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Metallic nanoparticles from heterometallic Co–Ru carbonyl clusters in mesoporous silica xerogels and MCM-41-type materials†

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Impregnation of a mesoporous xerogel or of MCM-41 with an organic solution of the heterometallic cluster [NEt$_4$][Co$_3$Ru(CO)$_{12}$], followed by thermal treatment under an inert atmosphere, leads to highly dispersed magnetic nanoparticles under milder conditions than when conventional metal salts are used as precursors.

The confinement of molecular clusters in the cavities of meso- or nano-porous inorganic matrices is attracting increasing interest as a way to stabilise highly dispersed metals in the form of atoms, clusters or colloids and prevent their coalescence into larger, ill defined aggregates. There are obvious implications for the fabrication of microelectronic devices[1] and for catalytic reactions whose selectivity will critically depend on the size and dispersion of the metal particles and also on the shape of the cavity in which they are embedded.[2] Numerous recent reports have emphasised the specific magnetic, optical, electrochemical, chemical and catalytic properties of nanostructures constructed from molecular clusters or colloids.[3] The sol–gel process is being increasingly applied to the design of new materials using functional building blocks[4] and it has already been used to incorporate mono- and bi-metallic species into inorganic matrices.[2c,5] Furthermore, solids with a template-based morphology control, such as zeolites and MCM-41, are currently attracting increasing attention as a way to stabilise highly dispersed metal particles endowed with unique properties (*e.g.* magnetic, catalytic, *etc.*).[6] A challenging development concerns the use of molecular mixed-metal clusters since microalloy particles could be obtained that would not be accessible by other, more conventional approaches.

With the aims of studying the influence of the structure of the inorganic matrix on the metal particles obtained after thermal treatment of confined molecular Ru/Co clusters, we have compared a mesoporous silica of the MCM-41 type with mesoporous silica xerogels.

A sample of MCM-41[7a] (pore diameter *ca.* 27 Å, specific surface area 1000 m^2 g^{-1}) was impregnated with a dark red saturated THF solution of [NEt$_4$][Co$_3$Ru(CO)$_{12}$],[8] resulting in a Co/Si molar ratio of 0.07 (EDX analysis). When a 1×10^{-3} M solution of the cluster was used, its discoloration from dark red to light red optically indicated adsorption of the cluster onto MCM-41. The solid was then rinsed with THF until the filtrate was colourless and drying under primary vacuum at room temperature (24 h) afforded an ochre powder which was kept under argon. The IR spectrum in the ν(CO) region contained the fingerprint absorptions of the molecular cluster.[8] X-Ray powder diffraction showed the absence of crystallised [NEt$_4$][Co$_3$Ru(CO)$_{12}$], consistent with a high dispersion of the molecular cluster. The typical IR *ν*(CO) pattern was lost around 200 °C whereas the unsupported cluster decomposes at *ca.* 150 °C, which is consistent with a stabilising effect of the matrix. Furthermore, for the first time to our knowledge, the thermal evolution of the impregnated MCM-41 was followed by magnetic measurements in original lab-built equipment allowing heating of the sample under either reducing (H$_2$, N$_2$–5% H$_2$) or inert atmospheres (Ar). Magnetisation at 1 Tesla progressively increases above 250 °C to reach a maximum at *ca.* 550 °C [Fig. 1(a)]. Further heating results in a decrease of the magnetisation consistent with a Curie point at *ca.* 980 °C. In comparison, a similar experiment on the pure cluster showed an increase in the magnetisation by 180 °C and a Curie temperature around 650 °C. In both cases, the Curie temperature is lower than in pure bulk cobalt (*ca.* 1115 °C), which may be interpreted as resulting from the formation of Co/Ru alloys and/or from the small size of the particles. This will be further investigated by variable temperature XRD experiments under an inert atmosphere.

A crushed mesoporous xerogel[9] (pore diameter *ca.* 35 Å along with microporous domains, specific surface area 750 m^2 g^{-1}) was impregnated, dried and thermally treated in the same manner. The Co/Si molar ratio was *ca.* 0.025 (EDX analysis). Magnetisation at 1 Tesla increases above 200 °C in a stepwise manner and reaches a maximum around 550 °C with a Curie temperature around 1000 °C [Fig. 1(b)]. For consistency, the magnetisation is expressed as per gram of cobalt to account for the different metal content in the samples.

