Pergamon

Materials Research Bulletin, Vol. 33, No. 4, pp. 663–667, 1998

0025-5408/98 $19.00 + .00

PII S0025-5408(98)00016-6

CARBON STRUCTURES OBTAINED BY THE DISPROPORTIONATION OF CARBON MONOXIDE OVER NICKEL CATALYSTS

A. Govindaraj[1]*, R. Sen[2], A.K. Santra[1], and B.V. Nagaraju[3]
[1]CSIR Centre of Excellence in Chemistry, Indian Institute of Science, Bangalore 560012, India
[2]Materials Research Centre, Indian Institute of Science, Bangalore 560012, India
[3]Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560064, India

(Refereed)
(Received May 3, 1997; Accepted May 15, 1997)

ABSTRACT

The disproportionation of CO over 18% Ni/MgO and 18% Ni/$AlPO_4$ catalysts has been studied at different temperatures. The nature of carbonaceous deposits over metal particles after the reaction has been examined by transmission electron microscopy. Carbon nanotubes are obtained by the disproportionation of CO over Ni/MgO at 700°C. *© 1998 Elsevier Science Ltd*

KEYWORDS: A. nanostructures, C. electron microscopy, D. catalytic properties

INTRODUCTION

The disproportionation of CO by the Boudouard reaction ($2CO \rightarrow CO_2 + C$) carried out in the presence of metals has been reported to yield carbon nanotubes. Several years ago, Audier et al. [1] reported filamenteous catalytic carbon in the form of simple tubes when the disproportionation of CO was carried out over Fe–Co and Fe–Ni alloys. These tubes contained metal particles at one end. In the light of more recent literature on carbon nanotubes [2], it would appear that Audier et al. had actually obtained carbon nanotubes with the metal particles at the tips. Martra et al. [3] studied the disproportionation of CO over Ni/MgO and found that the carbon produced by the Boudouard reaction at 200°C does not

*To whom correspondence should be addressed.

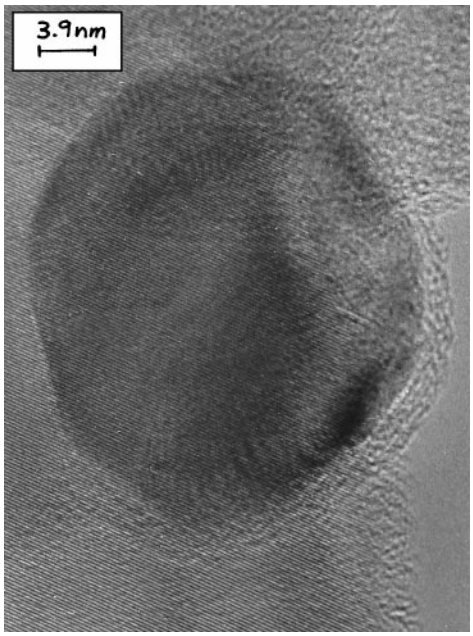

FIG. 1
TEM image of carbon coated Ni particles obtained by the disproportionation of CO at 400°C on 18% Ni/MgO.

appear on electron micrographs, suggesting that, under such mild conditions, it is very well dispersed to form carbide-like species. They found that at 400°C, CO disproportionation on Ni/MgO gives rise to Ni particles coated with graphitic carbon, as revealed by high-resolution electron microscopy. The disproportionation of CO over nanoparticles of Mo supported on fumed Al_2O_3 has recently been shown to give single-walled carbon nanotubes [4]. The disproportionation of CO at 460°C over an $Ni/Si_2–Al_2O_3$ catalyst gives rise to nanotubes or carbon filaments, depending on whether the reaction is carried out in the

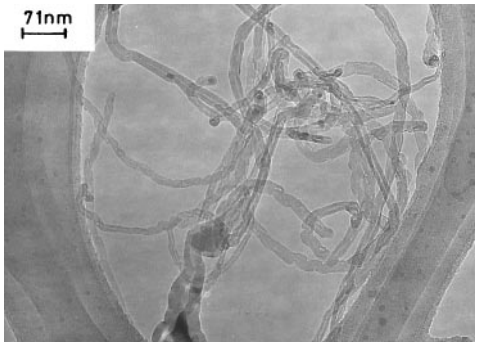

FIG. 2
TEM image of nanotubes obtained by the disproportionation of CO at 700°C on 18% Ni/MgO.

