# NOTE

# Influence of the Nature of the Catalyst Precursor on the Carbon Deposition Characteristics during Ethylene Decomposition over Copper–Cobalt

Selective poisoning with electronegative adatoms such as sulfur, halogens, or nitrogen has been shown to be a very effective method of modifying the activity and selectivity pattern of heterogeneous catalyst systems. The influence of sulfur has been most widely studied, and recent results from our laboratory have shown that addition of very small amounts of hydrogen sulfide to an ethylene gas stream can lead to a massive increase in activity for filamentous carbon formation from the reaction of cobalt and nickel metal powders with ethylene (1, 2). In catalytic reforming, the chlorine content derived from the metal precursor salt is thought to be directly related to the amount of coke that accumulates on the catalyst (3–5). Residual chlorine species from the catalyst preparation step have also been shown to alter the behavior of cobalt and copper for selective hydrogenation reactions (6–9). Nitta *et al.* (6) demonstrated that catalysts prepared by using cobalt chloride exhibited high selectivities to unsaturated alcohols during hydrogenation of $\alpha,\beta$-unsaturated aldehydes. They attributed this behavior to two factors; the notion that residual chloride species could give rise to a homogeneous particle size distribution of cobalt during hydrogen reduction step and the possibility that the presence of the halide suppressed the hydrogenation of the C=C bond in the aldehyde. Fujitsu *et al.* (7) observed a significant enhancement in activity of Rh/TiO$_2$ for the CO-H$_2$ reaction at 250°C when the catalyst was prepared from RhCl$_3 \cdot$ 3H$_2$O compared to that obtained from other precursor salts. More recently, Peri and Lund (10) reported that residual chlorine species in a Pd/SiO$_2$ catalyst exerted a profound effect on the ability of the noble metal to catalyze the oxidation of methane.

In the present study we have monitored the conversion of ethylene to filamentous carbon during interaction with copper–cobalt bimetallics prepared from both nitrate and chloride precursors in an attempt to determine any possible changes in the catalytic activity induced by the halide. The key steps involved in the formation of this type of carbon are as follows: (a) dissociative chemisorption of the hydrocarbon molecule at a certain set of faces of the metal particle, (b) diffusion of carbon species produced during

the decomposition reaction, through the catalyst particle, and (c) precipitation of solid carbon at other metal faces to create a fibrous structure (11, 12). It is generally accepted that carbon diffusion through the metal particle is the rate-controlling step in the growth process (13).

The two copper–cobalt powders were prepared via a previously described coprecipitation method (12, 14). Both powders contained a nominally equivalent cobalt to copper ratio of 75:25 wt%; however, the catalyst precursors were different for the two bimetallic samples. In the first preparation the respective nitrates of copper and cobalt were used as the catalyst precursors and in a subsequent method the bimetallic catalyst was synthesized from a mixture of copper and cobalt chlorides. Gas-flow experiments were performed in a quartz tube reactor located in a horizontal tube furnace into which the catalyst was placed in a ceramic boat. In all the experiments reported here, 50 mg of catalyst was evenly dispersed in the boat and the temperature raised to a desired level in a 10% hydrogen/helium mixture. The catalysts were held at the reaction temperature for two hours in hydrogen/helium to reduce any oxide possibly formed during the preparation of the bimetallic powders. Ethylene was then introduced into the system at a total flow rate of 40 ml/min, and the composition of the gas phase was analyzed before and during reaction by an on-line Varian 3400 gas chromatography unit. The solid carbonaceous product that formed on the catalyst during the hydrocarbon decomposition reaction was shown by transmission electron microscopy to consist almost entirely of filamentous carbon. These examinations were performed in a JEOL 100CX electron microscope fitted with a high-resolution pole piece. The carbon filaments were characterized by a combination of N$_2$ BET surface area measurements at −196°C and temperature-programmed oxidation studies in CO$_2$. The surface area measurements were performed with a Coulter Omnisorp 100CX unit, and the oxidation experiments were carried out in a Cahn 2000 microbalance reactor.

