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Origin of Filamentous Carbon Formation from the Reaction of Propane over Nickel

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Microscopic and gas-phase techniques have been used to study the decomposition of propane over nickel at 700°C. The structure of the carbonaceous deposit produced on nickel was found to be mainly filamentous in nature and was associated with the catalytic decomposition of the intermediate products, ethylene, propylene and benzene formed during pyrolysis of propane. The major product of the reaction, methane, did not influence the yield of filamentous carbon. Formation of filaments from these unsaturated hydrocarbon sources is in accord with the requirements of a previously postulated mechanism for growth of this form of carbon. The observation that filaments were not formed to any appreciable extent at low propane pressures is attributed to the reduction in yield of active hydrocarbon precursors under such conditions.

INTRODUCTION

Cracking of propane over nickel surfaces at elevated temperatures results in the formation of several forms of carbonaceous deposit. Most of the studies that have been made of this system have either been directed towards the kinetics of gaseous product formation (*1–3*) or the nature of the carbonaceous deposits (*4*) and there has been no attempt to relate gas and solid product formation.

Baird et al. (*4*) identified the formation of carbon filaments among the deposits produced from the interaction of nickel foils with propane at 700°C. In the postulated mechanism for the production of this form of carbon, one of the necessary requirements is that the hydrocarbon decomposition process imparts heat to the exposed faces of the metal catalyst particle (*5*). In the case of propane, the decomposition to elemental carbon and hydrogen is endothermic (*6*) and so it would appear that the conditions for filamentous carbon growth are never satisfied. In order to investigate this apparent anomaly both gas phase and microscopy techniques have been used in an attempt to identify the origin of carbon filaments formed in the propane/nickel system.

EXPERIMENTAL METHODS

Materials

The nickel used for the heterogeneous reactions was a spectrographically pure sheet of nickel foil 0.025 mm thick. The foil was cut into pieces 5 × 0.5 cm. Before each experiment the metal was ultrasonically cleaned in "Quadralene," rinsed in distilled water, acetone and finally dried. Prior to reaction with propane all specimens were weighed and then placed in a clean silica boat.

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The propane used in this work was Matheson Research Grade with a stated purity of better than 99.9%. Gas chromatographic analysis showed that it contained only a trace of higher hydrocarbons (<100 vpm) and approximately 700 vpm methane.

Methods

Static experiments were performed both in the presence and absence of nickel in a quartz reaction vessel. This reaction tube could be evacuated to a pressure of 10^{-5} Torr via a conventional calibrated glass vacuum system, and was located centrally in a furnace, maintained at 700 ± 10°C. A measured amount of propane, kept constant for each run at approximately 6×10^{-4} moles, was admitted to the reaction vessel. Reactions were performed for increasing time periods over the range 1–60 min. At the end of the experiment the reacting gas was expanded into, and then isolated in, a previously evacuated silica vessel, while the gas remaining over the nickel was quickly pumped away. This permitted representative gas samples to be taken and analyzed by gas chromatography.

After cooling, the nickel foil was carefully removed from the reaction vessel and re-weighed, the weight of deposited carbon being found by difference. Samples of the carbonaceous deposit were examined by transmission electron microscopy using a JEM 7A electron microscope. Observation of the filaments protruding over the edge of the Ni foil was made, and in some cases experiments were repeated with electron microscope grids of pure nickel, facilitating subsequent microscopic examination.

The formation of the carbonaceous deposit on nickel foils was also observed continuously by controlled atmosphere optical microscopy under conditions where propane was allowed to flow over the heated metal. The apparatus and technique have been described previously (*7*).

Experiments were performed at either 50 or 300 Torr, and at temperatures over the range ambient to 700°C. The reaction time for each run was 30 min. Samples of the carbonaceous deposits produced in these experiments were also examined by transmission electron microscopy. The techniques described earlier were used, but the majority of specimens were prepared by partial immersion of sections of reacted foils in 50% HCl, which after 12 hr had dissolved the underlying nickel. This left a residue of carbon which was then mounted on a microscope grid.

RESULTS

a. Static Experiments

The yield of products together with the decay of propane at 700°C is shown as a function of time in Figs. 1–3. The results obtained, both in the presence and absence of nickel, are plotted together, the filled-in symbols representing data from the former, and open symbols the measurements from the latter.

