Composition-tunable Metal–Alkyl Xerogels as Precursors for Homogeneously Dispersed Metals in Amorphous Silica Matrix

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Organometallic alkyls of Fe, Mo and W containing an $-Si(OEt)_3$ function are prepared and used for the synthesis of metal containing inorganic–organometallic hybrid materials by sol–gel processing with $Si(OEt)_4$.

The design of supported metal catalysts represents an important challenge in the field of heterogeneous catalysis.[1] In addition to the classical method of producing dispersed metal particles from metal salts and to more recent procedures involving organometallic species,[2] the considerable progress in transition metal cluster chemistry has made possible the use of heteropolymetallic complexes as precursors of highly dispersed bi- or poly-metallic particles of controlled composition.[3] However, this method does not allow a continuous variation of the intermetallic ratio in mixed-metal catalysts since it is strongly related to, and therefore limited by, that in the molecular precursor. Furthermore, the metal loading is sometimes difficult to control.

An elegant solution would be to be able to tune the metal composition at the molecular level, *i.e.* in solution, and to produce the solid matrix after the mixing of the components. This should be possible by the sol–gel process,[4] which has recently attracted considerable attention for the preparation of new supports in heterogeneous and hybrid catalysis. Indeed, it offers the possibility of preparing, under mild conditions, organic–inorganic hybrid xerogel materials of the type $x\mathrm{SiO_2}\cdot\mathrm{SiO_{3/2}(CH_2)}_n\mathrm{L}$, with controlled concentration of ligating functions L, by hydrolysis and co-condensation of $Si(OEt)_4$ (TEOS) with the substituted alkoxide $(EtO)_3Si(CH_2)_nL$. Depending on the nature of the metal species and on the metal anchoring conditions, both tethered metal complexes with catalytic activity[5] and supported metal particles[6] have been prepared from hybrid sol–gel materials.

In order to have suitable sol–gel precursors allowing a fine-tuning of the metal composition and dispersion without the often undesirable presence of ligating functions, we have attempted the synthesis of new metal alkyls containing the triethoxysilyl group, namely $(EtO)_3SiCH_2CH_2CH_2Fe(CO)_2(C_5H_5)$ **1**, $(EtO)_3SiCH_2CH_2CH_2Mo(CO)_3(C_5H_5)$ **2** and $(EtO)_3SiCH_2CH_2CH_2W(CO)_3(C_5H_5)$ **3**. We report here the preparation and characterisation of these compounds and the metal-containing inorganic–organometallic hybrid materials obtained by sol–gel processing **1–3** with TEOS.

Nucleophilic attack of the metallates $[Fe(CO)_2(C_5H_5)]^-$, $[Mo(CO)_3(C_5H_5)]^-$ or $[W(CO)_3(C_5H_5)]^-$ on $(EtO)_3SiCH_2CH_2CH_2I$ afforded the metal alkyls **1–3**, respectively, as dense, deep-coloured liquids which are stable under nitrogen at room temperature [eqn. (1); M = $(C_5H_5)Fe(CO)_2$ **1**, $(C_5H_5)Mo(CO)_3$ **2**, $(C_5H_5)W(CO)_3$ **3**].†

$$(EtO)_3SiCH_2CH_2CH_2I + Na[M] \longrightarrow (EtO)_3SiCH_2CH_2CH_2M + NaI \quad (1)$$

Sol–gel co-condensation of these complexes with TEOS yielded the new xerogels XGFe, XGMo and XGW, respectively, in which the unchanged alkyl moieties are covalently attached to the amorphous silica network. During the gelification only slight decomposition occurred, yielding the corresponding dimeric species $[\{(C_5M_5)M(CO)_x\}_2]$ and other unidentified carbonyl compounds, extracted by dichloromethane from the dried gel (evidenced by FTIR spectroscopy). Nevertheless the starting silicon : metal ratio was almost unchanged in the products as determined by energy dispersive X-ray microanalysis (EDX). Mixed-metal materials may be obtained in any ratio by starting from a mixture of **1**, **2** and **3**. As an example a 1 : 1 Fe–Mo xerogel (XGFeMo) was produced.‡

Identification of the tethered species was carried out by FTIR spectroscopy, comparing the solution spectra of the precursor with the spectra of the xerogels (Fig. 1 in the case of **1** and XGFe). Elemental analysis of the products was performed by EDX and the Si : metal ratios were found to correspond rather well to the ratio of the reagents.§ A composition distribution map was collected in the case of the mixed Fe–Mo xerogel; as expected a high homogeneity for both Fe and Mo was found.