The gases used in this investigation, ethylene, hydrogen and helium, all 99.999% pure, were supplied by MG Industries and used without further purification. Reagent
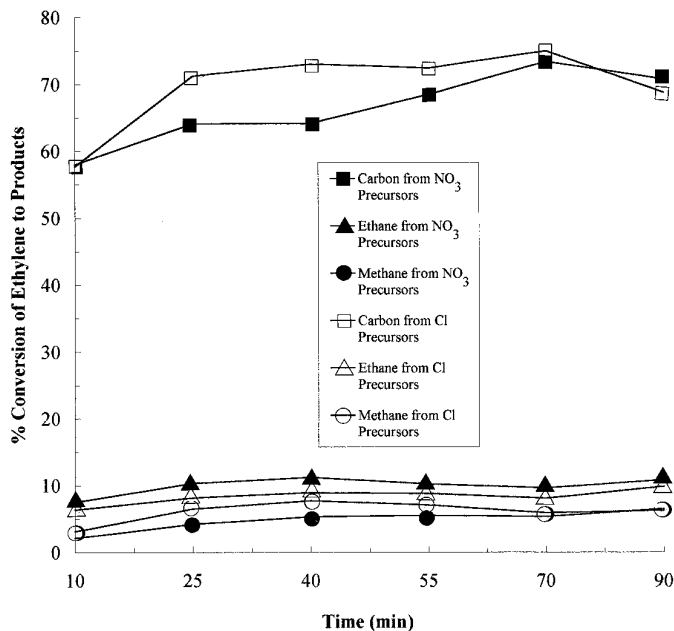
**FIG. 1.** Product distribution for the decomposition of ethylene over copper–cobalt (3:7) powders at 600°C.

grade cobalt nitrate $[Co(NO_3)_2 \cdot 6H_2O]$, cobalt chloride $[CoCl_2 \cdot 6H_2O]$, and copper chloride $[CuCl_2 \cdot 2H_2O]$ were supplied by Aldrich Chemical Co., and copper nitrate $[Cu(NO_3)_2 \cdot 2.5H_2O]$ was purchased from Fisher Scientific.

The first series of experiments were performed with the two catalyst samples being reacted in ethylene for 90 min at 600°C. The gas and solid phase product distributions for these systems are shown as a function of reaction time in Fig. 1. Inspection of these data indicate that over the first 60 min of reaction the bimetallic catalyst derived from the chloride salts is marginally more active than that prepared from the nitrate precursors. As the reaction is continued for longer periods of time, the behavior of the two systems becomes virtually indistinguishable. Examination of the solid carbon products from the two powders by transmission electron microscopy revealed that in both cases the deposit was mainly filamentous carbon. An example of the structural characteristics of this material are presented in the micrograph, Fig. 2, where it is evident that many filament limbs have been produced from a single catalyst particle. This type of filament conformation ("octopus-growth") has been observed by other workers following the reaction of modified nickel particles with various hydrocarbons (15, 16). Selected area electron diffraction analysis indicated that the structures obtained from the two catalyst samples were composed of carbon possessing short-range crystallographic order. Furthermore, the deposits appeared to have similar physical properties as evidenced by the close agreement of their surface area values (Table 1).

In a further set of experiments the reaction temperature was lowered to 500°C; under these conditions, subtle differences in both the catalytic activity and the structural characteristics of the carbonaceous deposit formed on the two bimetallic samples were found to exist. Figure 3 shows that at this temperature while the initial activities of the two samples with respect to carbon deposition were quite similar, after a period of about 40 min, significant differences in the reactivity patterns started to emerge. The catalyst prepared from the nitrate precursors was found to exhibit an appreciable drop in its ability to generate solid carbon, whereas the activity of the bimetallic derived from chloride precursors tended to increase as the reaction proceeded. From this plot, it is apparent that after 90 min on feed there is a 30% difference in the amount of solid carbon generated from the two systems. Furthermore, yields of methane were somewhat higher with the chloride prepared powder compared to those obtained from the nitrate precursor catalyst.

Estimates of the residual chloride species in the initial bimetallic powders and for the catalyst particles following reaction for 60 min at 500 and 600°C were determined by ion chromatography. In this method, samples containing the same weight of the bimetallic were treated in deionized water at 90°C overnight, and the chloride content of the resulting solution was measured using a Dionex 2010 unit. Analysis of the bimetallic powder prepared from the chloride salts was found to contain $14 \pm 2$ ppm of the halide, a value that is to be compared with those of $16 \pm 2$ and $5 \pm 1$ ppm obtained for the catalyst and solid carbon product after reaction at 500 and 600°C, respectively. These data indicate that while chloride species are retained on the catayst after reaction at 500°C, the same condition does not persist when the system is treated at 600°C.

