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Filamentous Carbon Growth on Nickel Surfaces Treated with Titanium Dioxide: Migration of Titania and Ramifications of Strong Metal–Support Interactions

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Controlled-atmosphere electron microscopy and gravimetric measurements were used to study the effects of depositing powdered TiO_2 on nickel surfaces with respect to the formation of filamentous carbon from acetylene and ethane. If the samples were heated directly in a hydrocarbon environment to temperatures near 1000 K, then filamentous carbon formation was initially suppressed on those portions of the nickel surface which contained titania. This inhibition of the formation of filamentous carbon was lost when the temperature was raised to ca. 1120 K, at which temperature the titania broke away from the nickel surface. In contrast, effective passivation of the nickel surface could be achieved at all temperatures by pretreating the TiO_2/Ni samples in hydrogen at ca. 770 K. During this treatment, the titania was observed to wet and spread over the nickel surface. This process could be reversed by heating in oxygen at 845 K, during which the nickel surface was uncovered and particles of TiO_2 were observed to form. The passivating effect of titania on nickel was thereby destroyed. These results provide direct evidence that reduced titania species migrate over metal surfaces under reducing conditions and collect into TiO_2 particles under oxidizing conditions. As such, these results support the idea that reduced titania species on metal surfaces may be the origin of strong metal–support interactions for titania-supported metal particles. Finally, a means of inhibiting filamentous carbon formation on nickel surfaces has been identified.

INTRODUCTION

The origin of strong metal–support interactions for titania-supported Group VIII metals has been a subject of investigation since the original discovery of these interactions by Tauster *et al.* (*1, 2*). The idea of electron transfer between the metal particles and the support has received considerable attention in the literature to explain these interactions (*3–8*). In contrast, it has also been observed that large metal particles (e.g., 10 nm in size) supported on titania may show behavior typical of strong metal–support interactions (*3, 9, 10*). In addition, for several systems which show these strong metal–support interactions, no clear evidence for electron transfer between the metal and the support was found by spectroscopic techniques (*9, 11, 12*). Thus, while electronic interactions between metals and supports may take place for very highly dispersed metal clusters, it has been suggested that the origin of strong metal–support interactions for larger metal particles is due to the presence of reduced titania species on the surfaces of the metal particles (*9, 13–15*). In fact, direct evidence for the presence of these reduced titania surface species has recently been provided by a variety of studies of model materials (*16–21*). An important question which remains as yet unanswered is how are these titania species transported from the support to the metal surface? For example, does this happen during the initial stages of catalyst preparation (e.g., in the aqueous solution used during catalyst impregnation) or are these species transported

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during treatment in hydrogen at elevated temperatures, as suggested by a number of investigators (*9, 13–15, 17, 19*). The present study addresses this important issue through the use of controlled-atmosphere electron microscopy, coupled with the formation of filamentous carbon from acetylene as a catalytic probe-reaction. These microscopy studies were supplemented by macroscale experiments of carbon formation from ethane decomposition in a flow reactor, where the weight of carbon deposited on the specimen was monitored as a function of temperature.

It is well established that the transition metals, iron, cobalt, and nickel, are among the most active catalysts for the growth of filamentary carbon (*22–25*). Nickel is the metal chosen for study in the present investigation. The formation of filamentous carbon is readily observable via controlled-atmosphere electron microscopy, and it is, therefore, an ideal reaction which allows electron microscopy to probe the properties of the metal catalyst surface as a function of position. Indeed, this catalytic reaction has been shown to be sensitive to the presence of titania on metal surfaces (*26*), with titania inhibiting the formation of filamentous carbon. In these experiments the titanium oxide was in the fully oxidized state and was an effective physical barrier toward filament formation, provided the temperature was kept below 920 K. Above this temperature the oxide tended to spall and as bare metal was exposed to the gas phase prolific filament growth occurred. Other workers (*27*) have shown that alloys containing titanium have a tendency to produce less carbon than those of similar composition but without titanium, when such samples were heated in hydrocarbons at 1070 K.

