


Fig. 3 Proposed intrazeolite chemistry of  $\text{Me}_3\text{SnMo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$  in the MCM-41 host (schematic)

the complex in MCM-41 (2019, 1948, and  $1921\text{ cm}^{-1}$ ) only moderate changes are observed (*in situ* FTIR spectroscopy; Fig. 1). This shows that there are no significant surface-CO interactions present such as those observed with carbonyl complexes in Na-containing zeolites (*e.g.* ref. 8). The hydroxyl region (monitored in the first overtone) shows a significant reduction of the intensity of the band at  $7328\text{ cm}^{-1}$ , supporting the idea that the trimethyl tin moiety reacts with the surface.

*In situ* FTIR-TPD experiments with the SnMo complex in MCM-41 show the striking stability of the above-mentioned triplet of CO stretching bands when heating up to about  $290^\circ\text{C}$  (Fig. 1). Only above  $320^\circ\text{C}$  is a slow decrease in intensity visible, and the subsequent destruction of the CO species between 320 and  $400^\circ\text{C}$  occurs without any significant change in band position, relative intensities, and without formation of intermediates. A slight increase of CO evolution becomes visible above about  $200^\circ\text{C}$ , with a maximum as high as  $350^\circ\text{C}$  (TPD-MS spectra). Methane evolution with a maximum at  $360^\circ\text{C}$  is also observed.

EXAFS data show the following: The bimetallic complex remains intact at the Mo moiety when adsorbed into the dry MCM host (Mo-CO, 3.4 ligands at  $3.15\text{ \AA}$ ). The Mo-edge shape is similar to that of the precursor. The tin coordination sphere is consistent with three C/O groups [Sn-C/O<sub>3.2</sub> at  $2.08\text{ \AA}$ ; Fig. 2(a)]. This distance is significantly shorter than that of the precursor ( $2.15\text{ \AA}$ ), indicating surface attachment with oxygen substitution at tin. This is confirmed by the Sn-edge shape that shows loss of Sn-C features. The second tin shell is assigned to Sn-Mo backscattering (reliable fits are difficult because of overlapping shells).

At  $300^\circ\text{C}$ ,<sup>†</sup> the Sn-edge EXAFS shows coordination to oxygen (3.5 O at  $2.08\text{ \AA}$ ), and a significant increase of the second-shell amplitude, due to metal backscattering [Fig. 2(b)]. These changes can be compared with a remarkable increase of absorption in the near IR spectra, and indicate the formation of metallic molybdenum-tin clusters in the MCM host after thermal decomposition of the precursor complex.

In summary, the reaction of  $\text{Me}_3\text{SnMo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$  with the walls of hexagonal mesoporous MCM-41 leads to intra-

channel attachment of the bimetallic species *via* removal of some of the methyl ligands already at room temp. The attached complex is extremely stable and starts to dissociate CO only above *ca.*  $200^\circ\text{C}$ , and converts into sub-nanometer size Sn-Mo metal clusters at about  $300^\circ\text{C}$ , as depicted in Fig. 3. Initial catalytic studies of this system show high activity of the intact, attached bimetallic complex for olefin hydrogenation.

The striking thermal stability of these encapsulated organometallic and metal cluster species permits further studies of their chemical reactivity and catalytic activity.

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### Footnote

<sup>†</sup> These temperatures can not be directly compared with the *in situ* IR measurements because batch processes take much longer than desorption from thin films.

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