conditions attempted by us. IR (neat film, cm^{-1}) 3059 (aromatic C–H str), 957 (trans vinyl C–H out-of-plane bend). UV (λ_{max}, nm) 218, 400. Anal. Calcd for $C_8H_4Br_2$: C, 36.98; H, 1.55; Br, 61.48; S, 0.00. Found: C, 36.89; H, 1.53; Br, 61.19; S, 0.23.

2-Fluoro PPV (4). Polymerization of a 0.2 M aqueous solution of monomeric salt **16** by the procedure described above results in a colorless solution of polyelectrolyte **20**. Film casting at 180 °C for 4 h as described above gave films that were flexible and slightly tacky. IR (neat film, cm^{-1}) 3042 (aromatic C–H str), 961 (trans vinyl C–H out-of-plane bend). UV (λ_{max}, nm) 200 (end absorption), 236 (shoulder), 420. Anal. Calcd for C_8H_5F: C, 79.99; H, 4.20; F, 15.82; S, 0.00. Found: C, 79.04; H, 4.29; F, 14.05; S, 0.44.

2,5-Difluoro PPV (5). Polymerization of 2 g of monomeric salt **15** in 21 mL of H_2O (0.2 M) by the procedure described above resulted in a slightly yellow solution of polyelectrolyte **21**. Film casting at 250 °C for 4.5 h as described above gave reddish films that were somewhat brittle. IR (neat film, cm^{-1}) 3100 (aromatic C–H str), 1260, 1155 (Ar–F str), 960 (trans vinyl C–H out-of-plane bend). UV (λ_{max}, nm) 240, 420 nm. Anal. Calcd for $C_8H_4F_2$: C, 69.57; H, 2.92; F, 27.51; S, 0.00. Found: C, 69.35; H, 2.89; F, 27.28; S, 1.08.

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Registry No. **6**, 19036-27-2; **7**, 35335-16-1; **8**, 69857-33-6; **9**, 35335-08-1; **10**, 696-01-5; **11**, 1736-88-5; **12**, 1737-69-5; **13**, 452-94-8; **14**, 135789-45-6; **15**, 135789-46-7; **16**, 135789-47-8; **17**, 135789-48-9; **18**, 135789-55-8; **19**, 135789-57-0; **20**, 135789-58-1; **21**, 135789-59-2; 2,5-dichloro-*p*-xylene, 1124-05-6; 2,5-dibromo-*p*-xylene, 1074-24-4; 2,5-dimethylaniline, 95-78-3; 2,5-dimethylbenzenediazonium tetrafluoroborate, 2192-32-7; tetrahydrothiophene, 110-01-0.

Preparation of Nickel Carbide Ultrafine Particles by Metal Vapor Methods

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Highly reactive nanoscale nickel particles were prepared by nickel atom clustering in low-temperature pentane. During this process some carbonaceous material was incorporated due to attack on pentane of the highly reactive growing clusters. These nickel particles could be converted cleanly and completely to Ni_3C by treatment with additional carbon sources (e.g., octene, octane, or methyl methacrylate) at 200 °C. Similar results have been observed with palladium. Comparisons with other activated forms of nickel (or palladium) reveal that the metal vapor method is most satisfactory. Active forms of both Ni and C are necessary for metal carbide formations.

Introduction

Metal vapor synthesis (MVS) has proven to be a good method for the production of nanoscale metal particles that have shown fascinating physical, magnetic, chemical, and catalytic properties.[2] This procedure involves the low-temperature clustering of metal atoms in organic media. As matrices of metal atoms trapped in alkanes or aromatics are warmed, a competition between two processes is set up:[2b,3] cluster growth vs. reaction of the forming clusters with the low-temperature organic host. Depending on the metal, the organic host (solvent), dilution effects, and rate of warmup, control of the size, composition, and properties of the resultant metal clusters/particles can be achieved. All the extremes have been realized, from formation of organometallic cluster compounds[4,5] to colloidal particles[6-8] to catalysts[2d] to large crystalline metal particles.[9]

In some cases the forming metal clusters are so reactive that even relatively "inert" organic hosts react at low temperature. Examples include nickel, cobalt, iron, and chromium alkane deposits.[2,10] In these cases the final product is a black, pyrophoric "pseudoorganometallic" powder that contains about 2–8% by weight carbonaceous fragments. These fragments are mainly C_1 species distributed throughout the nanoscale metallic particles but are not in the form of interstitial carbidic carbon.[2b]

The picture that has evolved for these extremely reactive materials is that of nearly amorphous metal particles interspersed with CH_3, CH_2, CH plus other reactive carbon species, leading to the conclusion that both "activated" metal and "activated" carbon exist simultaneously. The question arises as to whether these materials could be of use in the preparation of ultrafine particles of metal carbides with a small distribution in particle size. Such materials could be very useful in a variety of technological areas. The work described herein deals with this possibility for the nickel and palladium cases.