In this paper it will be shown that following reduction in hydrogen at 770 K, titanium oxide is an effective inhibitor for carbon deposition from hydrocarbons. In contrast, following oxidation in oxygen at 845 K, titania has an almost negligible effect on the subsequent rate of carbon deposition. These effects are interpreted in terms of the ability of reduced titanium oxide to wet and spread on the surface of a metal, such as nickel. Accordingly, reduced titania surface species suppress the formation of filamentous carbon, which normally forms when a hot metal surface is exposed to hydrocarbons, by covering surface metal atoms and by decreasing the average ensemble size of the remaining, exposed metal surface sites. During subsequent oxidation of the sample, the reduced titania surface species react to form TiO_2 particles, thereby reexposing the metal surface to the gas phase and destroying the passivating effect of titania toward the formation of filamentous carbon.

EXPERIMENTAL

The microscopy experiments described here were performed in the controlled-atmosphere electron microscope described elsewhere (*28*). The nickel specimens were in the form of electron microscopy grids, which were first rinsed in acetone and then washed in deionized water before being spot welded across the specimen hole in a platinum heater ribbon. The titanium oxide was obtained from Degussa (P-25), and was introduced onto the nickel grids by the following procedure: the oxide powder was ultrasonically dispersed in *n*-butanol and a portion of the resulting mixture was applied to the grid as an atomized spray and then allowed to dry in air. Although these specimens were too thick to allow penetration by a 100-keV electron beam, it was possible to follow the reactions occurring at the edges by observing the changes in shape of the silhouette as a function of time and temperature.

The gases used in this part of the study, hydrogen, oxygen, and acetylene, were obtained from Scientific Gas Products, Inc. with stated purities of >99.5% and were used without further purification.

The flow experiments of ethane decomposition were carried in a quartz U-tube, 40 cm in total length, where one arm was 12 mm diameter and the other, 4 mm. Specimens in the form of foils (0.01 cm thick, and cut into rectangles, ~3.5 × 0.6 cm) were loaded into the wider portion of the tube. The reactor tube was then placed in a Thermolyne "mini-melt" furnace, the temperature of which was measured by a Pt/Pt13% Rh thermocouple connected to an Omega heat controller unit. One end of the U-tube was attached to an ethane cylinder via a flow controller, while the other end was connected via a variable leak valve to a UTI-mass Model 100C spectrometer. With this arrangement it was possible to sample the gas-phase products at regular intervals during the reaction.

Prior to each run a fresh sample of nickel foil (Material Research Corp., Orangeburg, N.Y., marz grade) was firstly rinsed in acetone, washed in deionized water, and dried. Samples where the effects of titanium oxide additions were being investigated were prepared by spraying both sides of the foil with the same mixture as that used to prepare the electron microscopy specimens. The coated specimens were allowed to dry, subsequently weighed, and then placed in the reactor tube. The apparatus was evacuated to 10^{-4} Torr and heated to the desired reaction temperature in the presence of argon. The argon was replaced by ethane (Scientific Gas Products, Inc., C.P. grade) at a flow rate of 50 cm^3/min, and allowed to react for 1.0 h. In some experiments this procedure was modified to include a reduction step before the hydrocarbon treatment. This involved heating the sample to 870 K for 1.0 h in a flowing 10% hydrogen/argon mixture. Hydrogen was subsequently removed from the reactor tube by flushing with argon at room temperature for 1.0 h, followed by reaction with ethane in the manner described above. Reactions were performed at 870, 970, and 1070 K using the following three types of samples: pure nickel, nickel with titanium oxide, and nickel with reduced titanium oxide. Following reaction in ethane, the samples were cooled and reweighed. The weight of carbon deposited on a given sample was determined from the weight difference and is expressed as grams of carbon per square centimeter of nickel.

RESULTS

Controlled-Atmosphere Electron Microscopy Studies

(*a*) *Nickel/acetylene.* When the pure-nickel grids were heated in 5.0 Torr acetylene the observed pattern of events paralleled that found in an earlier study performed at a lower hydrocarbon pressure (*22*). At about 870 K the original smooth surface of the grid became rough and this transformation was followed by the onset of filamentous carbon formation. At these conditions the filaments were between 5 and 10 nm in width and up to 150 nm in length. Continuous observation of the reaction showed that all filaments had a nickel catalyst particle located at their tip and that the width of the particle was about the same as that of the filament. During the filament growth process the nickel catalyst particle was carried away from the bulk metal surface.