Examination of the solid carbon products formed on the two bimetallic powders showed that in both cases the deposit consisted of carbon filaments that had grown via a multidirectional mode, similar in nature to the example shown in Fig. 2. Controlled oxidation experiments performed in $CO_2$ demonstrated that the structural perfection of the carbon deposit generated from the catalyst derived from chloride precursors was significantly higher than that of the nitrate analog, as evidenced by the difference in weight loss profiles, Fig. 4. Consistent with these conclusions is the finding that $N_2$ BET surface area measurements showed that when chloride was used as the catalyst precursor salt then the surface area of the carbon filaments produced was lower than when using nitrate (Table 1).

It is clearly apparent that changing the catalyst precursor from the nitrate to the chloride resulted in subtle changes in the nature of the filamentous carbon produced and in the activity of the catalysts when the ethylene decomposition reaction was allowed to proceed over a prolonged time period at 500°C. In contrast, after about 60 min reaction
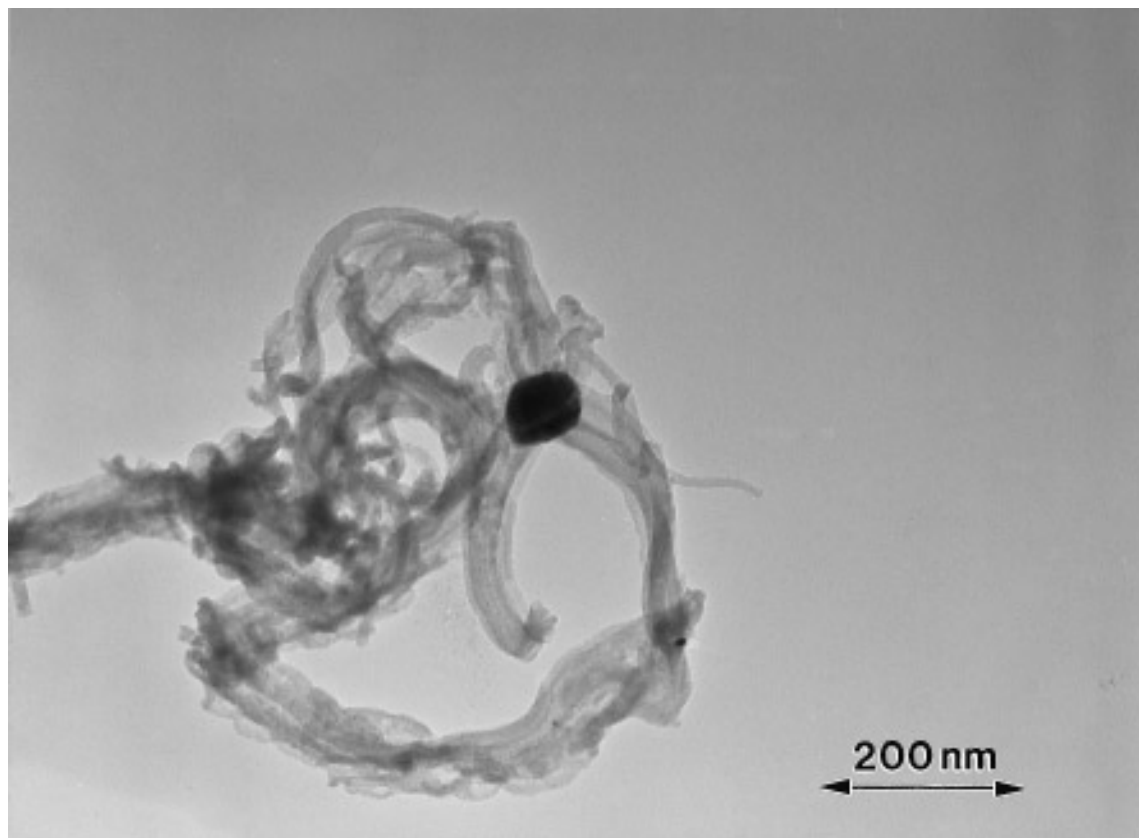
**FIG. 2.** Transmission electron micrograph showing the appearance of several carbon nanofibers emanating from a single copper–cobalt (3:7) catalyst particle after reaction in ethylene at 600°C.

at 600°C the catalysts exhibited a similar reactivity pattern, and the carbonaceous deposits produced appeared to have comparable physical characteristics as evidenced by their similar growth form and close agreement of BET surface area values. This indicates that after 60 min at 600°C any residual chloride species are effectively desorbed and that the surface of the two bimetallic powders are essentially the same, both in composition and electronic character. On the other hand, when the reactions were performed at

### TABLE 1

Nitrogen BET Surface Area Measurements of the Solid Carbon Produced from the Interaction of Ethylene with Copper–Cobalt (1:3) Powders Prepared from Different Precursor Salts

| Catalyst precursor | Reaction temperature (°C) | BET Surface area (m² g⁻¹) |
|---|---|---|
| Nitrate | 600 | 316 |
| Chloride | 600 | 309 |
| Nitrate | 500 | 292 |
| Chloride | 500 | 243 |

500°C then dramatic differences in behavior were observed with the two catalyst systems. It is not unreasonable to assume that the observed variations in both catalytic activity and in the characteristics of the solid carbon produced from the two powders under these conditions was related to the presence of Cl species at the surfaces of the copper–cobalt particles.