The thermal decomposition of the carbonyl species in the xerogels XGFe and XGMo were monitored in a DRIFTS (diffuse reflectance FTIR spectroscopy) heatable cell, under a nitrogen flux. In the case of the iron xerogel, the $Fe(CO)_2(C_5H_5)$ moiety decomposes in the range 180–220 °C, giving no other carbonyl species. The morphology of the micrometric glassy grains of the materials does not change even after thermal treatment at 600 °C (Fig. 2). In the case of XGMo, decomposition begins at 180 °C, but other carbonyl fragments [ν(CO) cm^{-1} 1967w, 1894s, 1858s] are formed in the matrix, highly similar to those found in the case of adsorption of $[(C_5H_5)_2Mo_2(CO)_4]$ on silica.[7] Unlike the iron xerogel, the molybdenum system allows the formation (favoured by the high

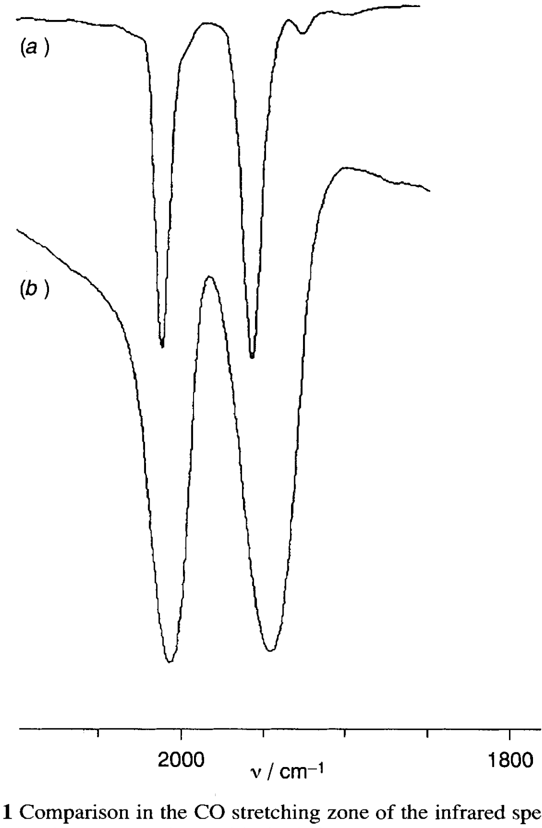

Fig. 1 Comparison in the CO stretching zone of the infrared spectrum of **1** [(*a*), hexane solution] with the infrared spectrum of XGFe [(*b*), KBr pellet]