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Table I. Elemental Analyses of Ni and Pd Composites from Pentane Codepositions

sample	metal	% M	% C	% H	%O[a]	atomic ratios M:C:H:O
1	Ni	82.3	6.04	0.66	11	2.8:1.0:1.3:1.4
2	Ni	86.4	3.53	<0.5	9.6	5.0:1.0:1.3:2.1
3	Ni	92.4	1.76	<0.5	5.4	11:1.0:1.3:2.4
4	Pd	91.2	1.76	<0.5	6.5	6.0:1.0:1.3:3.0

[a] By difference: composition is due to adventitious oxygen incorporation even though handling was under airless conditions as much as possible.

Conventional synthesis of transition-metal carbides from the metals or metal oxides reacting with elemental carbon generally requires high temperatures, and these extreme thermodynamic conditions are not conducive to the production of small particles.[11] Also, fine transition-metal carbide powders produced by ball milling are invariably contaminated by the materials constituting the grinding equipment.[12]

Nickel carbide, Ni_3C, is a rather unusual carbide in that it is not stable at high temperatures, and so it cannot be formed by "brute force" methods. Indeed, it is usually prepared by the reaction of some activated form of nickel metal with carbon monoxide (the Boudouard reaction).[13] When hydrocarbons are employed, carbon deposits on the surface of the Ni metal.[14] These deposits can have a variety of structures and morphologies, including amorphous, graphitic, and filamentous carbon. This carburization of Ni has been extensively studied since it is of importance in catalytic applications of nickel. Surface monatomic carbon appears to be the precursor to catalytic coking, but it is also the intermediate in methanation reactions. Since much information on carburization of Ni metal is available, and there are many data available also on nickel vapor/organic composites, Ni was chosen for most careful study in the present work.

With regard to palladium, a stable, stoichiometric palladium carbide has not been reported. However, carburizing Pd black with C_2H_4 or C_2H_2 has been found to produce a PdC_x phase, $0.13 \leq x \leq 0.15$.[15] This is not a true interstitial carbide like Ni_3C but is best described as a supersaturated solid solution of carbon in Pd, which is kinetically stable but thermodynamically unstable. The PdC_x phase has a structure closely related to that of Pd metal, but the cubic close packed lattice of Pd atoms is expanded slightly to accommodate the carbon atoms in the octahedral holes.[16]

Results

Ni–FOP and Pd–FOP. When Ni or Pd vapor are codeposited with high molar excesses of pentane at 77 K, followed by slow warming and vacuum removal of volatile materials, the final product composites contain the elemental compositions shown in Table I.

It can be seen that the amount of carbon incorporated is somewhat variable; this is a sensitive parameter and depends on Ni–pentane starting ratio as well as warmup procedure. Even though experimental conditions were carefully standardized, these variations were the norm. We also note that the atomic ratios formed usually showed a deficiency in carbon when considering the metal carbide stoichiometries we wished to produce.

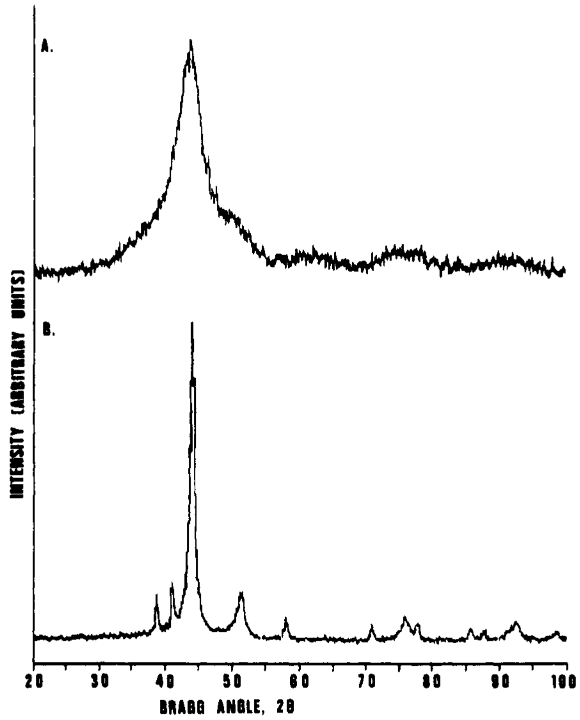

Figure 1. (a) Powder X-ray diffraction pattern of Ni–FOP powder exposed slowly to air. (b) Powder X-ray diffraction pattern of Ni–FOP powder heated to 200 °C.