As the temperature was progressively raised to 1120 K both the size and number of filaments increased. At 1120 K some filaments were 100 nm in width and up to 2.0 μm in length. At any given temperature it was found that filaments produced from small nickel particles grew at a faster rate than those formed from large particles. After holding at 1120 K for 5 min, deposition of carbon became so intense that it was impossible to follow the progress of any individual filament and so experiments were usually terminated at this stage.

(*b*) *Nickel–titanium oxide/acetylene.* In a second series of experiments, nickel grids onto which powdered titanium oxide had been applied were heated directly in 5.0 Torr acetylene. The presence of the titanium oxide was readily detectable as isolated, ragged aggregates of particles against

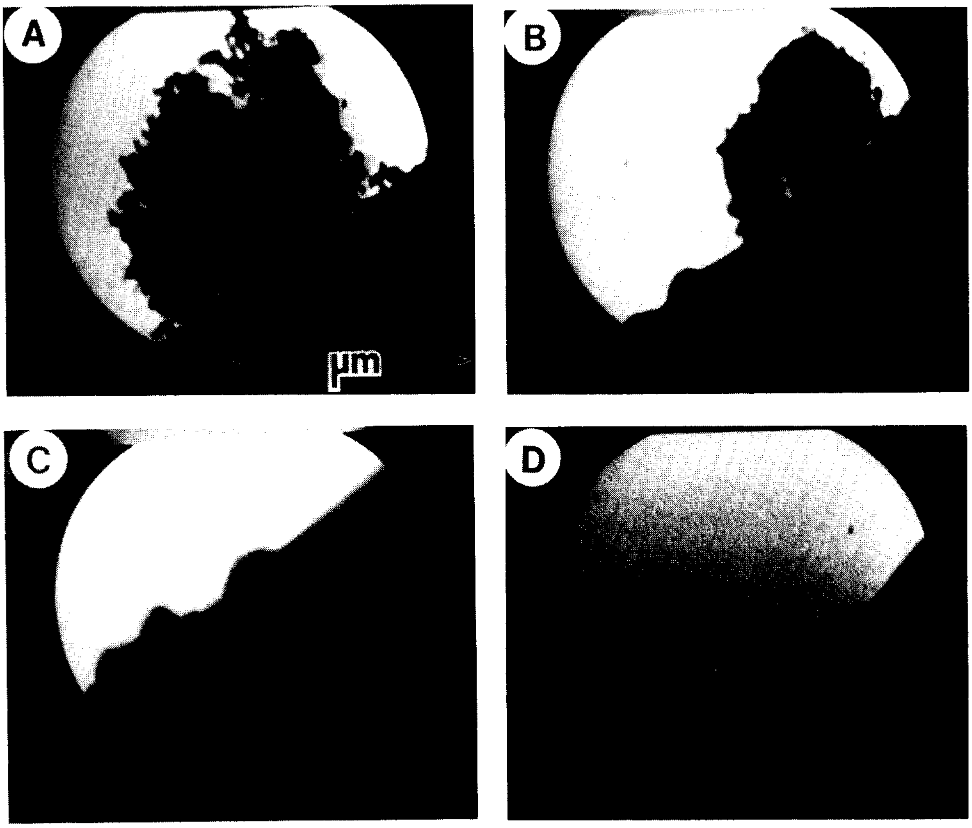

FIG. 1. Sequence (A–D) showing the transformation of titanium oxide aggregates during reaction in 1.0 Torr hydrogen at 870 K. Time interval between (A) and (D) is 60 min.

the smooth, uniform nickel edges. The form of this initial profile was maintained until the temperature was raised to 890 K, at which stage filamentous carbon was observed to form. At this temperature the filaments grew only in regions remote from the patches of titanium oxide. Although the number of filaments was far fewer than that produced on the pure-nickel specimens under comparable conditions, it was evident that their mode of growth was identical to that found on the untreated surface.