It is generally accepted that one of the roles of Cl in reforming reactions is that of inducing hydrogen spillover, which in turn leads to removal of some of the carbonaceous overlayer from the catalyst surface. One might argue that in the present study the sustained high activity exhibited by the catalyst prepared from the chloride precursors as compared to its nitrate prepared counterpart, at 500°C, is being brought about by enhanced dissociation of hydrogen at the catalyst surface facilitated by strongly adsorbed Cl species at the surface of the catalyst. This action would result in the removal of any carbonacoeus overlayer produced leaving the catalyst surface clean. A gradual build-up of carbon at the surface of the catalyst sample devoid of chloride would lead to premature catalyst deactivation. This explanation, however, fails to account for the observed differences in the structural characteristics of car-
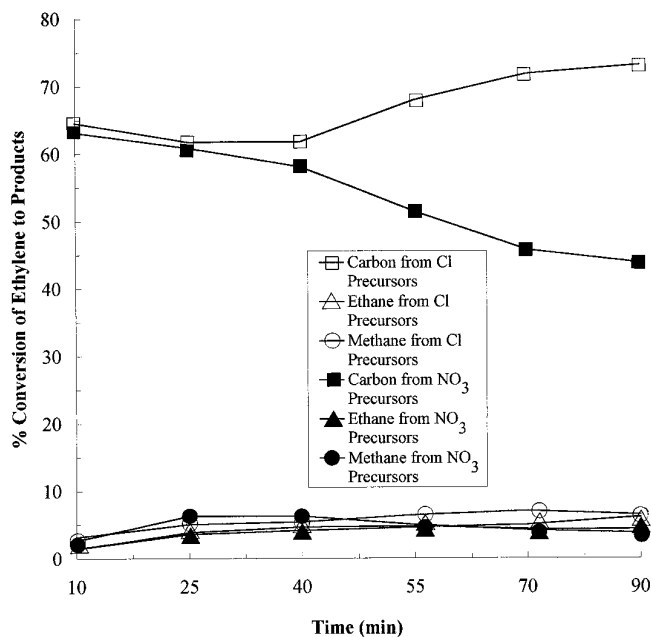
**FIG. 3.** Product distribution for the decomposition of ethylene over copper–cobalt (3:7) powders at 500°C.

bon filaments generated from the two catalysts at 500°C, and it also assumes that catalyst deactivation is due to the formation of graphitic overlayers. Recent experimental data from our laboratory indicate that for several bimetallic catalyst systems, deactivation is not due to an accumulation of carbon at the surface, but rather induced by a net depletion of one of the components from the active faces of the catalyst particles, which is enhanced by the preferential segregation of the atoms to the metal/carbon filament interface (12, 17).

The addition of electronegative adatoms to transition metals in many ways mimics the behavior of the promoter metal in bimetallics and modifications in catalytic activities and selectivity patterns exhibited by Cl-doped metal particles are generally explained by selective site blocking or electronic interactions (18, 19). It is possible that the presence of chloride species facilitates the maintenance of a high concentration of cobalt at the catalyst surface and as such is responsible for the observed enhancement in activity over extended time periods. A more plausible explanation however, may rest in the ability of adsorbed chloride species to induce reconstruction of the bimetallic surface to create a face that is more favorable for dissociative chemisorption of ethylene and less susceptible to deactiva-
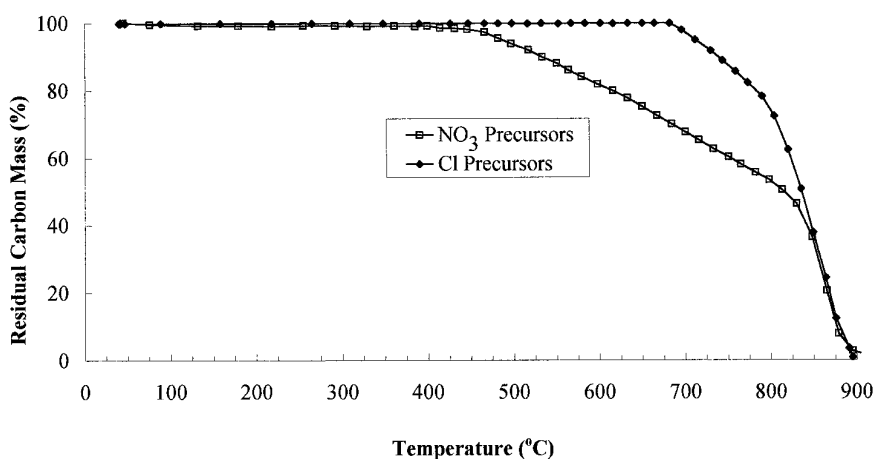