Earlier work on the Ni–pentane system showed that heating of the composite (which we labeled Ni–FOP, or nickel–fragments of pentane) to 200 °C yielded predominantely CO_2 as the volatile product.[2b] The present work reconfirmed this and water was also detected.

X-ray diffraction analysis of the starting Ni–FOP showed the presence of very small Ni and NiO crystallites. (It should be noted that complete protection from air was not possible during the XRD measurements, and so surface NiO formation would be expected.) After 200 °C heat treatment, XRD indicated the presence of larger Ni crystallites plus Ni_3C, and the NiO was greatly diminished (see Figure 1 and Table II). There was no evidence of a metastable Ni–C solid solution, as has been observed in molten Ni/C systems that have been rapidly quenched.[17] After 300 or 400 °C treatments, only Ni crystallites were detected. As expected, surface areas progressively decreased while crystallite sizes increased with higher temperature treatments. Also, the samples progressively became more uniform in spite of the differences in elemental composition of the starting Ni–FOP samples.

For the samples heated to 200 °C without prior air pacification (samples stored under argon atmosphere), the percent Ni_3C formed ranged from 28 to 40%, the remainder being Ni crystallites. When the Ni–FOP samples were slowly pacified prior to 200 °C treatment (samples allowed to come into contact with air over a 10-min period), the percent of Ni_3C dropped to 18%. Interestingly, no NiO remained, however.

The Ni/Ni_3C samples prepared in this way were also sensitive to air. Indeed, rapid exposure showed that they were pyrophoric. However, slow pacification yielded stable particles suitable for XRD and other analysis techniques.

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Table II. Particle Size Data on Ni–FOP and Pd–FOP Samples

		unheated			200 °C			300 °C			400 °C		
sample	identification	species detected by XRD	metal crystallite size, nm	surface area, m² g⁻¹	species detected by XRD	metal crystallite size, nm	surface area, m² g⁻¹	species detected by XRD	metal crystallite size, nm	surface area, m² g⁻¹	species detected by XRD	metal crystallite size, nm	surface area, m² g⁻¹
1	Ni–FOP	Ni/NiO	1.7	29	Ni/Ni_3C	7.4	22	Ni	12	19	Ni	15	21
2	Ni–FOP	Ni/NiO	1.8	62	Ni/Ni_3C	6.2	28	Ni	12	22	Ni	16	22
3	Ni/PMMA	Ni/NiO	1.9	21	Ni/Ni_3C	6.9	13	Ni	12	19	Ni	19	16
4	Pd–FOP	Pd	3.9	59	Pd	6.3	17	PdC_x	7.5	9.0	Pd	8.3	6.6

Table III. Relative Atomic Concentrations from Auger Electron Spectroscopy

			surface %			interior %		
sample	treatment	species assigned by XRD	O	Ni	C	O	Ni	C
Ni–FOP	Ni–FOP pacified slowly in air	Ni/NiO	54	41	4.9	9.2	80	10
Ni–FOP	Ni–FOP/PMMA pacified slowly in air	Ni/NiO	11	21	67	2.6	62	35
Ni–FOP	Ni–FOP/PMMA heated to 200 °C	Ni/Ni_3C	6.2	37	57	3.2	67	30
Ni–FOP	Ni-FOP/MMA heated to 200 °C	Ni_3C	6.2	32	61	2.8	61	36

It is apparent though that with slow pacification only very thin oxide coatings were formed since NiO was not evident by XRD; only Ni and Ni_3C were evident.

Higher temperature treatments caused the decomposition of the Ni_3C to Ni and graphite, consistent with literature reports.

Palladium behaved somewhat differently. No PdO was detected in the starting Pd–FOP, crystallite sizes grew upon 200 °C treatment, and then at 300 °C a PdC_x phase formed. Treatment at 400 °C caused decomposition of this phase to Pd and graphite.