As the temperature was raised gradually to 1000 K, it became clear that any passivation of the metal toward carbon deposition was only a temporary effect. Much of the titanium oxide was observed to break away from the surface, exposing fresh regions of metal which rapidly became engulfed in carbon filaments. Continued heating to 1120 K resulted in a similar pattern of behavior to that described for the pure-nickel specimens.

(*c*) *Nickel–titanium oxide/hydrogen/acetylene.* In these experiments, nickel grids which had been sprayed with the solution containing dispersed titanium oxide were heated in 1.0 Torr hydrogen prior to reaction studies with acetylene. No changes in appearance of the specimen silhouette in hydrogen were observed until the temperature was raised to about 770 K. At this temperature over a period of 1 h, the morphology of the oxide aggregates first changed from a rugged to a smooth outline, followed by a decrease in particle height and a corresponding increase in particle width. This behavior is indicative of an increased mobility of titania particles and it suggests that reduced titania species may be spreading over nickel. It was significant to find that the smaller particles appeared to exhibit this transformation first. As the temperature was gradually increased to 870 K the oxide spread to such an extent that it was impossible to locate the position of some of the original aggregates. Figures 1A–D is a sequence taken from the TV monitor showing the transformation of a titanium oxide aggregate as it is heated in hydrogen at 870 K.

When these samples were subsequently treated in 5.0 Torr acetylene they exhibited a different behavioral pattern to that observed with the previous two systems. Although there were isolated regions of the surface where sparse accumulations of carbon filaments were detected at 870 K, over 95% of the surface remained unchanged. This condition persisted even when the temperature was eventually raised to 1120 K. An important finding was that if the initial pretreatment in hydrogen was performed at temperatures of about 570 K for 1 h instead of at 770 K, then no morphological transformation of the titanium oxide occurred and mitigation of filamentous carbon growth was *not* achieved to any significant extent when specimens were subsequently reacted in acetylene.

In some experiments, the ostensibly inert samples were cooled and the hydrocarbon replaced by 5.0 Torr oxygen. Upon reheating, the smooth rippled surface was seen to undergo a dramatic change at 845 K, restructuring into a saw-toothed form. Figure 2 shows the typical appearance of a specimen after such a treatment. If these samples were reheated in acetylene, then prolific carbon filament formation ensued at 870 K. If, however, an intermediate reduction step in hydrogen at 870 K was employed, then the surface structure reverted to its smooth, rippled form and showed no tendency to catalyze filament formation when subsequently treated with acetylene at temperatures up to 1120 K.

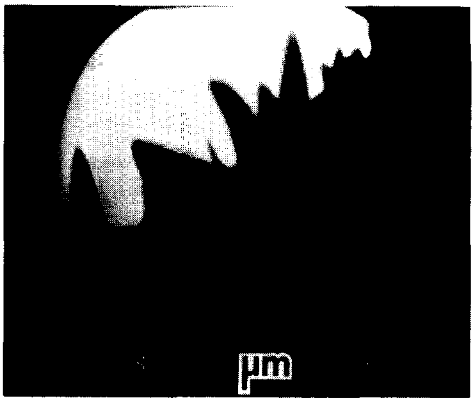

FIG. 2. Saw-toothed appearance of titanium oxide after heating a reduced nickel/titanium oxide sample in 5.0 Torr oxygen at 845 K for 5 min.

Figure 3 is a schematic representation of the effect of the various surface treatments of nickel on its ability to catalyze the growth of filamentous carbon when subsequently reacted in acetylene.

