Preparation of a Microporous Organometallic Material

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Zeolites[1] and transition-metal organometallic complexes[2] have found widespread application as heterogeneous and homogeneous catalysts, respectively, the former on account of their microporosity and the latter on account of their selective reactivity toward organic molecules under mild conditions. Materials combining the properties of both classes of compounds are therefore of great interest and have been studied in the form of zeolite-supported organometallic complexes.[3] We report here a new approach to this type of material where the microporous framework itself is organometallic. This approach is based on the observation that many zeolite frameworks are comprised of large aluminosilicate cages linked together into cross-linked, three-dimensional polymers and the idea that microporous organometallic analogues might be prepared by linking together organic cages in a similar fashion using transition-metal complexes. We describe here a successful implementation of this approach using C_{60} cages and $-Ir(C_2H_4)(\mu_2\text{-}Cl)_2(C_2H_4)Ir-$ linkages. C_{60} was selected as the cage unit due to its large size and its ability to bind up to six transition metals octahedrally in molecular[4] and possibly in polymeric[5] systems; $[(C_2H_4)_2Ir(\mu_2\text{-}Cl)_2Ir(C_2H_4)_2]$ was selected as the linkage precursor since its ethylene ligands are easily displaced by other olefins.[6]

Microporous organometallic Ir/C_{60} materials were prepared in an inert argon or nitrogen atmosphere using the following type of two-step procedure: First, a solution of C_{60} (104 mg, 0.144 mmol) in 70 mL of benzene was added to 4.3 equiv of $[Ir_2Cl_2(C_2H_4)_4]$ (354 mg, 0.622 mmol) in 12 mL of benzene at 25 °C with stirring over 2 min. A brown precipitate appeared, and the suspension was stirred for 4 h. The precipitate was then collected by filtration, washed with 15 mL of benzene, and dried in vacuo to yield 355 mg of material having a nitrogen BET surface area of <10 m^2/g.[7] A 350 mg sample of this material was suspended in 28 mL of dry, degassed 1,2,4-trimethylbenzene and heated to reflux (168 °C) with stirring for 5 days while slowly bubbling ethylene gas through the suspension. The solid sample was then isolated by filtration, washed with 20 mL of benzene, and added to 25 mL of benzene. This suspension was heated to 80 °C for 1 h in an ethylene stream, and the suspended material was isolated by filtration and dried in vacuo (0.05 Torr) yielding 299 mg of an air-sensitive product.[8] This brown material had a nitrogen BET apparent surface area of 250−300 m^2/g, with the precise value depending largely upon the degassing procedure followed (see below) and the reaction stoichiometry employed. When larger amounts of $[Ir_2Cl_2(C_2H_4)_4]$ were used, i.e., 6−8 equiv, the trimethylbenzene solution formed in the second step of the preparation was replaced with fresh solvent after 1 day.

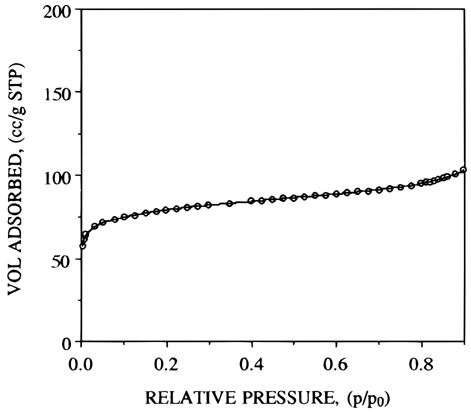

Figure 1. Nitrogen adsorption isotherm measured at liquid nitrogen temperature for C_{60}/Ir material prepared as described in the text using 4.3 equiv of $[Ir_2Cl_2(C_2H_4)_4]$.

Nitrogen gas sorption isotherms identify the Ir/C_{60} materials just described as high surface area, microporous materials. The nitrogen-adsorption isotherm shown in Figure 1 was measured from a sample prepared using 4.3 equiv of $[Ir_2Cl_2(C_2H_4)_4]$ after outgassing for 2 h at 110 °C and 10^{-3} Torr. The type I/type II composite isotherm shows no hysteresis in the 0−0.8 relative pressure range, and BET analysis yielded an apparent surface area of 297 m^2/g. Two features of the BET analysis suggested sample microporosity:[9] the BET *C* value was very high (ca. 2000), and the BET plot was linear only up to $p/p_0 = 0.10$ and therefore did not extend into the region where the isotherm was linear ($0.25 < p/p_0 < 0.65$). Microporosity was confirmed by *t*-plots[9] using both Harkins-Jura[10] and Halsey[11] standard isotherms. The Harkins-Jura *t*-plot yielded an external surface area of 36 m^2/g and a 0.11 cm^3/g effective micropore volume; the Halsey *t*-plot gave similar values of 47 m^2/g and 0.10 cm^3/g, respectively.