From Fig. 1, it is clear that the presence of nickel does not affect the rate of decomposition of propane at 700°C, which was found to follow the following kinetic

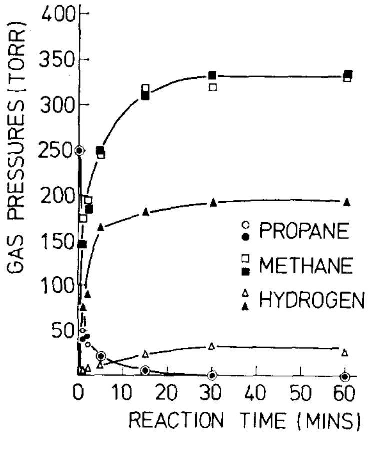

FIG. 1. Change of propane, methane and hydrogen partial pressures with time at 700°C.

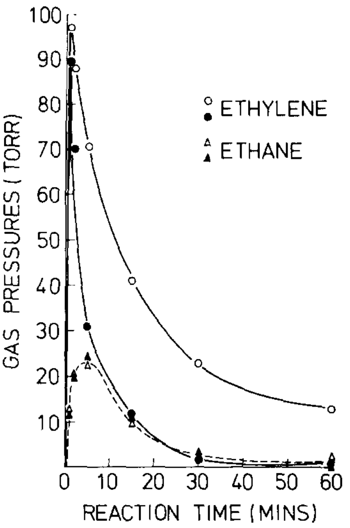

Fig. 2. Change of ethane and ethylene partial pressures with time at 700°C.

expression:

$$-\frac{dP_{C_3H_8}}{dt} = kP_{C_3H_8}{}^{1.30}.$$

This relationship has also been found to hold at lower temperatures (*1*). Examination of the gaseous product distributions obtained in the two systems shows that the yields of C_2H_4, C_3H_6, and C_6H_6 are all reduced in the presence of nickel and this is reflected by an increase in the H_2 component. The yields of CH_4 and C_2H_6 remain unaffected by the presence of nickel. The stability of methane under these experimental conditions was confirmed in a further experiment; 350 Torr methane was in contact with nickel for 60 min at 700°C. The results showed that, within experimental error, the pressure of methane remained unaltered at the end of the experiment and that there was no detectable formation of carbon on the nickel surface under these conditions.

At the end of each experiment the reaction vessel was dismantled and cleaned in order to remove a nonvolatile residue which tended to collect on the walls of the coolest regions of the vessel. Although the weight of this deposit was not determined it is thought to be small since mass balance of reactant and products was obtained to within 5%.

Figure 4 shows the yield of carbon deposit produced on nickel as a function of time. It is evident that carbon accumulates on the nickel surface at an appreciable rate

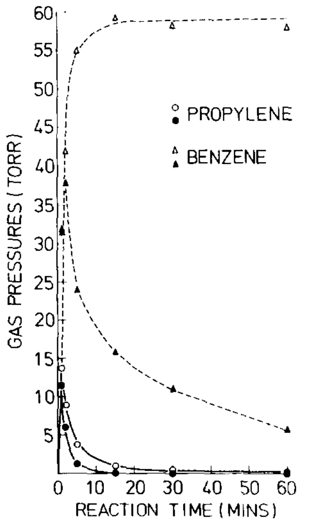

Fig. 3. Change of propylene and benzene partial pressures with time at 700°C.

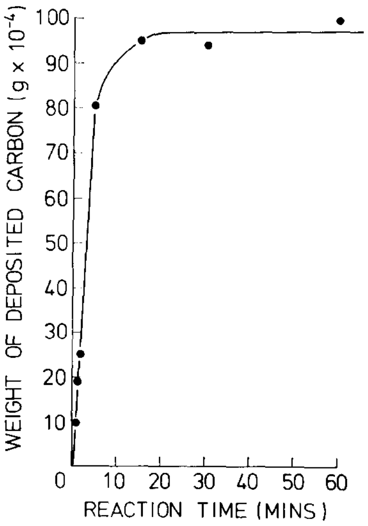

Fig. 4. Increase in the amount of deposited carbon with time at 700°C.