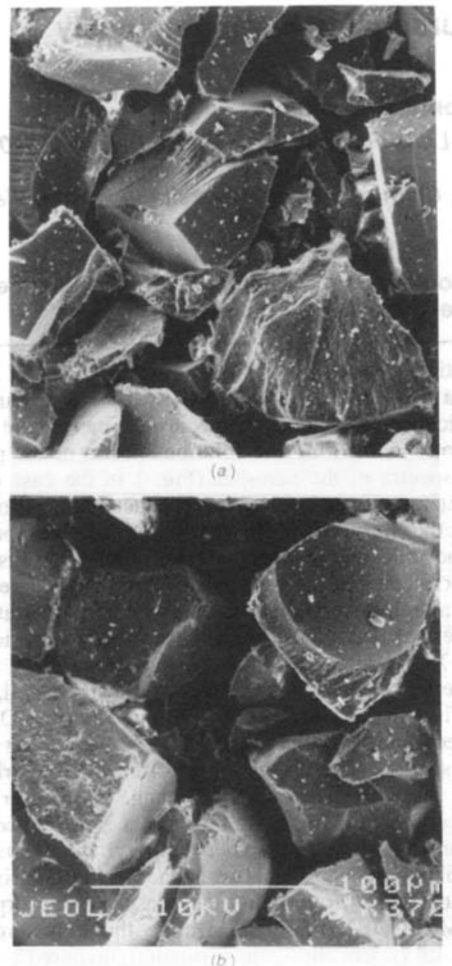

Fig. 2 SEM photographs of the xerogel XGFe before (*a*) and after (*b*) thermal treatment under nitrogen at 600 °C

level of metal loading in the xerogel) of stable dimeric species, still present at 300 °C. For all the xerogels, treatment at 600 °C under a nitrogen flux leaves no organic or carbonyl species on the silica.

A sample of XGFe was reduced in a steel reactor under a hydrogen flux at 500 °C. The material obtained has a metal loading of *ca.* 10% m/m (EDX analysis), and adsorbs carbon monoxide at 150 °C. In conclusion these materials, which are easy to synthesize, should become interesting catalytic metal systems with easily tunable composition and properties. In order to understand better the nature of the surface metal species in the mono- or poly-metallic xerogels at different loading, XPS experiments are planned.

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Footnotes

† Compounds **1–3** were prepared by addition of a THF solution of the iodoalkyl to a THF solution of the metallate at 0 °C. The temperature was raised to 25 °C and the mixture was stirred for 2 h (**1**) or 5 d (**2**, **3**). Yields calculated on the purified products varies from 65 to 40%. **1**, IR (hexane): ν(CO) cm^{-1} 1999s, 1941s. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.7 [5H, s, $Fe(C_5H_5)$], 3.79 (6H, q, $CH_3C\mathit{H}_2O$), 1.53 (2H, br s, $C\mathit{H}_2CH_2Fe$), 1.49 (2H, br s, $CH_2C\mathit{H}_2Fe$) 1.23 (9H, t, $C\mathit{H}_3CH_2O$), 0.72 (2H, m, $SiC\mathit{H}_2$). **2**, IR (hexane): ν(CO) cm^{-1} 2018s, 1934s. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.27 [5H, s, $Mo(C_5H_5)$], 3.8 (6H, q, $CH_3C\mathit{H}_2O$), 1.67 (4H, br s, CH_2CH_2Mo), 1.22 (9H, t, $C\mathit{H}_3CH_2O$), 0.76 (2H, m, $SiCH_2$). **3**, IR (hexane): ν(CO) cm^{-1} 2009s, 1912s br. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.37 [5H, s, $W(C_5H_5)$], 3.8 (6H, q, $CH_3C\mathit{H}_2O$), 1.63 (4H, br s, CH_2CH_2W), 1.21 (9H, t, $C\mathit{H}_3CH_2O$), 0.72 (2H, m, $SiCH_2$).

‡ Typical sol–gel conditions are TEOS : $(EtO)_3Si(CH_2)_3M$ = 5 : 1, in methanol, with NH_4F as catalyst. These conditions give a high concentration of the metallic moiety inside the matrix, thus allowing easy characterisation.

§ XGFe: IR (KBr pellet): ν(CO) 2003s, 1943s cm^{-1}; EDX, Si : Fe = 5.6 : 1 (soln. = 5.9 : 1), 10% m/m. XGMo: IR (KBr pellet): ν(CO) 2013s, 1917s br cm^{-1}; EDX, Si : Mo = 5.85 : 1 (soln. = 6 : 1), 15% m/m. XGW: IR (KBr pellet): ν(CO) 2009s, 1918s br cm^{-1}; EDX, Si : W = 5.9 (soln. = 6 : 1), 25% m/m. XGFeMo: IR (KBr pellet): ν(CO) 2014s, 1935s br cm^{-1}; EDX Si : Fe = 13 : 1, Si : Mo = 10.9 : 1, Fe : Mo = 0.83 (soln. = 10, 10, 1 : 1).

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