**FIG. 4.** Comparison of the gasification characteristics in $CO_2$ of carbon nanofibers generated from the interaction of copper–cobalt (3:7) powders derived from nitrate and chloride precursor salts with ethylene at 500°C.

tion. In addition, adsorption of the electronegative ad-atoms at the carbon precipitating faces of the particle may also be involved in modifying the crystallographic orientation to produce an atomic arrangement that promotes formation of a relatively well ordered carbon deposit structure. Some of these arguments have been invoked by Iyagba *et al.* (20) to account for the observed enhancement in selectivity toward methane formation during Fischer–Tropsch synthesis when residual chloride species were present on supported ruthenium catalysts. We plan to continue these studies by monitoring the effect of chlorine addition to the gas phase during the ethylene decomposition reaction to produce filamentous carbon over selected bimetallic catalysts.

## REFERENCES

1. Kim, M. S., Rodriguez, N. M., and Baker, R. T. K., *J. Catal.* **143,** 449 (1993).
2. Owens, W. T., Rodriguez, N. M., and Baker, R. T. K., *Catal. Today* **21,** 3 (1994).
3. Verderone, R. J., Pieck, C. L., Sad, M. R., and Parera, J. M., *Appl. Catal.* **21,** 239 (1986).
4. Parera, J. M., Figoli, N. S., Jablonski, E. L., Sad, M. R., and Beltramini, J. J., *in* "Catalyst Deactivation" (B. Delmon and G. F. Froment, Eds.), p. 571. Elsevier, Amsterdam, 1980.
5. Bishara, A., Murad, K. M., Stanislaus, A., Ismail, M., and Hussain, S. S., *Appl. Catal.* **7,** 337 (1983).
6. Nitta, Y., Hiramatsu, Y., and Imanaka, T., *J. Catal.* **126,** 235 (1990).
7. Fujitsu, H., Ikeyama, N., Ishibashi, H., and Mochida, I., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), p. 689. Chem. Inst. Canada, Ottawa, 1988.
8. Miura, H., Hondou, H., Sugiyama, K., Matsuda, T., and Gonzalez, R. D., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), p. 1307. Chem. Inst. Canada, Ottawa, 1988.
9. Chambers, A., 1994 Ph.D. Thesis, University of Glasgow, Glasgow, UK.
10. Peri, S. S., and Lund, C. R. F., *J. Catal.* **152,** 410 (1995).
11. Kim, M. S., Rodriguez, N. M., and Baker, R. T. K., *J. Catal.* **131,** 60 (1991).
12. Chambers, A., Rodriguez, N. M., and Baker, R. T. K., *J. Phys. Chem.*, **99,** 10581 (1995).
13. Baker, R. T. K., *Carbon* **27,** 315 (1989).
14. Best, R. J., and Russell, W. W., *J. Am. Chem. Soc.* **76,** 838 (1954).
15. Bernardo, C. A., Alstrup, I., and Rostrup-Nielsen, J. R., *J. Catal.* **96,** 517 (1985).
16. Rostrup-Nielsen, J. R., *J. Catal.* **85,** 31 (1984).
17. Rodriguez, N. M., Kim, M. S., and Baker, R. T. K., *J. Catal.* **140,** 16 (1993).
18. Bartholomew, C. H., Agrawal, P. K., and Katzer, J. R., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 31, p. 135. Academic Press, New York, 1982.
19. Kuhn, W. K., Campbell, R. A., and Goodman, D. W., *in* "The Chemical Physics of Solid Surfaces" (D. A. King and D. P. Woodruff, Eds.), p. 157. Elsevier, London, 1993.
20. Iyagba, E. T., Hoost, T. E., Nwalor, J. U., and Goodwin, J. G., *J. Catal.* **123,** 1 (1990).

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