

Application of Carbon Nanotubes as Supports in Heterogeneous Catalysis

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With the discovery of nanometer-scale carbon tubules¹ and their large-scale synthesis,² attention is now being focused on their potential applications in various fields of materials research, such as superconductivity, catalysis, etc. In the field of heterogeneous catalysis, numerous carbon materials have been used to disperse and stabilize metallic particles.³ Catalytic properties of these solids are known to be dependent upon the interaction between the carbon support and the metal particles. Solid-state chemistry of fullerene-based materials is of much interest due to the novel electronic properties both of the intercalation compounds of solid C₆₀^{4,5} and of C₆₀ monolayers deposited on nonalkali metals.^{6,7} Furthermore, strong interaction was found to exist between nickel clusters and multilayer films of C₆₀.⁸ For carbon nanotubes, theoretical calculations show that, depending upon the fiber geometry and the curvature of graphitic planes, the nanotubes have metallic or semiconducting properties.^{9,10} The aim of the present study is to show the potential of carbon "nanotubes" as a support for metal catalysts.

The classical preparation method of fullerenes, direct current arc discharge evaporation of graphite in a helium-filled vessel, was employed. This produces fullerenes (C₆₀, C₇₀, and other higher analogs), together with a carbonaceous deposit on the cathode which contains graphitic tubules of nanometer dimensions. The bulk cylindrical deposit was grained and sieved to yield a powder. As described before,¹ this material, known as carbon nanotubes, contains graphitic carbon needles, ranging from 4 to 30 nm in diameter and up to 1 μm in length, in addition to polyhedral carbon particles with onionlike shell structures, 5–20 nm in diameter. The surface area of this solid was determined by N₂ physisorption at 77 K and is about 27 m² g⁻¹. The supported Ru catalysts were prepared by adsorption of a ruthenium precursor

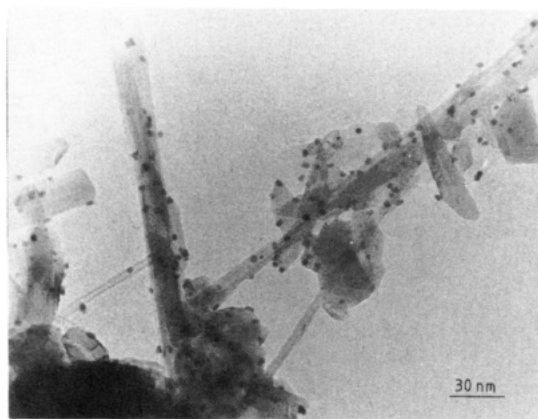


Figure 1. TEM micrograph of the Ru/nanotube catalyst (magnification $\times 10^5$). Dark spots are assigned to ruthenium clusters with sizes in the range 3–7 nm.

in toluene solution. Ruthenium 2,5-pentanedionate (31.85 mg, Aldrich) was dissolved in toluene (4 cm³, SDS, 99.3%) and then contacted for 72 h with carbon nanotubes material (0.8 g); it was found that this carbon material is insoluble in toluene. Toluene was removed by evaporation, and the residue dried in a vacuum desiccator at 353 K overnight. The resulting solid was treated for 3 h under a stream of nitrogen at 523 K and then reduced for 1 h in a stream of diluted hydrogen (H₂/N₂ = 10/90 mol/mol) according to published procedures.¹¹ The Ru/nanotubes catalyst contains 0.2 wt % Ru as determined by chemical analysis. The catalyst was characterized by hydrogen chemisorption and transmission electron microscopy. The hydrogen chemisorption was carried out in a static volumetric apparatus. The adsorption isotherm was determined at 373 K in the 6.6–33 kPa pressure range. The hydrogen monolayer coverage was calculated by extrapolating to zero pressure. From this value and using unity H/Ru stoichiometry, the percentage of ruthenium atoms present at the surface was determined (dispersion = 30%; Ru particle size \approx 3.5 nm). For the purpose of TEM characterization, a Ru/nanotube suspension in ethanol was sonicated and deposited on a copper grid covered with a carbon film; the examinations were carried out with a JEOL 200 CX apparatus with an accelerating voltage of 100 kV. We distinguish from the TEM image (Figures 1 and 2) a spacially random distribution of dark spots with a uniform distribution of sizes. From the diffraction patterns of these spots, we could assign them unambiguously to metallic ruthenium. The metallic particles range in diameter from 3 to 7 nm. The diffraction patterns of the carbon support show only the 002-type reflection ($d = 0.353$ nm) characteristic of the distance between two graphitic planes. On TEM images (Figure 1), many carbon tubules but also some polyhedral particles can be observed. External diameters and graphitic sheets numbers can be quite different. High-resolution pictures obtained with a TOPCON 002B transmission electron microscope operating at 200 kV (Figure 2) shows (i) the homogeneous distribution of metallic clusters on the nanotubes and (ii) that ruthenium clusters are deposited on the external surface of the tubes.