Ni–FOP and Pd–FOP/Poly(methyl methacrylate) and Other Organic Additives. The most remarkable finding of this study is that complete conversion to Ni_3C (or PdC_x solid solution) could be attained by heating the appropriate Ni–FOP (or Pd–FOP) sample under an argon atmosphere in the presence of a polymer or liquid organic compound, e.g., poly(methyl methacrylate), methyl methacrylate, 1-octene, or *n*-octane. As well as bringing about complete conversion to Ni_3C, 1-octene and methyl methacrylate reduced the temperature for formation of Ni_3C to 174 °C. When no organic compound was present, Ni_3C formation began at 181 °C. Octane did not reduce this temperature. It was observed that the onset of Ni_3C formation coincided directly with the reduction of NiO in all cases. The physical properties of the Ni_3C powders were *not* found to be dependent on the organic reagent used.

According to XRD the samples were made up of pure Ni_3C (or PdC_x). However, elemental analyses showed the presence of a slight excess of non-carbidic carbon. Thus, C found ranged from 7.7 to 9.0 wt %, and the expected value is 6.4 wt % (for a typical Ni_3C sample: % Ni = 90.7, %C = 7.7, % H $\leq$ 0.5). The XRD determined crystallite sizes varied over the narrow size range 19–24 nm. Thus, the Ni_3C crystallite sizes were relatively large compared with Ni crystallite sizes formed under the same conditions in the absence of an organic reagent. The range of surface areas of the Ni_3C samples was 18–26 m²/g.

Other Forms of Ni and Pd. To determine if our metal vapor prepared samples were unique in this carbide-forming reactivity, we tested a series of other Ni and Pd samples. Typical samples of Ni powder or NiO powder heated at 200 °C with excess methyl methacrylate yielded no Ni_3C, nor did Raney Ni of surface area 80–100 m²/g. A partial reaction was observed for an active Ni sample prepared by the procedure of Rieke and co-workers (lithium reduction of a nickel salt under anhydrous conditions).[18] However, fine palladium black (crystallite size ≈11 nm) did successfully react fully to produce the PdC_x solid solution.

Spectroscopic Studies of Ni–FOP, Pd–FOP, and Products Ni_3C and PdC_x. In an attempt to understand why Ni–FOP is so reactive, a detailed study by Auger spectroscopy was undertaken to learn more about the chemical state of the metal and carbonaceous groups. In particular we wanted to reexplore the question of whether the starting Ni–FOP or Pd–FOP contained carbidic or graphitic carbon. Depth profiling by Ar ion bombardment was used to explore the interior of the particles. (It should be noted, however, that because the Ni particles/crystallites were so small, the AES spectra recorded after etching are simultaneously representative of the interior *and* the exterior of the particles, since the etching beam is larger than the individual particles.) These studies enabled us to determine the relative atomic concentrations of Ni, C, and O for surface and bulk (Table III). An air-pacified Ni–FOP sample showed by far the highest surface oxygen concentration, as would be expected. However, interior oxygen was much lower. Interestingly, this sample also showed a much lower surface and bulk concentration of carbon compared with samples that had been treated with organic reagents, again an expected result. Note, however, that for the Ni–FOP sample the surface carbon was less than half that found in the interior.

For a Ni–FOP sample possessing a thin coating of poly(methyl methacrylate) (PMMA), a much lower surface oxygen concentration was found even though PMMA itself contains oxygen. Of course this sample showed a high surface carbon concentration but a much lower interior carbon concentration. These results indicate that the PMMA resides on the surface and serves to protect the Ni particles from atmospheric oxidation. As this sample was heated to 200 °C both the carbon and oxygen surface concentrations decreased. The XRD showed that the starting crystallites of Ni/NiO converted to Ni/Ni_3C.

For the optimum conversion to Ni_3C it was found that monomeric methyl methacrylate (MMA) served best, and the final surface concentrations of carbon and oxygen were similar for the PMMA- and MMA-treated samples. The significantly higher surface carbon coupled with low oxygen amounts suggests that surface carbon is graphitic.

