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NOTES

Evidence for Temperature-Driven Carbon Diffusion Mechanism of Coke Deposition on Catalysts

INTRODUCTION

The formation of carbon filaments on supported catalysts and polycrystalline metal surfaces is of scientific as well as commercial interest. The carbon filaments generally have a small diameter, e.g., less than 0.1–0.2 μm, and a catalyst particle of the same diameter is usually found at the tip of the filament (*1, 2*). A generally accepted mechanism for the growth of carbon filaments is the diffusion of carbon through the catalyst particles. The carbon formed on the front-exposed face of the particle dissolves in and diffuses through the catalyst particle, and subsequently precipitates on the rear face to form the body of the filament. The nature of the driving force for diffusion is, however, a subject of current debate. Baker *et al.* (*3*) suggested that the heat of decomposition (exothermic) on the front-exposed face is removed by the endothermic process of carbon deposition from the metal on the rear face of the particle. Thus a temperature gradient should exist across the particle, and it serves as the driving force. Rostrup-Nielsen and Trimm (*4*) suggested that a concentration gradient is the driving force for diffusion. This is due to a difference between the solubilities of carbon in metal from the hydrocarbon vapor (on the front-exposed face) and from graphite (on the rear face).

Evidence for the temperature-driven carbon diffusion mechanism was reported in a previous study involving carbon formation on a thin film (ca. 500 Å) of MoS_2 (*5*) from exothermic and endothermic decompositions. This note reports the results using an improved experimental technique on the carbon formation on a thin nickel film from four hydrocarbon compounds.

EXPERIMENTAL

The experimental procedure is illustrated in Fig. 1. The size of the Ni/graphite sample was approximately 2 mm. The Ni film, vacuum-evaporated/deposited on the basal plane of the single crystal graphite, was approximately 400 Å thick. This was estimated from the amount of Ni wire evaporated and the distance between the graphite face and Ni source by assuming a spherical distribution of the vapor. The single crystal

TABLE 1

Coke Formation at 700°C on a Nickel Film of Approximately 400 Å Thickness

Vapor	ΔH at 1000 K, (kcal/mol)	Partial press. (atm); exposure time (min)	Coke formed
Methane	+21.4	0.60; 180	Nearly graphitic islands (ca. 0.5 μm in size) formed on exposure face of Ni.
n-Hexane	+49.0	0.18; 40	Graphitic islands formed on the exposure face of Ni
Benzene	−14.7	0.12; 60	Islands of ca. 0.5 μm formed on the rear face of Ni, none formed on the exposure face.
Toluene	−5.4	0.04; 90	Islands of ca. 0.5 μm formed on the rear face of Ni, none formed on the exposure face.

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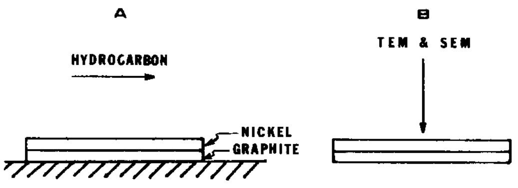

FIG. 1. Experimental procedure. The double film consists of a Ni film of ca. 400 Å thickness, vacuum evaporated/deposited on the basal plane of a single-crystal graphite film of ca. 500 Å. The double film, supported on a sapphire plate, is exposed to a hydrocarbon for coking (A). The coked sample is examined by TEM and SEM (B).

of Ticonderoga natural graphite was cleaned and cleaved to a layer approximately 500 Å thick by a standard procedure (*6*). The Ni face was then exposed to a hydrocarbon at 700°C in a quartz reactor. The coked sample was examined by both TEM and SEM. Any coke deposits could be seen in the TEM as the Ni/graphite film was thin enough to be transparent. Subsequent SEM examination would identify the exact locations of the coke deposits, and pinpoint the deposits that were sandwiched between the Ni and graphite films. The penetrating power of the SEM was approximately 100 Å in Ni at 30 keV, which was used in this study.

An O_2-free N_2 (<0.5 ppm O_2, Linde), further purified through copper turnings at 550°C, was used as a carrier gas. The hydrocarbons were generated by bubbling the N_2 carrier through the liquids at 20°C. The partial pressures and exposure times are given in Table 1.