The catalytic properties of this new material for liquid-phase cinnamaldehyde hydrogenation have been tested. It is well established that the hydrogenation of α,β -unsaturated aldehydes occurs through the classical pathway shown in Figure 3. Our results are fully in line with this network of parallel and consecutive reactions. The experimental setup and the reaction conditions were reported in detail previously.¹¹ In short, the reaction was carried out in a 100 cm³ batch reactor. The prerduced Ru/nanotubes sample (0.26 g) was reactivated in situ in 2-propanol (40 cm³) at 383 K and under 4.5 MPa of H₂ pressure for 2 h.

(11) Coq, B.; Kumbhar, P. S.; Moreau, C.; Moreau, P.; Warawdekar, M. G. *J. Mol. Catal.* 1993, 85, 215–228.

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(1) Ijima, S. *Nature* 1991, 354, 56–58.

(2) Ebbesen, T. W.; Ajayan, P. M. *Nature* 1992, 358, 220–222.

(3) Ryländer, P. N. *Catalytic Hydrogenation in Organic Synthesis*; Academic Press: New York, London, 1979.

(4) Fischer, J. E.; Heiney, P. A.; Smith, A. B., III. *Acc. Chem. Res.* 1992, 25, 112–118.

(5) Haddon, R. C. *Acc. Chem. Res.* 1992, 25, 127–133.

(6) Lang, H. P.; Thommen-Geiser, V.; Frommer, J.; Bernier, P.; Güntherodt, H. J. *Europhys. Lett.* 1992, 18, 29–32.

(7) Ohno, T. R.; Chen, Y.; Harvey, S. E.; Kroll, G. H.; Weaver, J. H.; Hauffler, R. E.; Smalley, R. E. *Phys. Rev. B* 1991, 44, 13747–13755.

(8) Vijayakrishnan, V.; Santra, A. K.; Seshadri, R.; Nagarajan, R.; Pradeep, T.; Rao, C. N. R. *Surf. Sci.* 1992, 262, L87–L90.

(9) Saito, R.; Fujita, M.; Dresselhaus, G.; Dresselhaus, M. S. *Phys. Rev. B* 1992, 46, 1804–1811.

(10) Mintmire, J. W.; Dunlap, B. I.; White, C. T. *Phys. Rev. Lett.* 1992, 68, 631–634.

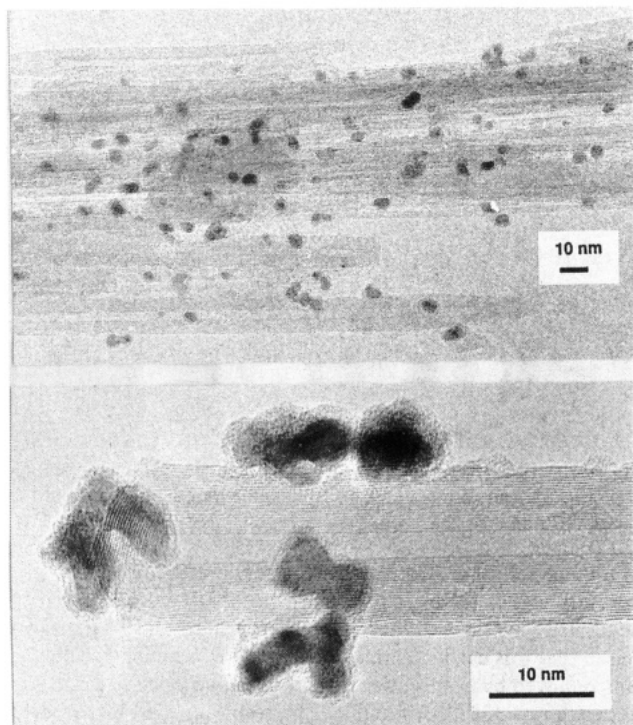


Figure 2. HRTEM pictures of the Ru/nanotube catalyst. Ruthenium clusters (dark spots) have sizes in the range 2–6 nm. They appear to be located on the external surfaces of the carbon tubes, possibly even on their closures. Sample was examined using a high-resolution TOPCON 002B transmission electron microscope operating at 200 KeV.