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[8] Elemental analysis consistently showed >1% each of C, H, Ir, and Cl, with Ir/Cl mole ratios >1. A sample of material prepared using 7.6 equiv of $[Ir_2Cl_2(CH_2CH_2)_4]$, for example, showed an Ir/Cl ratio of 2.1: C, 35.41%; H, 1.50%; Ir, 56.83%; Cl, 4.89%.

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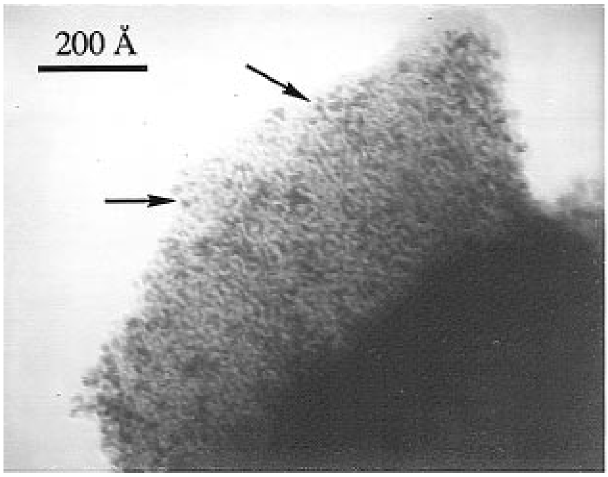

Figure 2. Bright-field STEM micrograph taken at 100 keV of C_{60}/Ir material prepared as described in the text using 6.94 equiv of $[Ir_2Cl_2(C_2H_4)_4]$. Arrows point at dark spots identified as nanocrystalline iridium metal by selected area electron diffraction.

Horváth-Kawazoe analysis[12] of high-resolution nitrogen adsorption isotherms measured in the $10^{-6} < p/p_0 < 10^{-1}$ region yielded a median pore diameter of 6.1 Å. The absorption capacity of the microporous Ir/C_{60} materials at $p/p_0 = 0.4$, 0.10−0.13 cm^3/g is comparable with that of molecular sieves such as $AlPO_4$-11 (0.085 cm^3/g[13]), $AlPO_4$-5 (0.146 cm^3/g[13]), and ZSM-11 (0.16 cm^3/g[14]). Their 250−300 m^2/g nitrogen BET apparent surface areas are also quite high, in the range observed for pillared layered materials such as pillared interlayered clays (250−400 m^2/g[15]), pillared titanium phosphates (80−250 m^2/g[16]), polyoxoanion-pillared layered double hydroxides (107−155 m^2/g[17]), and silica pillared layered oxides (280−600 m^2/g[18]). Given the high surface area and microporosity observed for the C_{60}/Ir materials and the catalytic activity of surface metal atoms observed in C_{60}-supported Pd ("$C_{60}Pd_n$"[19]), the microporous organometallic materials of the type reported here offer a potential as catalytic materials.

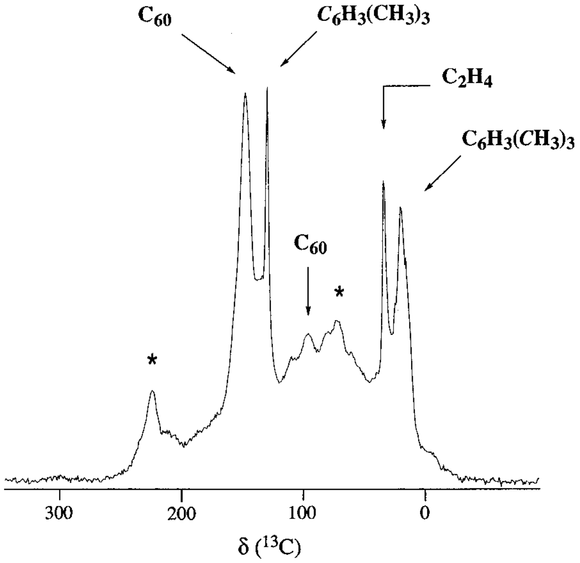

Figure 3. The 75.4 MHz ^{13}C CPMAS NMR spectrum of C_{60}/Ir material prepared as described in the text using 6.94 equiv of $[Ir_2Cl_2(C_2H_4)_4]$. The resonances labeled with asterisks are spinning sidebands of the δ 147.4 resonances.