Thermal treatments under argon were realised at 250, 350 and 500 °C on both materials. In all cases, TEM observations showed metal particles which for MCM-41 were well dispersed with a narrow size distribution (Table 1) whereas in the xerogels, the dispersion is less regular. At 500 °C, the small particles (*ca.* 30 Å) coalesce to form larger, ill defined aggregates (*ca.* 200 Å). This clearly points to a structural effect

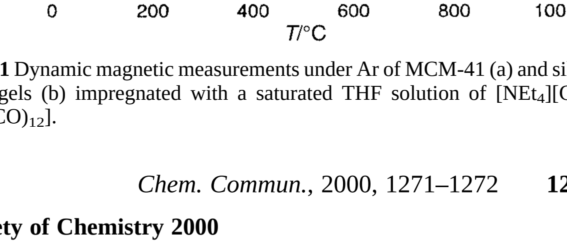

Fig. 1 Dynamic magnetic measurements under Ar of MCM-41 (a) and silica xerogels (b) impregnated with a saturated THF solution of [NEt$_4$][Co$_3$Ru(CO)$_{12}$].

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† Dedicated to the memory of Professor O. Kahn, who made so many brilliant contributions to inorganic chemistry.

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Table 1 Sizes of the particles (Å) observed by TEM on MCM-41 and xerogels, after 1 h treatment under Ar at different temperatures

	T/°C		
	250	350	500
MCM-41	10	15	80
Xerogel	30	60	30/200

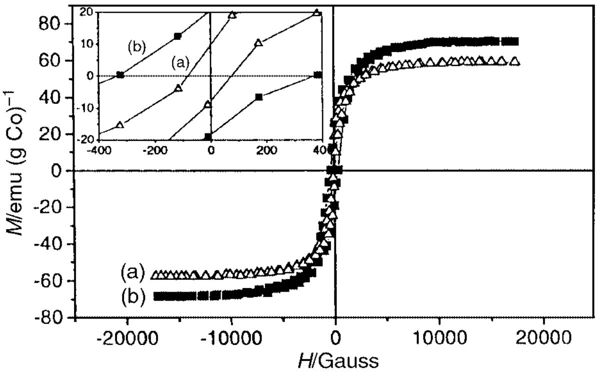

Fig. 2 Isothermal magnetic measurements at room temperature of MCM-41 (a) and silica xerogels (b) impregnated with a saturated THF solution of $[NEt_4][Co_3Ru(CO)_{12}]$, after 1 h treatment under Ar at 500 °C. Inset: expansion near zero shows an increase of the coercitivity for the monoliths.

of the inorganic matrix. Electron diffraction patterns performed on the particles observed after a thermal treatment at 500 °C show the presence of three different metallic phases: pure hexagonal cobalt, pure fcc cobalt, and pure hexagonal ruthenium; no alloy was formed at such low temperature. In contrast, X-ray diffraction after thermal treatment at 900 °C showed that a Co/Ru hexagonal alloy is also present besides pure metallic fcc cobalt and hexagonal ruthenium. Using Vegard's law, we have determined the composition of this alloy to be 86 atom% Co.

Hysteresis loops recorded at ambient temperature on the different samples are consistent with the particles sizes, since no open loop is observed for the doped MCM-41 treated below 350 °C. The xerogels show a ferromagnetic behaviour when treated at or above 350 °C (Fig. 2). In the other samples, superparamagnetic behaviour is observed. Particularly noteworthy is that, irrespective of the matrix, metal particles could be obtained at such a low temperature, without the use of a reductive atmosphere, which cannot be achieved when metal salts [*e.g.* cobalt(II) nitrate][10] are used since a hydrogen atmosphere is required to generate metallic behaviour. This is clearly due to the low oxidation state of the molecular precursor used.

Finally, the differences observed, on the one hand between the impregnated and the unsupported precursor and on the other, between the two impregnated materials, clearly indicate that the magnetic properties originate from particles inside the porous materials and not from intact molecular precursor or metal salts resulting from its decomposition, present at the external surface of the grains.