RESULTS AND DISCUSSION

The cokes deposited from four hydrocarbons (two were endothermic and two were

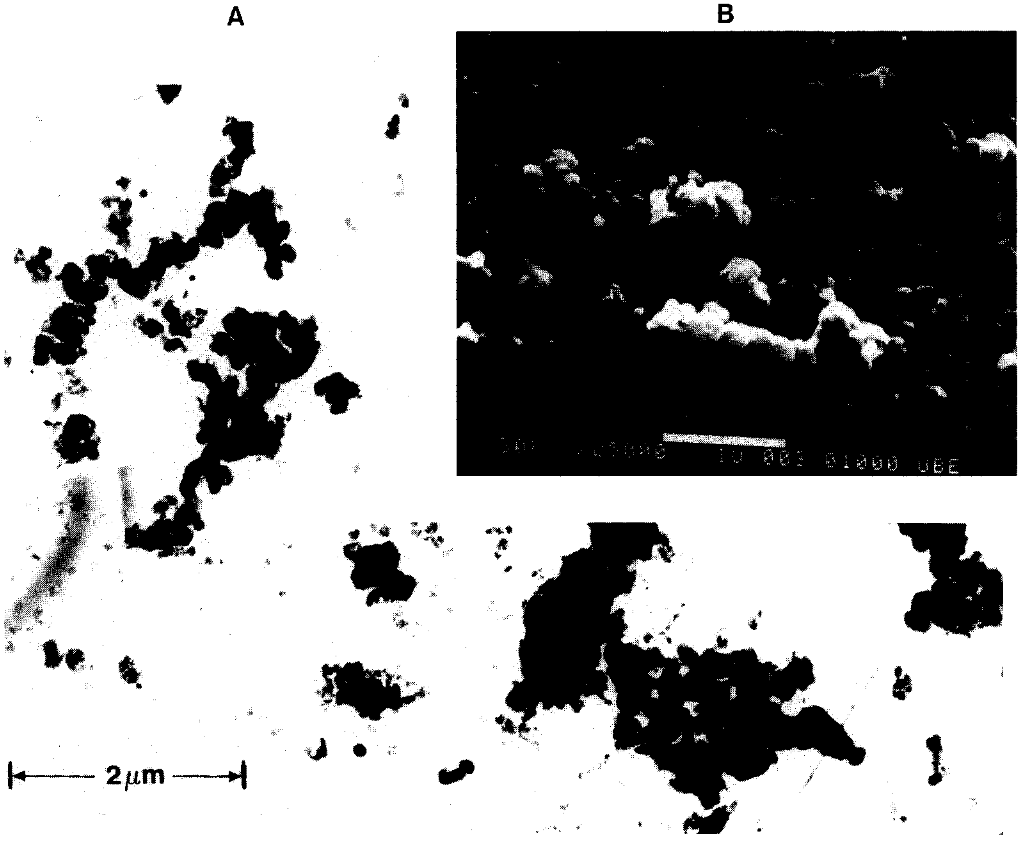

FIG. 2. Coke islands formed by n-hexane at 700°C on the Ni/graphite double film. (A) TEM; (B) SEM on the exposed Ni face.

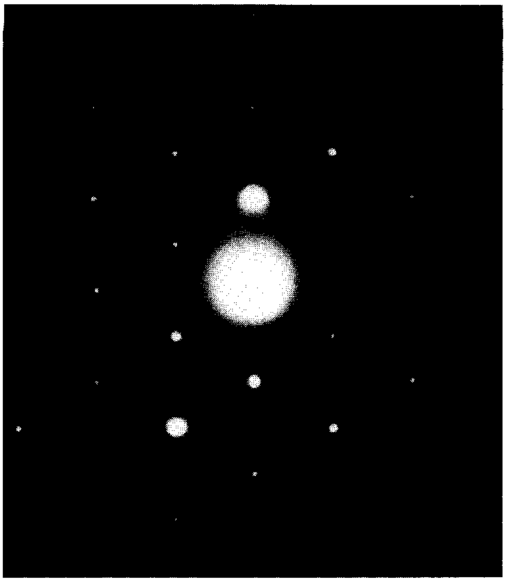

FIG. 3. Selected-area electron diffraction pattern of the coke islands formed by n-hexane on Ni, showing graphitic structure.

exothermic in decomposition) were studied at 700°C by using the technique illustrated in Fig. 1. The results are summarized in Table 1.

The coke islands formed from n-hexane at 700°C are shown in Fig. 2. The random-shape particles were seen in both TEM and SEM. The SEM picture were taken from a tilted angle (24°) on the nickel surface, which was previously exposed to n-hexane. Selected-area electron diffraction patterns were also taken on the coke islands. All patterns were identical to that of single-crystal graphite. The pattern is shown in Fig. 3. Comparing the SEM and TEM pictures, it appeared that all islands were deposited on the exposed nickel surface. Based on the estimated densities of the particles in the SEM and TEM pictures, no particles seemed to have been deposited on the rear-unexposed Ni face.