Scanning transmission electron microscopy (STEM), $^{13}C\{^1H\}$ CPMAS NMR, and X-ray powder diffraction (XRPD) were used to characterize the Ir/C_{60} material just described and suggest that it is a composite material containing iridium nanocrystals and $-Ir(C_2H_4)(\mu_2\text{-}Cl)_2(C_2H_4)Ir-$ cross-linked $[Ir(C_2H_4)(\mu_2\text{-}Cl)_2Ir(C_2H_4)(C_{60})]_n$ polymers. The material prepared as described above was comprised of aggregated particles having 100−300 nm dimensions, and STEM bright-field images (see Figure 2) showed dark spots of high electron density within a spaghetti-like matrix of light chains having relatively low electron density. Selected area electron microdiffraction identified the dark spots as nanocrystalline iridium: spotty ring diffraction patterns were observed with *d* spacings and intensities corresponding to ccp iridium metal.[20] The *ca.* 10 Å width of the chain structures matches the van der Waals diameter of C_{60},[21] suggesting the presence of C_{60} coordination polymer chains, an interpretation consistent with $^{13}C\{^1H\}$ CP-MAS NMR and XRPD measurements. As shown in Figure 3, the ^{13}C CPMAS NMR spectrum of a sample prepared using 7.6 equiv $[Ir_2Cl_2(C_2H_4)_4]$ shows five intense resonances. The narrow δ 147.4 and very broad δ 96 resonances are assigned to uncoordinated and coordinated C_{60} carbon atoms, respectively, by analogy with $C_{60}[Pt(PEt_3)_2]_6$, where the corresponding resonances appear at δ 142.1 and 153.8 and at δ 79.2.[4] The δ 33.1 resonance is assigned to coordinated ethylene by comparison with the δ 47.9 shift observed for solid $[Ir_2Cl_2(C_2H_4)_4]$, and the δ 129.3 and 19.3 resonances are assigned to sorbed 1,2,4-trimethylbenzene ring and methyl carbon atoms whose resonances appear at δ 130.4, 129.4, and 126.3 and δ 20.7, 19.5, and 19.1, respectively, in $CDCl_3$ solution. These assignments are supported by ^{13}C CPMAS NMR spectra of Ir/C_{60} samples prepared using smaller amounts of $[Ir_2Cl_2(C_2H_4)_4]$. When 4.3 equiv was employed, for example, the intensities of the δ 33.1 coordinated ethylene carbon and δ 96 coordinated C_{60} carbon resonances were reduced relative to the intensity of the δ 147.4 uncoordinated C_{60} carbon resonance. The Cu Kα XRPD pattern of material prepared using 7.6 equiv of $[Ir_2Cl_2(C_2H_4)_4]$ showed two broad features, a reflection at about $2\theta = 40.5°$ with a 13.4° line width (fwhm), and a second reflection having about 3 times the peak intensity at $2\theta = 6.0°$ with a 7.6° line width (fwhm). The peak at 40.5° is the Ir 111 reflection[20] from the nanocrystalline iridium identified

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by selected area electron diffraction (see above). The more intense reflection arises from a *d* spacing of about 14.7 Å, and this distance matches the 14 Å repeat estimated[22] for linear segments of $[Ir(C_2H_4)(\mu_2\text{-}Cl)_2Ir(C_2H_4)(C_{60})]_n$ polymers where each C_{60} is coordinated to two Ir centers using a pair of its trans C═C double bonds.

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(22) Structural parameters from the $C_{60}[Pt(PEt_3)_2]_6$[4] and $[Rh_2Cl_2(1,5\text{-cyclooctadiene})_2]$[23] structures were used to estimate the repeat distance for the polymer.

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