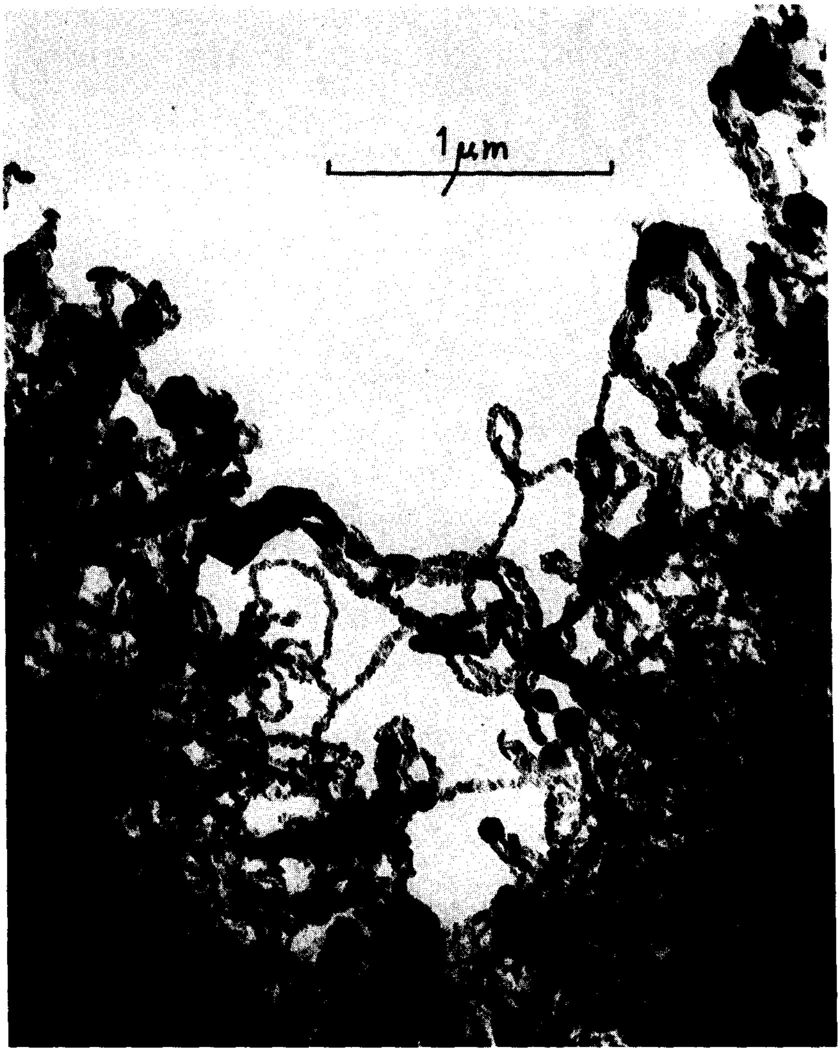

FIG. 5. Carbon filaments from propane/nickel at 700°C.

initially and then tends to slow down in the later stages of the reaction.

Examination of the carbonaceous deposit by transmission electron microscopy showed it to be mainly filamentous in nature (Fig. 5). The filaments were similar to those produced from acetylene/nickel (*5*) in that the catalyst particles responsible for their formation had been carried away from the surface of the metal by the growing filaments and as a consequence remained at the filament tips.

b. Optical Microscopy Experiments

Continuous observation of the deposition process by optical microscopy showed that carbon formation was dependent on the pressure of propane. At low pressures (<30 Torr) no carbon was detected over a 30 min period at temperatures up to 700°C. At higher pressures (around 300 Torr) carbon was initially observed to collect in the vicinity of grain boundaries on the metal surface after a period of 10 min at 450°C. The rate of carbon formation increased rapidly as the temperature was progressively raised to 700°C and was accompanied by a reduction in the induction period preceding growth. Unfortunately the resolution of the optical microscope was not sufficient to enable identification of the particular form of carbon which was being produced. Post-reaction examination in the transmission electron microscope revealed that the deposit consisted mainly of carbon filaments at all temperatures over the range 450–700°C.