The approach presented here, which involves in the impregnation of well defined heterometallic, low oxidation-state, organometallic clusters into a given porous silica matrix, followed by thermal treatment under an inert atmosphere leads to the formation of magnetic metal particles at temperatures as low as 250 °C. The differences observed between the two kinds of materials concerning the repartition and sizes of the nanoparticles, as well as their magnetic behaviour highlights the structural effect of the inorganic matrix that should allow control of the particle size in the nanometer range and, accordingly, their magnetic properties.

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Notes and references

1 U. Simon, *Adv. Mater.*, 1998, **10**, 1487; G. Schmid and L. F. Chi, *Adv. Mater.*, 1998, **10**, 515; U. Simon, in *Metal Clusters in Chemistry*, ed. P. Braunstein, L. A. Oro and P. R. Raithby, Wiley–VCH, Weinheim, 1999, vol. 3, p. 1342.

2 (*a*) P. Braunstein, R. Devenish, P. Gallezot, B. T. Heaton, C. J. Humphreys, J. Kervennal, S. Mulley and M. Ries, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 927; (*b*) S. Kawi and B. C. Gates, in *Clusters and Colloid. From Theory to Applications*, ed. G. Schmid, Wiley–VCH, Weinheim, 1994, ch. 4, p. 298; (*c*) D. S. Shephard, T. Mashmeyer, B. F. G. Johnson, J. M. Thomas, G. Sankar, D. Ozkaya, W. Zhou, R. Oldroyd and R. G. Bell, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2242; (*d*) B. F. G. Johnson, S. A. Raynor, D. S. Shephard, T. Mashmeyer, J. M. Thomas, G. Sankar, S. Bromley, R. Oldroyd, L. Gladden and M. D. Mantle, *Chem. Commun.*, 1999, 1167; (*e*) R. Raja, G. Sankar, S. Hermans, D. S. Shephard, S. Bromley, J. M. Thomas, B. F. G. Johnson and T. Maschmeyer, *Chem. Commun.*, 1999, 1571; (*f*) E. Lindner, T. Schneller, F. Auer and H. A. Mayer, *Angew. Chem., Int. Ed.*, 1999, **38**, 2154; (*g*) M. Sasaki, M. Osada, N. Higashimoto, T. Yamamoto, A. Fukuoka and M. Ichikawa, *J. Mol. Catal. A: Chem.*, 1999, **141**, 223.

3 N. Toshima and T. Yonezawa, *New J. Chem.*, 1998, 1179; *Metal Clusters in Chemistry*, ed. P. Braunstein, L. A. Oro and P. R. Raithby, Wiley–VCH, Weinheim, 1999.

4 R. J. P. Corriu and D. Leclercq, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1420; N. Hüsing and U. Schubert, *Angew. Chem., Int. Ed.*, 1998, **37**, 22, and references therein.

5 P. Braunstein, D. Cauzzi, G. Predieri and A. Tiripicchio, *Chem. Commun.*, 1995, 229; J. P. Carpenter, C. M. Lukehart, S. B. Milne, S. R. Stock, J. E. Wittig, B. D. Jones, R. Glosser and J. G. Zhu, *J. Organomet. Chem.*, 1998, **557**, 121.

6 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710; J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10 834; A. Corma, *Chem. Rev.*, 1997, **97**, 2373; J. H. Clark and D. J. Macquarrie, *Chem. Commun.*, 1998, 853; J. Y. Ying, C. P. Mehnert and M. S. Wong, *Angew. Chem., Int. Ed.*, 1999, **38**, 56.

7 (*a*) A. C. Voegtlin, A. Matijasic, J. Patarin, C. Sauerland, Y. Grillet and L. Hure, *Microporous Mater.*, 1997, **10**, 137; (*b*) Molar composition: 1 SiO_2 : 0.8 NaOH : 0.2 C_{16}TMABr : 135 H_2O : 0.59 HCl.

8 P. Braunstein and J. Rosé, *Inorg. Synth.*, 1989, **26**, 356.

9 N. Viart and J. L. Rehspringer, *J. Non-Cryst. Solids*, 1996, **195**, 223; molar composition: 1 TMOS : 4 MeOH : 1 $HCONH_2$: 0.45 HNO_3 : 4.5 H_2O.

10 T. Lutz, C. Estournes and J. L. Guille, *J. Sol–Gel Sci. Technol.*, 1998, **13**, 929.