Flow Reactor Studies

The amount of carbon deposited on the various nickel specimens following reaction in ethane at temperatures from 870 to 1070 K is presented in Table 1. Examination of these data shows that at 870 K, titanium oxide provides an effective barrier toward carbon deposition with or without hydrogen pretreatment; however, at higher temperatures only titanium oxide which had

TABLE 1

Amount of Carbon Deposited on Nickel Specimens Which Have Been Reacted at Various Temperatures in 1 atm Ethane for 1.0 h

Specimen	Weight of carbon deposited ($g. 10^{-4} cm^{-2}$)		
	870 K	970 K	1070 K
Virgin nickel	1.9	26.2	27.7
Nickel/titanium oxide	0.2	24.5	25.0
Nickel/reduced titanium oxide	0.2	10.0	6.4

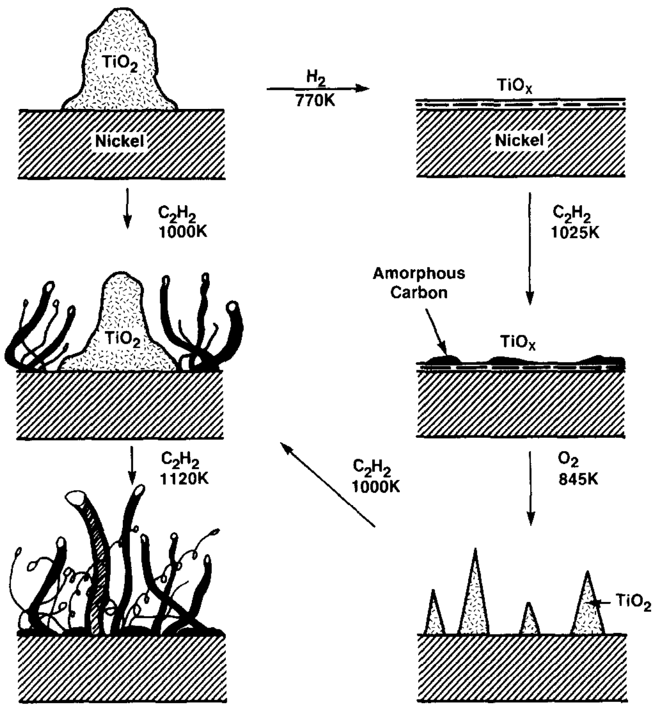

FIG. 3. Schematic representation of the suppression of filamentous carbon growth on nickel by reduced titanium oxide.

been pretreated in hydrogen exhibits an inhibiting effect.

Optical microscopy examination of the titanium oxide-passivated nickel foils which had been pretreated in hydrogen and reacted in ethane showed that the majority of deposited carbon had formed at the edges of the metal samples. These regions were probably not coated to any significant degree by the oxide spray. In contrast, the other two specimens which had been reacted in ethane at temperatures in excess of 870 K exhibited fairly uniform carbon deposition over the entire metal surface.

DISCUSSION

This investigation has revealed important aspects of the behavior of titanium oxide particles on nickel when this system is heated in hydrogen. The dramatic change in morphology of the titanium oxide particles observed when specimens were heated to 770 K in hydrogen coincides with conditions where strong metal–support interactions are induced for nickel supported on titanium oxide (*29, 30*). Furthermore, the restructuring of the reduced titanium oxide from a highly wetting to nonwetting configuration during treatment in oxygen at 845 K correlates with the restoration of normal chemisorption properties of metals supported on titanium oxide after exposure of reduced samples to oxygen at 870 K (*31*).

For restructuring of a particle to occur, an appreciable degree of mobility must exist. Previous studies have shown that when metal/titanium oxide systems are heated in hydrogen to temperatures of about 770 K, the support is reduced to Ti_4O_7. Although one may postulate that the transformation of TiO_2 to Ti_4O_7 occurs when the present system is heated to 770 K in hydrogen, an examination of the physical properties of the oxides involved raises difficulties in accounting for the observed mobility. The lowest temperature at which mobility is generally observed coincides with the Tammann temperature of a material, which is calculated from 0.52 times the bulk melting point. Based on the phase diagram given in Ref. (*33*), the Tammann temperatures for TiO_2 and Ti_4O_7 are 1090 and 1015 K, respectively. Since the transformation in particle morphology observed in the present study takes place at about 250 K lower than either of these values it would appear that the observed mobility is associated with some other intermediate Ti–O species. Alternatively, it may be suggested that the temperature at which wetting and spreading occur is lower than the Tammann temperature. Indeed, platinum particles have been reported to change morphology on titanium oxide at a temperature of 770 K (*31, 32*), this being about 290 K lower than the Tammann temperature of platinum.