These studies also allowed at least partial clarification of the form of the interior carbon in the Ni–FOP powders

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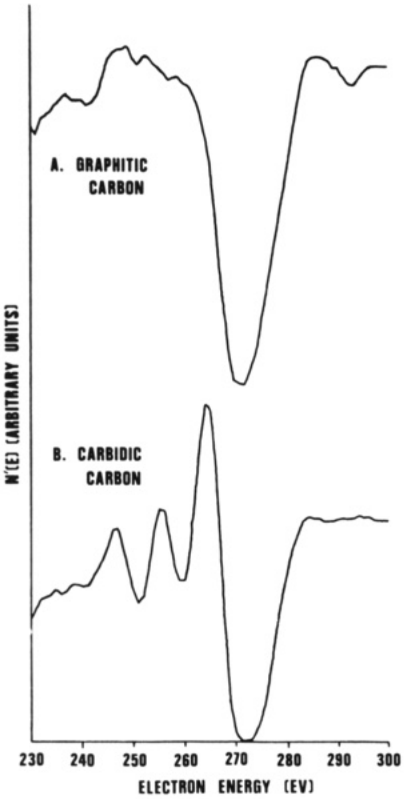

Figure 2. Carbon Auger electron signal of Ni–FOP before etching. (b) Carbon Auger electron signal of Ni–FOP after argon ion etching.

that were not heat treated. Earlier X-ray photoelectron studies suggested that this carbon was in the form of species such as CH_3, CH_2, or CH and not carbidic. However, XPS is not highly sensitive to the differences in such species and especially not to the difference between carbidic and graphitic carbon. AES, on the other hand, can easily distinguish between carbidic and graphitic carbon but cannot easily distinguish between carbidic carbon and other monatomic carbon species.

The exterior carbon of all the samples, whether heat treated or not, was found to be graphitic. In contrast, the interior carbon for all *heat-treated* samples exhibited the fine structure of carbidic carbon (Figure 2).[19] The interior carbon of *unheated* samples also showed the same fine structure associated with carbidic carbon, but whether this was due to chemisorbed CH_3, CH_2, and CH species or carbidic carbon, is not clear.

Scanning Electron Microscopy Studies of Ni–FOP and Product Ni_3C. The SEM picture of a Ni–FOP powder pacified by slow exposure to air showed a highly dispersed solid with no definite particle size (Figure 3). A Ni_3C sample formed by heating Ni–FOP with methyl methacrylate at 200 °C had a quite different morphology. The Ni_3C particles were in the form of short fibers and much larger in size. Thus, although the actual particle size of the Ni_3C cannot be described as nanoscale, XRD evidence indicates that these fibers are made up of many small Ni_3C crystallites, with a diameter of 19–24 nm.

Discussion

During formation of the Ni–FOP and Pd–FOP, it is clear that carbonaceous fragments were incorporated into the forming clusters. XPS and AES studies of these materials are not conclusive regarding the questions of whether Ni_3C is an initial product or not. According to XRD only very small Ni and NiO crystallites are initially present, and no Ni_3C.

The carbon that is incorporated appears to be distributed throughout, while oxygen is located on the surface of the particles. This is also indicative of the carbon being incorporated during metal cluster formation, while the oxygen is obtained later from adventitious sources.

Our experiments with polymers were originally intended to be a means of protecting the active particles from oxygen by forming a protective physical barrier. Polymer solutions were carefully added to the freshly prepared Ni–FOP particles followed by solvent removal. If carefully done with dilute polymer solutions, it was indeed possible to deposit a thin coat of polymer that was quite successful in decreasing surface oxidation of the particles. The AES results clearly show, for example, that Ni–FOP coated with PMMA did minimize NiO formation from attack by adventitious oxygen.

To our initial surprise, heating of the Ni–FOP samples (without added polymer or other organic reagent) caused a decrease in the NiO/Ni ratio as evidenced by XRD, and the evolution of CO_2 (also H_2O). The FOP portion of Ni–FOP was providing carbon for the reduction of adventitiously formed NiO. Since two oxygens are taken up by each carbon atom, there are ample amounts of carbon present to carry this reduction to completion:

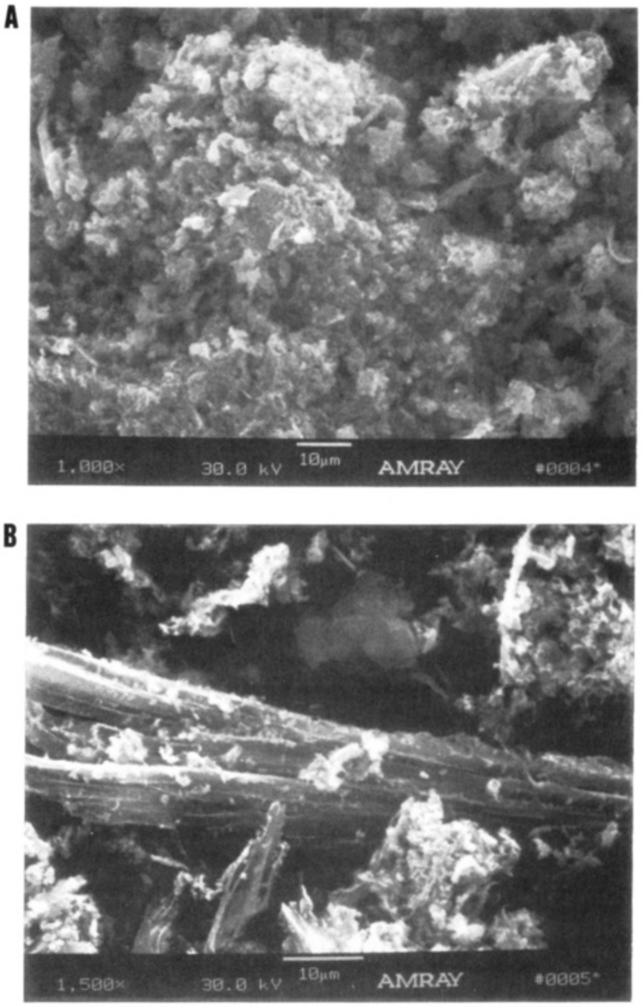

Figure 3. (A) Scanning electron micrograph of Ni–FOP powder (pacified by slow exposure to air). (B) Scanning electron micrograph of Ni_3C powder (formed by heating Ni–FOP with methyl methacrylate at 200 °C).

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$$\text{Ni–FOP/NiO} \xrightarrow{200\ °C} \text{Ni} + CO_2$$

(about 85% metal, 6% C, and 9% O by weight; see Table I). Therefore, some carbon would remain so that Ni_3C could also be formed. However, in this reaction the carbon remaining would be the limiting reagent:

$$9Ni + C \rightarrow Ni_3C + 6Ni$$

This example is a realistic one since we estimate by XRD peak intensities that a typical Ni–FOP sample after 200 °C treatments yielded a Ni/Ni_3C ratio of about 6, and this is quite reasonable considering the amount of carbon sacrificed in reducing NiO. Now considering an air-pacified sample where more surface NiO was formed, the final ratio of Ni/Ni_3C turned out to be 8, showing that more carbon was sacrificed in order to reduce the surface NiO to Ni.

Up to this point our results had shown that the incorporated carbon in Ni–FOP would readily react upon mild heating to give Ni_3C unless the more thermodynamically favorable process, NiO reduction, was an available pathway. We also had learned how to protect the metal particle surfaces with thin polymer coats.

When these coated materials were heat treated, the results truly surprised us; complete conversion to carbide was attained and at relatively low temperatures! When we learned this, we immediately set out to determine how general the reaction was, and so we used different polymers (PMMA and polyethylene) and then monomers such as MMA, 1-octene, and *n*-octane. Again, to our surprise, it did not matter if functional groups were present or not in the organic compound. They all allowed complete formation of Ni_3C at 200 °C, although the presence of certain functional groups did slightly lower the formation temperature of the Ni_3C. Actually, the monomers worked better than the polymers in that lower temperatures still led to complete conversions. It is apparent that the Ni particles in Ni–FOP are capable of activating essentially any organic compound so that carbon atoms become available for carbide formation.

Previous studies of PdC_x formation from Pd particles and C_2H_2 or C_2H_4 at 200 °C have been carried out and a mechanism proposed.[16] First, the hydrocarbon is adsorbed followed by dissociative chemisorption of C–H bonds. The C_2 species form a carbonaceous layer from which carbon atoms diffuse into the palladium lattice. This last step is rate determining, and the driving force is the continuing formation of the carbonaceous layer on the metal surface.

The results we observe tend to support a similar sequence of events. Alkanes, alkenes, or esters all react with these small particles in such a way that carbonaceous groups form on the surface followed by carbon atom migration into the particle interior. When the Ni_3C stoichiometry has been reached, migration stops, and probably a thin layer of carbonaceous material remains on the surface, which could explain the small overrichness in carbon in our Ni_3C samples, according to elemental analyses.

In our system, however, it is not obvious what is the rate-limiting step. Temperature studies indicate that the reduction of NiO occurs simultaneously with the production of Ni_3C whether organic reagents are present or not. It is therefore possible that the reduction of NiO is the rate-limiting step, as once the NiO has been removed, Ni_3C formation occurs rapidly. In the presence of organic additives the removal of NiO by reaction with the organic reagent would leave active Ni sites where carburization and subsequent C atom migration could take place rapidly. When no functional group is present, i.e., with *n*-octane, this reduction takes place at a slightly higher temperature than when functional groups are present, i.e., with 1-octene or methyl methacrylate.

