The Formation of Nanoparticulate Cobalt Carbide, Co₂C, Encapsulated in an Amorphous Siliceous Matrix

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Reaction of octahydridooctasesquisiloxane with $Co_2(CO)_8$ in hexane affords the complex $[Si_8O_{12}H_6]\{Co(CO)_4\}_2$ which on pyrolysis at 300 °C *in vacuo* gives nanoparticulate Co_2C encapsulated in an amorphous siliceous matrix; the magnetic coercivity of this material is 3.5 kOe.

Electrical, magnetic and optical properties of nanosized materials are markedly dependent on the size of the particles. Magnetic properties of nanosized clusters of ferromagnetic metals have been investigated extensively in recent years because of their interesting properties which are of practical significance. In particular, nanoparticles of iron and/or cobalt have applications in high density magnetic recording devices because of their high coercivity and saturation magnetization characteristics. In contrast, nanosized iron[1] and cobalt carbides,[2] which should also have interesting magnetic properties, have been little explored. In addition, cobalt carbides in particular have been implicated as the reactive sites in cobalt-based Fischer–Tropsch catalysts[3] and isolated carbides of cobalt, *e.g.* Co_2C, have been studied mainly in connection with the Fischer–Tropsch process.[4] Unfortunately, further development of these materials as catalysts has been hindered by the lack of suitable preparative routes. The preparation of Co_2C is lengthy and protracted,[5] and involves exposing finely divided cobalt metal to carbon monoxide at temperatures below 225 °C, but takes 400 h for complete reaction. Great care needs to be excercised with the exact conditions since at only moderately higher temperatures the carbide Co_3C_2 and elemental carbon are formed. More sophisticated preparative techniques such as carbon ion implantation[6] and rf magnetron sputtering[2] have been employed to obtain films of cobalt carbides, but are not suitable for the preparation of single-phase material in bulk. Thus, a convenient route to Co_2C is desirable in view of its potential magnetic and catalytic properties.

In this communication we describe an unusual route for the formation of particulate cobalt carbide, Co_2C, encapsulated in an amorphous siliceous matrix *via* a complex formed from dicobalt octacarbonyl and the cubane octahydridooctasesquisiloxane I. This material not only exhibits an unexpectedly high coercivity value but also has potential as a Fischer–Tropsch catalyst. We believe this method provides a convenient synthesis of Co_2C in a useful form.

Rather surprisingly, the reactivity of the Si–H bonds of the octahydridooctasesquisiloxane I appears to be significantly lower than might be expected by comparison with simple hydridosilanes such as $SiHX_3$ (X = Cl, OMe), and only a few reaction types have been described for this molecule. However, reaction of I with dicobalt octacarbonyl (molar ratio 1 : 1) in dry, oxygen-free hexane results in the formation of a clear brown solution after stirring at ambient temperature for 24 h. Removal of the solvent affords a brown waxy product which microanalytical and spectroscopic data indicated to be the complex II

as a hexane solvate. The ¹H NMR spectrum of II (hexane solution) exhibits two resonances at δ 4.19 and 4.35 in the ratio 2 : 1 and therefore are assigned to the two types of hydrogen atom H_A and H_B, respectively, of structure II. The ²⁹Si NMR spectrum exhibits four resonances at δ −87.9, −86.3, −50.5 and −48.3 relative to $SiMe_4$. The peaks at δ −87.9 and −86.3 are assigned to cage silicon atoms bonded to hydrogen atoms H_A and H_B. The resonances at δ −50.5 and −48.3 are assigned to the two cage silicon atoms bearing $Co(CO)_4$ groups. That these are magnetically inequivalent suggests some steric interaction between the two $Co(CO)_4$ groups. The ¹³C NMR spectrum exhibits a single resonance at δ 196.5 relative to $SiMe_4$ [*cf.* $Co_2(CO)_8$ in CH_2Cl_2, single resonance at δ 202.5] indicating the fluxional nature of the carbonyl groups. In the IR carbonyl bands are observed at 2112m, 2049m, 2018s, br, 1984w, sh and 1861vw, br cm⁻¹ {*cf.* bands at 2112m, 2095s, 2054m, 2036m, 2020m, 2014w, sh and 1992vw cm⁻¹ for $[Co(CO)_4]_2SnBr_2$}, with cage Si–H stretching bands at 2300w, sh, 2293m and 2272w, sh cm⁻¹ [*cf.* bands at 2300w, sh and 2293m cm⁻¹ for $Si_8O_{12}H_8$]. The mass spectrum (70 eV) exhibits high mass fragments at *m/z* values of 680 {[$Si_8O_{12}H_6$]-$Co_2(CO)_5^+$ (10%)}, 652 {[$Si_8O_{12}H_6$]$Co_2(CO)_4^+$ (2%)}, 624 {[$Si_8O_{12}H_6$]$Co_2(CO)_3^+$ (2%)}, 596 {[$Si_8O_{12}H_6$]$Co_2(CO)_2^+$ (8%)}, 568 {[$Si_8O_{12}H_6$]$Co_2(CO)^+$ (4%)}, 540 {[$Si_8O_{12}H_6$]Co_2^+ (7%)} and 423 {[$Si_8O_{12}H_7$]⁺ (100%)}.