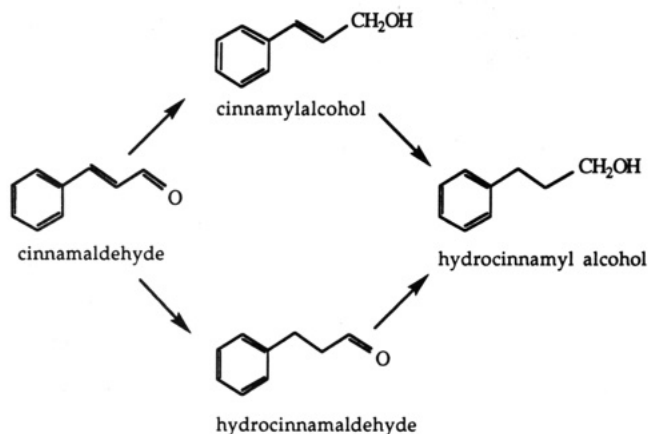


Figure 3. Cinnamaldehyde hydrogenation scheme.

After being cooled to room temperature, the cinnamaldehyde was charged and the reaction started at 383 K under 4.5 MPa of H_2 pressure with a reactant concentration of 7.9×10^{-4} mol

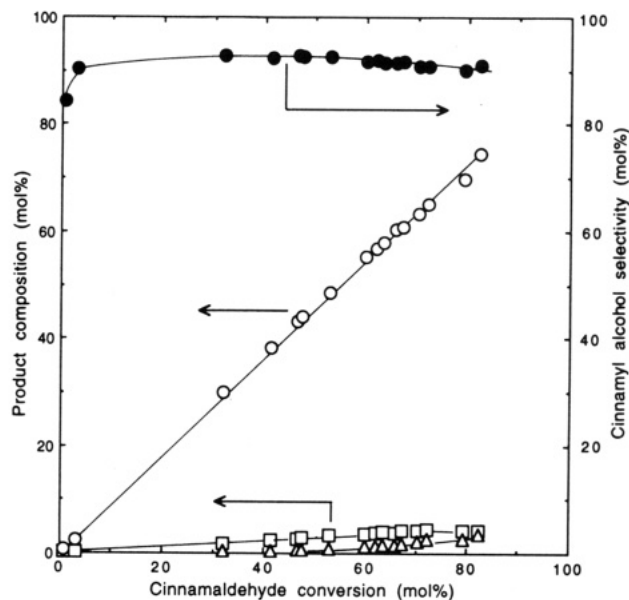


Figure 4. Composition of products and selectivity for cinnamyl alcohol for the hydrogenation of cinnamaldehyde over Ru/nanotube catalyst as a function of cinnamaldehyde conversion. (O) Cinnamyl alcohol; (□) hydrocinnamaldehyde; (Δ) hydrocinnamyl alcohol; (●) cinnamyl alcohol selectivity. T_R , 383 K; $C_{\text{cinnamaldehyde}}$, $7.9 \cdot 10^{-4}$ mol cm^{-3} ; P_{hydrogen} , 4.5 MPa; catalyst weight, 0.26 g.

cm^{-3} . Microsamples were withdrawn and analyzed on a gas chromatograph (Varian 3300 equipped with FID detector) using a DB wax capillary column (30 m \times 0.32 mm i.d.). The calibration was done by using synthetic mixtures of pure components. Figure 4 shows the composition of products as a function of cinnamaldehyde conversion. It is noteworthy that the high selectivity for cinnamyl alcohol (up to 92%) is maintained to 80% conversion of cinnamaldehyde. Under the same conditions, we found a cinnamyl alcohol selectivity of 20–30% on Ru/ Al_2O_3 catalysts with similar-sized Ru particles.¹¹ Galvagno *et al.*¹² reported 30–40% cinnamyl alcohol selectivity on carbon supported Ru with a similar dispersion. It appears that the carbon nanotubes material could induce a metal/support interaction of a different kind than that which exists for Ru supported on Al_2O_3 or active carbon. For the moment, the nature of this interaction remains unclear. More precisely, the respective role of electronic effects (d-band modification) and/or geometric effects (particle morphology) needs to be clarified.

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(12) Galvagno, S.; Capanelli, G.; Neri, G.; Donato, A.; Pietropaolo, R. *J. Mol. Catal.* **1991**, *64*, 237–246.