When no organic reagent is present, a slightly different mechanism would be in operation. This would involve loss of H_2 from the FOP portion of the powder (or H_2O as the surface NiO is reduced). However, removal of NiO again may be the rate-limiting step. If carbon atom migration were the rate-limiting step, formation of Ni_3C from Ni–FOP with no organic additive would be expected to occur at lower temperatures than in the presence of organic additives, since the carbon is already dispersed in the interior of the Ni–FOP particles.

More quantitative measurements of Ni_3C formation from Ni–FOP/PMMA indicate that PMMA does not speed up Ni_3C formation at 200 °C. (Actually, at 200 °C PMMA slowly breaks down to monomer MMA.) However, PMMA does enhance the yield of Ni_3C, perhaps simply by restricting the amount of NiO formation in Ni–FOP and hence preserving more of the carbon in Ni–FOP for eventual Ni_3C formation. When 300 °C was employed (using an autoclave), Ni–FOP/PMMA samples converted totally to Ni_3C, and it was noted that PMMA was degrading to monomer rather rapidly as well. It seems likely that the monomer would be more mobile and would dissociatively chemisorb more rapidly than PMMA, and so monomer formation would be beneficial overall.

The ability to form carbidic phases under these relatively mild conditions appears to be unique to metal samples with very small crystallite sizes; indeed Ni–FOP seems to be unique in this process. Other reactive forms of Ni metal, such as Raney Ni, do not form carbides under these conditions. However, metal particles formed by metal salt reduction are also somewhat reactive. Metal particles formed by metal vapor synthesis and by metal salt reduction are known to form very small, almost amorphous particles with very small crystallite sizes. It is also known that organic material as fragments of the solvent are incorporated throughout. Thus, we have metal particles possessing many imperfections and dislocations in the metal lattice and the presence of CH_x species throughout the particles. This means that many reactive sites are present for dissociative chemisorption processes to take place, and carbon does not need to migrate far for carbides to form. In fact, perfect crystalline samples of Ni probably would not allow migration of C species at a temperature below the decomposition temperature of Ni_3C.

The chemical state of the carbon is also important. No enhancement of carbide phase formation was observed when "activated carbon" (carbon black, (50–200 mesh)) was employed as the carbon additive. So unlike graphitic carbon, carbon species formed by dissociative chemisorption are in a reactive state. *The formation of carbide phase under relatively mild conditions is therefore facilitated not only by an active form of metal particle but also by a reactive form of carbon.*

Experimental Section

The metal atom vapor reactor for the preparation of Ni–FOP powders has been described previously.[2,3,20] Organic solvents were freshly distilled under argon from suitable drying agents prior to use. All subsequent manipulations involving solvents or solutions were undertaken using a Schlenk line, an argon gas supply, and standard vacuum/inert atmosphere techniques. Manipulation of air-sensitive solids was done in an inert-atmosphere box

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(Vacuum/Atmospheres HE-43 series, Dri-Lab).

Ni-FOP Powder Preparation. Ni shot (1.0–2.5 g, 99.5%) was loaded into a crucible constructed from 1.5-mm Mo wire and alumina cement;[20] the crucible insulated with alumina wool (Saffil, I.C.I.). The reactor was assembled with the crucible in the appropriate position and evacuated to <10^{-3} Torr. The reactor vessel was cooled to −196 °C with liquid nitrogen, and the flow of pentane vapor started. After 20–30 cm^3 of pentane had coated the inner walls of the reaction flask, Ni vaporization was begun. A typical reaction proceeded for 2 h with 150 cm^3 of pentane being condensed with 1.5–2.0 g of Ni, giving a black matrix.

Once the codeposition was completed, the liquid nitrogen source was removed and the reaction flask isolated from the vacuum system. The matrix was allowed to melt down yielding a black Ni slurry. This was stirred magnetically as it warmed, and then transferred via a Teflon cannula onto a glass filter frit. Filtration of the slurry yielded the black Ni-FOP powder, which was dried under vaccum (10^{-3} Torr) for several hours.