Thermolysis of the complex II (sealed tube, 300 °C, *in vacuo*, 24 h) results in the conversion into a shiny bluish-black powder III which exhibits a metallic lustre. The IR spectrum of III shows that it still incorporates some residual Si–H function [v(Si–H) at 2264 cm⁻¹] but no carbonyl bands remain. XRD (Cu-Kα, λ = 1.54250 Å) showed that the only crystalline component of the product III was the cobalt carbide Co_2C [Fig. 1(*a*)] with *d*-spacings (relative intensities in parentheses) at 2.3927 (24.5), 2.1747 (40.1), 2.1008 (100), 1.9751 (53.9), 1.6115 (21.9), 1.5499 (4.5), 1.4384 (6.5), 1.3173 (8.3), 1.2401 (7.7), 1.2140 (6.0), 1.1616 (9.5), 1.1238 (5.2), 1.0895 (2.7) and 0.9618 (3.5) Å [*cf.* lit.⁵ᵇ,⁸ᵃ values 2.4137 (20), 2.3287 (10),
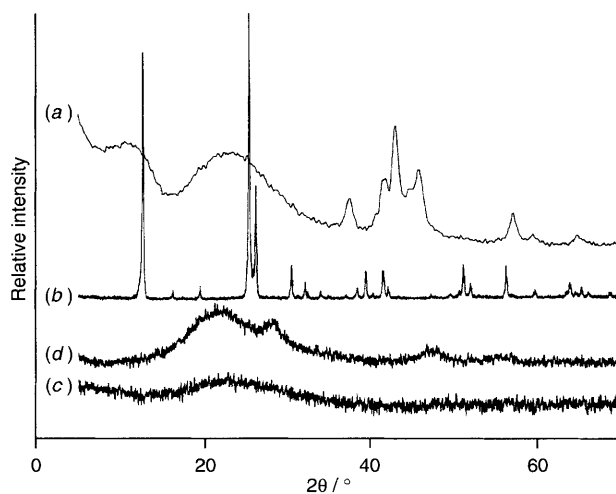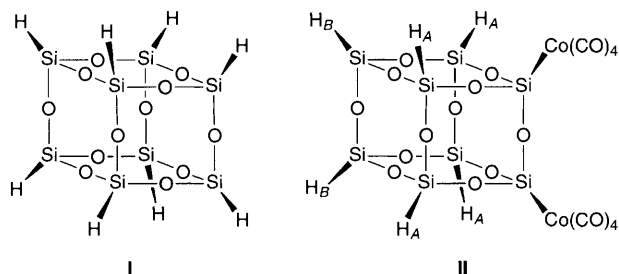

Fig. 1 Powder XRD patterns for III (*a*), and [$Si_8O_{12}H_8$] heated for 24 h at (*b*) 300, (*c*) 600 and (*d*) 1000 °C

2.1712 (20), 2.1127 (100), 1.9826 (80), 1.6244 (60), 1.5558 (10), 1.4454 (20), 1.3166 (60), 1.2469 (60), 1.2187 (40), 1.2053 (40), 1.1680 (80), 1.1267 (80), 1.0754 (10), 1.0638 (10), 1.0565 (10), 0.9949 (60) and 0.9895 (10) Å]. Neither cobalt metal[5b,8b] [d-spacings expected at 2.165 (20), 2.023 (60), 1.910 (100), 1.480 (1), 1.252 (80), 1.149 (80), 1.083 (20), 1.066 (80), 1.047 (60), and 1.015 (20) Å (hexagonal) and at 2.046 (100), 1.772 (40), 1.253 (25), 1.068 (30) and 1.023 (12) Å (cubic)] nor Co₃C[8c] [d-spacings expected at 2.496 (1), 2.359 (20), 2.339 (18), 2.222 (16), 2.176 (14), 2.070 (35), 2.029 (35), 1.997 (100), 1.943 (30), 1.854 (20), 1.825 (35), 1.736 (12), 1.676 (3), 1.665 (8), 1.611 (5), 1.558 (9), 1.518 (2), 1.487 (5), 1.391 (4) and 1.328 (3) Å] are observed. In addition to the peaks due to crystalline Co_2C, the X-ray diffractogram exhibits very broad diffuse bands at 2θ values of ca. 10 and 22°. It is noteworthy that at the temperature at which the complex II decomposes (300 °C) the parent hydride I is totally stable and exhibits an XRD spectrum with very sharp peaks [Fig. 1(b)], and only undergoes thermal degradation above 400 °C giving an XRD spectrum containing a broad featureless band at a 2θ value of ca. 22° with additional bands appearing at 29 and 48° at 1000 °C [Figs. 1(c) and (d)].