There were some apparent differences in the structural characteristics of these filaments compared to those formed from acetylene, as seen from the high magnification micrograph of a typical filament formed after 5 min reaction at 700°C (Fig. 6), the specimen having been prepared by dissolution of the metal in acid. The filaments had an irregular outline and in most cases there was a complete absence of a hollow central channel. Oxidation experiments indicated that the structure was largely amorphous carbon surrounded by a thin layer of more oxidation-resistant carbon. The widths of the filaments were approximately twice those of the catalyst particles at their heads, the shape of which were generally of a hexagonal form, rather than "pear-shaped" (*5*).

The pressure dependence was confirmed by controlled atmosphere electron microscopy investigations where no filamentous carbon formation was observed when supported nickel particles were exposed to a limiting pressure of 30 Torr propane at 700°C.

DISCUSSION

The present results show that at 700°C, nickel does not affect the decomposition kinetics of propane, but does alter the fate of some of the products. From their study of the thermal decomposition of propane at 530–670°C, Laidler *et al.* (*8*) presented a very comprehensive mechanistic scheme

FIG. 6. Carbon filament formed in optical microscope at 700°C.

to account for the production of H_2, CH_4, C_2H_6, C_2H_4, and C_3H_6, which involved the participation of H, CH_3, and C_3H_7 radicals. While the present results do not enable us to throw any further light on these mechanisms, inspection of the relationship between the rate of formation of benzene and the concentration of propylene (Fig. 7) reveals that benzene is probably formed by a second order process from propylene.

It is evident that the only hydrocarbon yields which are affected by the presence of nickel in the system are those of ethylene, propylene and benzene. Indeed, one can account for all the carbon deposited on the metal by the loss of carbon from these gas-phase products, as demonstrated in Fig. 8. Calculations indicated that the main source of carbon in the early stages of the reaction was ethylene and propylene, while decomposition of benzene resulted in most of the carbon produced after 5 min, at 700°C. Decomposition of methane is not a contributary factor to carbon deposition under these conditions, a fact supported by separate experiments.

The filamentous nature of the deposit was established by electron microscopy and because it has been demonstrated that only the ethylene, propylene and benzene are responsible for deposit formation, there is no conflict with the postulated mechanism for filamentous carbon growth (*5*) as these hydrocarbons decompose to produce carbon by an exothermic process [$-\Delta H_f$ for C_2H_4 = 9.4 kcal mole^{-1}; $-\Delta H_f$ for C_3H_6 = 0.05 kcal mole^{-1}; and $-\Delta H_f$ for C_6H_6 = 14.8 kcal mole^{-1} (*6*), at 1000°K].

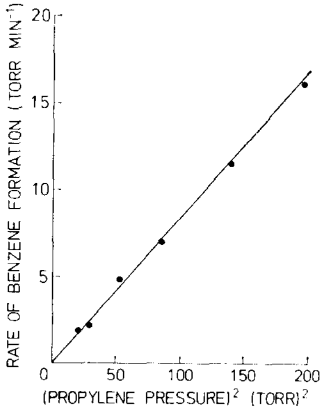

FIG. 7. Rate of benzene formation vs (propylene pressure)^2.

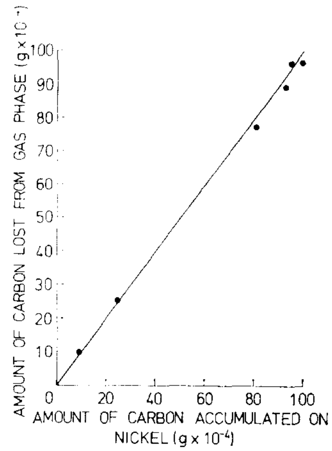

FIG. 8. Amount of carbon loss from the gas-phase vs amount of carbon accumulated on nickel.

At low propane pressures, the partial pressures of the products, C_2H_4, C_3H_6 and C_6H_6 will be correspondingly reduced, probably to a level where they will not induce filament formation to any appreciable extent during the time-scale of controlled atmosphere microscopy experiments (typically 60 min).

Finally, care must be exercised before drawing any firm conclusions about the structure of the filaments examined after exposure to aqueous environment. Absorption of water causes swelling of the structure and fracturing of the filament skin resulting in a ragged outline (*9*), features which were apparent with filaments examined in this work. Perhaps the most interesting and at present unexplainable aspect is the existence of a hexagonal-shaped catalyst particle at the filament head.

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