Alternatively, if a Ni-FOP/PMMA powder was required, the still-cold metal slurry from the meltdown of the Ni/pentane matrix was transferred via a Teflon cannula into a precooled Schlenk flask. It was then refrozen. As it thawed the PMMA (Aldrich, medium MW) was added as a toluene solution to the rapidly stirred metal slurry. Typically, 10 wt % of PMMA was added compared to the amount of metal evaporated. The slurry was then allowed to warm, filtered, and dried as previously described. Analysis of the filtrate indicated all the PMMA remained with the solid Ni powder phase.

Pd-FOP Powder Preparation. The above procedure was employed for the Pd-FOP powder production, with 0.5 g Pd being codeposited with 120 cm^3 of pentane.

Heat Treatments. The heating experiments for production of carbide phases from the Ni-FOP and Pd-FOP powders were done in a quartz tube (length = 15 cm, diameter = 0.8 cm) sealed at the bottom. At the other end, the tube could be connected to a Schlenk line via a vacuum valve (Young's tap), allowing the heating to be done with an overpressure of argon. Connection of the gas supply to a bubbler prevented excess pressure buildup in the apparatus. A thermocouple was inserted directly into the 50–100 mg of sample contained in the quartz tube. For temperatures <200 °C, the bottom of the tube was placed in a silicone oil bath set at the required temperature, while for temperatures >200 °C, heating tape controlled by an electronic temperature controller was wrapped around the tube. The desired temperature was reached in 1–2 min and maintained for 30 min. For complete conversion of the Ni-FOP and Pd-FOP powders to the carbide phases, 5–10 drops of the appropriate organic liquid was added prior to heating.

When required, the volatile gases evolved on heating the powders were collected in liquid nitrogen cooled traps, a flow of helium gas over the sample being used. The gaseous mixtures were analyzed by mass spectroscopy.

X-ray Powder Diffraction. Powder X-ray diffraction was done using a Scintag XDS 2000 scanning diffractometer over the range 20–100° at a rate of 2 or 5°/min. The metal or metal carbide crystallite size was calculated by using the Scherrer equation with reference to an internal KCl reference. Phase identification was done by comparison to the JCPDS powder diffraction file.[21] The relative amounts of Ni:Ni_3C were calculated by comparing the peak intensities of the Ni and Ni_3C mixtures, with a previously constructed calibration curve.

Quantitative Elemental Analyses. Carbon and hydrogen analyses for all samples and nickel analyses for Ni_3C samples, were obtained from Galbraith laboratories. Metal analyses for Ni-FOP and Pd-FOP samples were determined by a gravimetric procedure.[22] The amount of oxygen was determined by subtracting the percentage values obtained for the metal, carbon, and hydrogen from 100% and is therefore less accurate than values for the other elements present in the samples.

BET Surface Area. The BET surface area values for the samples were obtained with a Micrometrics Flowsorb II 3000 apparatus.

Auger Electron Spectroscopy. The AES spectra were obtained with a Physical Electronics PHI 610 scanning auger spectrometer with a base pressure of 5×10^{-9} Torr. The spectrometer is equipped with a single-pass cylindrical mirror analyzer with a coaxial electron gun. Auger spectra were recorded with an energy resolution of 0.6%. Surface compositions were analyzed in the "as received" state and after different sputtering times at 3-keV primary electron energy and with a 50-mA beam current.

Composition depth profiles of the near surface layers were obtained in the AES analysis. The spectra were collected after sputtering with a differentially pumped ion gun employing argon as the sputtering gas. AES depth profiles were obtained using a 3-keV Ar^+ ion beam rastered over an area 2 mm × 2 mm. Under these conditions the sputtering rate for SiO_2 was 50 Å/min. The powder sample was pressed into indium foil, and the foil was then sandwiched between a metal mask and sample holder so as to ensure good electrical contact. AES data analyses and manipulations were carried out using built-in software by Physical Electronics.

The digitally stored AES data were differentiated numerically for quantification since the data were collected in the direct $N(E)$ mode. The Auger peak-to-peak height (APPH) was used as a measure of sample composition. The atomic percentage concentrations of the individual components were obtained from the APPHs and employing the sensitivity factors provided by United Technologies[23] and Physical Electronics.[24]

Scanning Electron Microscopy. Electron micrographs of the Ni-FOP and Ni_3C powders were taken by using an AMRAY 1810D scanning electron microscope. The samples were mounted by using carbon paste on aluminum stubs.

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Registry No. Ni_3C, 12012-02-1; Pd, 7440-05-3; Ni, 7440-05-3; C, 7440-02-0; Pd carbide, 102726-88-5; methyl methacrylate, 80-62-6; pentane, 109-66-0.

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