A transmission electron micrograph of a demagnetized sample of III is illustrated in Fig. 2, and shows the material to consist of individual spherical particles of Co_2C of diameter ca. 50–60 nm embedded in the lower electron-dense siliceous matrix. Closer examination of the siliceous matrix shows there
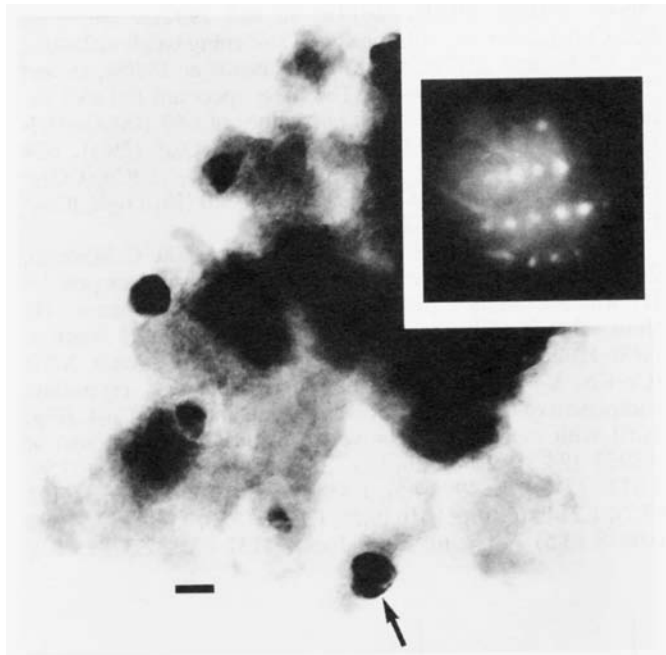

Fig. 2 Transmission electron micrograph of III. The electron diffraction pattern shown is that recorded for the electron-dense particle arrowed. The scale bar represents 50 nm.

to be similar particles of dimensions as low as a 2–3 nm. EDXa analysis of the large spherical particles show them to contain only cobalt and carbon, whilst electron diffraction shows a pattern characteristic of a single crystal (Fig. 2 inset).

Magnetic measurements using a vibrating magnetometer showed the magnetic coercivity of III to be 3.5 kOe. This compares with a value ca. 2.5 kOe reported for iron particles of nanometer dimensions (1.7–7.0 nm) embedded in a silica glass matrix.[9,10] Ultrafine (10 nm) particles of composition $Fe_{63}Ni_{24}B_{13}$ have a coercivity of 1.275 kOe,[11] but finely dispersed Fe–Co alloy particles exhibit a value of only 0.23 kOe.[12]

The high observed coercivity in the present case is a result of the particle size approaching the dimension of a single domain. When particles have dimensions of the order of that of a single domain, the coercivity of the assembly is related to the size of the particle by the expression[13] $H_c = 2K/M_s[1 - (25kT/KV)^{1/2}]$ where K is the anisotropy energy density constant, M_s the saturation magnetization, k the Boltzmann constant, and V the particle volume. For cobalt metal the single domain range is ca. 30 nm[13] whilst for iron the single domain size is ca. 20 nm.[9] Thus, in the present case it would appear that the particles of Co_2C exist as single domain, single crystallites embedded in the siliceous matrix.

As a Fischer-Tropsch catalyst, III exhibits promising activity. In a typical experiment using a catalytic microreactor charged with 0.5 g of III, a flow of 10% CO, 40% H_2 and 50% He (50 ml min⁻¹) gave 1.9% conversion of CO (65% overall selectivity towards hydrocarbons; selectivities for CH_4 37%, alkenes 30%, and alkanes 32%) at 503 K.

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