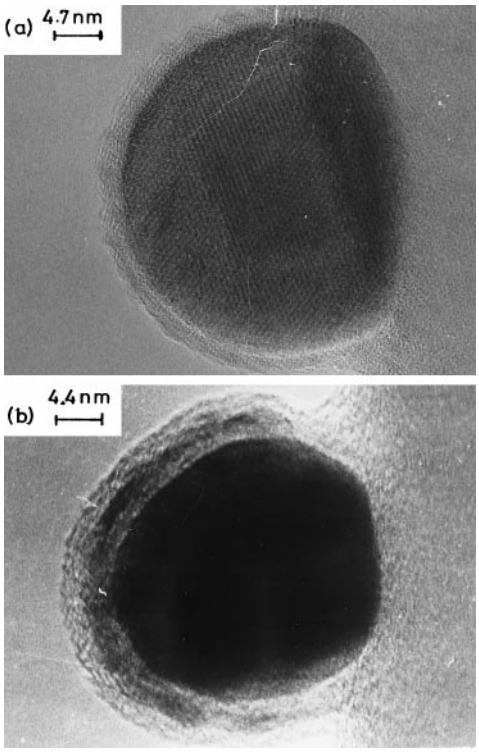

FIG. 3
TEM images of carbon-coated Ni particles on 18% Ni/$AlPO_4$ catalyst wherein the disproportionation of CO was carried out at (a) 400°C and (b) 600°C.

presence of H_2 [5]. Therefore, we considered it useful to carry out a comparative study of the disproportionation of CO over supported Ni catalysts such as Ni/MgO and Ni/$AlPO_4$.

EXPERIMENTAL

$AlPO_4$ was prepared from an aqueous solution of $Al(NO_3)_3 \cdot 9H_2O$ and H_3PO_4 (85%) by precipitation at 0°C with the dropwise addition of aqueous ammonia at a controlled pH. The final pH of the solution after complete precipitation was maintained at 6.8. After filtration, the product was washed several times with distilled water and propan-2-ol, dried at 200°C for 12 h, and then calcined at 800°C for 8 h. The powder X-ray diffraction pattern of the prepared $AlPO_4$ matched that reported in the literature [6]. High-purity MgO (E-Merck, India) was used for the catalyst preparation.

Ni/MgO and Ni/$AlPO_4$ catalysts were prepared by impregnating MgO or $AlPO_4$ with an appropriate amount of nickel acetylacetonate in a methanol solution and then evaporating the solvent with a rotavapor. The catalysts were calcined at 400°C for 16 h in air. The loading of nickel was 18%.

The disproportionation of CO was carried out in a horizontal tubular furnace. A weighed quantity (100 mg) of the catalyst was placed in a quartz tube located inside the furnace. The

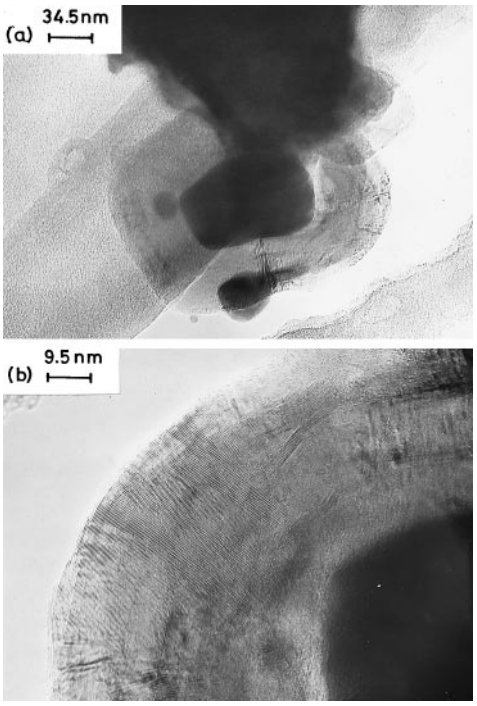

FIG. 4
(a) TEM image of a carbon-coated Ni particle obtained by the disproportionation of CO with 5% H_2 over $Ni/AlPO_4$ at 700°C. (b) High-resolution electron microscopic image of the same particle showing the graphitic nature of the carbon coating.