Random-shape islands were also seen in both TEM and SEM of the samples coked by methane at 700°C. However, these islands were larger and similar to those formed from benzene (to be shown later). The electron diffraction patterns of these islands were the same and shown in Fig. 4. The pattern was similar to that of graphite, but differed in *d* spacings. The structure of these coke islands is not known. However, it appeared to be similar to a graphitic structure.

The TEM pictures showed islands in both samples coked by benzene and toluene. The SEM, however, failed to see these islands on the exterior faces—the surface was bare in the SEM. The islands formed by benzene are shown in TEM (Fig. 5). The same sized islands, but fewer in number, were also seen in the sample coked by toluene due to the low toluene partial pressure. Since the resolution of the SEM (ca. 40 Å) was well below the sizes of the islands, it was concluded that these islands were in the interior of the Ni/graphite sample, most likely on the inner face of Ni. (No opaque islands were seen in the TEM pictures of the uncoked samples.)

The thickness of the Ni film, i.e., approx-

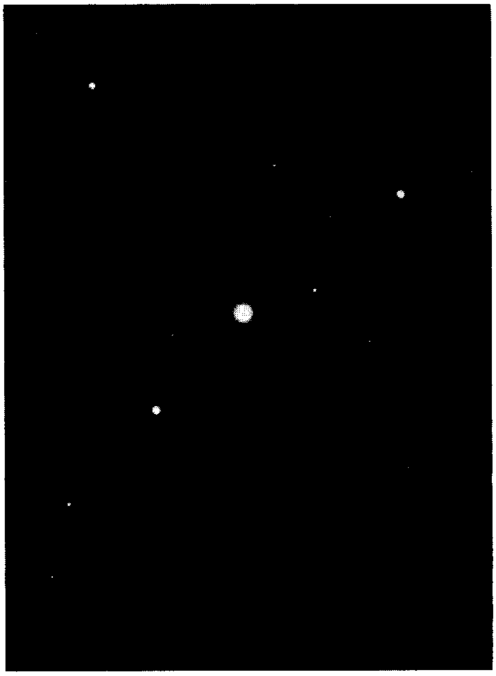

FIG. 4. Selected-area electron diffraction pattern of coke islands formed by methane on Ni, showing a near graphitic structure.

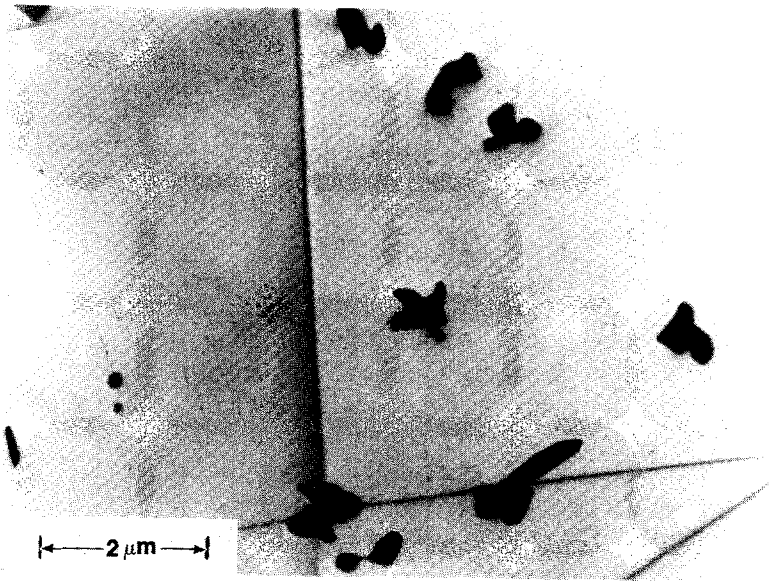

FIG. 5. TEM showing coke islands formed by benzene at 700°C on Ni.

imately 400 Å, was the same as the supported Ni particles, which were most favorable for the formation of carbon filaments (*1, 2*). The experiments described here provided an ideal test to distinguish between the two proposed driving forces for carbon diffusion. The results, as shown in Table 1, provide strong evidence that the exothermic heat of decomposition is the driving force for carbon diffusion through Ni.

ACKNOWLEDGMENT

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