Direct evidence of the spreading of reduced titanium oxide on nickel is seen from the suppression of filamentous carbon growth when specimens which had been treated in hydrogen at 770 K were subsequently reacted in acetylene. The finding that this suppression was not observed when the reduction was performed at 570 K points either to the existence of a lower temperature limit for the spreading of Ti–O species on nickel or to the fact that the rate of spreading is temperature dependent, with higher temperatures being required to spread the reduced titanium oxide over greater distances. This would suggest that the surface diffusion of these species on nickel is an activated process.

The observations of this study are consistent with reported catalytic properties of titania-supported metal particles for various hydrocarbon conversion reactions following reduction at elevated temperatures. Meriaudeau and co-workers (*4, 34*) reported that the activity of various metals supported on titanium oxide for ethylene, benzene, and styrene hydrogenations, cyclohexane dehydrogenation, and butane hydrogenolysis decreased after a high-temperature reduction (770 K) compared to the catalytic activity obtained after a low-temperature reduction (420 K). Other workers have found similar trends for titanium oxide-supported metal systems both in alkane hydrogenolysis (*15, 35–39*) and isomerization of methylpentane reactions (*40*). Importantly, it has been reported that the presence of titania species on metal particles has a greater inhibiting effect on metal-catalyzed reactions which require larger ensembles of metal atoms as active sites (*15, 38*). Furthermore, it has been proposed that the formation of filamentous carbon on nickel requires large ensembles of nickel atoms, since this reaction can be effectively suppressed by addition of small amounts of sulfur to the nickel surface (*41*). In this respect, it appears that the role of reduced titania species may be to cover a fraction of the nickel surface and to decrease the average ensemble size of the remaining, exposed nickel surface atoms.

A further similarity exists between the present results and those relating to the catalytic activity of titania-supported metal systems: the effect of an oxidation step following the initial high-temperature reduction treatment. It has been reported that after reduction at elevated temperatures, oxidation of catalysts followed by a low-temperature reduction restored the catalytic activity of the system to 80% of its original value (*4*). In the present study, treatment of an ostensibly inert nickel/reduced titanium oxide sample in oxygen at 870 K resulted in reformation of discrete titanium oxide structures and a consequent restoration of the catalytic activity for filamentous carbon formation when such samples were reacted in acetylene. It should be noted that treatments in oxygen at lower temperatures may have similar effects, but on shorter length scales. This would explain why several investigators (*4, 9*) have observed that exposure of titania-supported metal catalysts to oxygen at nominally room temperature can restore the chemisorptive and catalytic properties of small metal particles which are inhibited by strong metal–support interactions. It should also be remembered that the actual temperatures of these metal particles may be significantly higher than room temperature during this exposure to air at ambient conditions, due to the exothermic nature of the reoxidation process.

Another observation of the present study was that smaller titania particles underwent structural modifications before the larger particles when the samples were heated in hydrogen. This may be due to the fact that the binding energy of titania is lower in smaller particles or that the smaller particles are reduced before the larger particles, due to spillover of atomic hydrogen from the nickel surface to the titania particles. Indeed, the importance of hydrogen spillover in the reduction of titania has been previously documented (*42*). Finally, in addition to providing valuable information regarding the origins of so-called strong metal–support interactions, this investigation has led to the discovery of a new application based on these interactions. The flow reactor experiments have confirmed that the passivating effect of reduced titanium oxide on nickel toward catalytic carbon formation observed in the controlled-atmosphere electron microscope persists on a larger scale. Furthermore, these data are in line with earlier studies which indicated that titanium oxide was an effective barrier toward carbon deposition on metal surfaces at temperatures below 920 K (*26*). Here we have demonstrated that the passivation can be extended to higher temperatures by performing an intermediate reduction step at 770 K prior to exposing the nickel/titanium oxide samples to a hydrocarbon environment.

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