catalysts were reduced in H_2 flow at 700°C for 1 h prior to the disproportionation step. CO disproportionation was carried out over 18% Ni/MgO and 18% $Ni/AlPO_4$ at appropriate temperatures. The flow rate of the gases was monitored by unit mass flow controllers.

The products of CO disproportionation were dispersed in acetone and then loaded onto holey carbon copper grids and observed with a transmission electron microscope (Jeol JEM3010) operating at 300 kV.

RESULTS AND DISCUSSION

The disproportionation of CO at 400°C on Ni/MgO gives Ni particles with graphitic coatings. In Figure 1, we show a typical transmission electron microscopy (TEM) image of a nickel particle covered by graphitic carbon layers. These Ni particles reside at the edges of the MgO crystal surfaces and have a nearly spherical morphology. When CO disproportionation was carried out at 700°C over Ni/MgO, we obtained a high yield of carbon nanotubes. In Figure 2, we show a typical TEM image revealing the presence of a large number of nanotubes produced by this method. The Ni particles are found at the tip of the nanotubes and act as the catalyst for nanotube formation. Some of the Ni particles seem to have come out from their MgO support.

Figure 3a shows a TEM image of a carbon-coated Ni particle obtained by the disproportionation of CO at 400°C over the $Ni/AlPO_4$ catalysts. The disproportionation of CO on $Ni/AlPO_4$ at a higher temperature (600°C) also yielded graphitic carbon-coated metal particles, as shown in Figure 3b. The coverage of carbon was higher at higher temperatures, as observed by Martra et al. [3].

The disproportionation of CO on $Ni/AlPO_4$ in the presence of a small percentage of hydrogen also yielded graphitic carbon-coated metal particles. In Figure 4a, we show a typical TEM image of a Ni particle coated with carbon obtained by the disproportionation of CO with 5% H_2 at 700°C over $Ni/AlPO_4$ catalyst. Figure 4b shows a high-resolution electron microscopic image of the same carbon-coated nickel particle, clearly revealing the graphitic nature of the coating.

The formation of carbon nanotubes is considered to be associated with the movement of the metal particles [7], the movement increasing with increasing temperature as well as gas flow rate. Therefore, it is understandable that we obtained nanotubes by the disproportionation of CO over the Ni/MgO catalyst only at higher temperatures. We observed nanotubes only with Ni/MgO and not with the $Ni/AlPO_4$, possibly because the nickel particles are less strongly embedded in the former.

ACKNOWLEDGMENT

We thank Prof. C.N.R. Rao for suggesting the problem and for guidance.

REFERENCES

1. M. Audier, A. Oberlin and M. Coulon, *J. Cryst. Growth* **55**, 549 (1981).
2. S. Iijima, *Nature* **354**, 56 (1991).
3. G. Martra, L. Marchese, F. Arena, A. Parmaliana, and S. Coluccia, *Topics in Catalysis* **1**, 63 (1994).
4. H. Dai, A.G. Rinzler, P. Nikolaev, A. Thess, D.T. Colbert, and R.E. Smalley, *Chem. Phys. Lett.* **260**, 471 (1996).
5. J. Jiao and S. Seraphin, *Chem. Phys. Lett.* **249**, 92 (1996).
6. J.M. Campelo, A. Garcia, D. Luna, and J.M. Marinas, *J. Catal.* **111**, 106 (1988).
7. R.T.K. Baker and P.S. Harris, in *Chemistry and Physics of Carbon*, ed. P.L. Walker and P.A. Thrower, Vol. 14, p. 83, Marcel Dekker (1978).