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Clustering of Metal Atoms in Organic Media. 8. Low-Temperature Cleavage of Alkanes by Small Nickel Particles Resulting in Stable Nickel–Organic Composites with the Unusual Magnetic and Chemical Properties

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Abstract: Nickel crystallites formed by clustering of metal atoms in alkane media at low temperature were studied. The powders produced contained crystallites of very small sizes (<35 Å). The average crystallite size was not influenced significantly by the choice of alkane used in their preparation or the degree of dispersion of the metal atoms in the −196 °C matrix. However, the magnetic properties of the particles were very sensitive to the preparative conditions employed. Stable ferromagnetic or stable nonferromagnetic powders could be produced at will, depending upon preparative details. Slow warm-up of the Ni–alkane matrix favored the formation of nonferromagnetic powders. A large amount of carbonaceous material (C, H) was found to be present in the Ni–alkane powders. Slow warm-up (−130 °C for 2 h, then warm to 25 °C) procedures resulted in more carbonaceous material in the powders than a rapid warm-up (−196 to 25 °C), suggesting that alkane cleavage occurs at very low temperatures (<−130 °C). Analysis of the carbonaceous layer by hydrogenation of the surface species revealed that it is composed primarily of C_1 fragments (i.e., CH_3, CH_2, CH, or C). Surface area measurements by H_2 chemisorption and N_2 adsorption and X-ray diffraction studies indicate the presence of particles $\gtrsim$100 Å consisting of aggregates of crystallites <35 Å. A model is proposed for the formation of nickel particles by clustering of metal atoms in alkane media which accounts for the observed properties.

Introduction

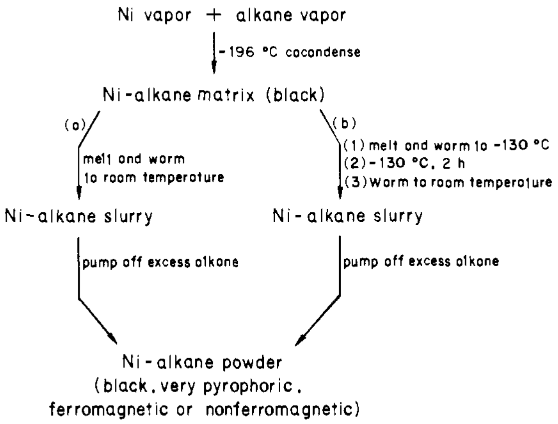
The interaction of alkanes with transition-metal surfaces at elevated temperatures has been studied rather extensively by catalysis researchers due to the importance of catalytic reactions such as hydrogenolysis, skeletal isomerizations, and cracking. A survey of the literature reveals that the nature of a metal surface (especially cleanliness) has a pronounced effect on the facility of dissociative chemisorption of alkanes. For example, Maire, Anderson, and Johnson[1] reported dissociative chemisorption of methane and ethane on single-nickel-crystal surfaces at 20 °C, resulting in the formation of a carbonaceous layer, thought to consist of C_1 units. Later studies of Maire and Legare[2] indicated dissociative adsorption of propane and neopentane on "clean" Ni(III) surfaces to form residues of the type CH_x.

Merta and Ponec[3] observed some cracking of cyclopropane at 0 °C over polycrystalline nickel films. Anderson and Baker[4] pointed out that clean films are very easily self-poisoned as compared to supported metals, indicating that the initial surfaces of supported metals are not as clean as those of metal films.

An early report of propane cracking on nickel powders by McKee[5] showed product formation at 65 °C. Martin and Imelik[6] reported that dissociative adsorption of methane, ethane, propane, and butane on Ni/SiO_2 catalysts occurs most readily on initially "clean" metal surfaces at low hydrocarbon coverage. However, even on these "clean" surfaces cracking was first observed at 300 °C for methane, 50 °C for ethane, 90 °C for propane, and 100 °C for butane.

These discrepancies in reactivities of various nickel surfaces for alkane dissociative adsorption and cracking are probably due, in part, to differences in surface cleanliness (impurity poisoning such as oxide formation) as well as structural and electronic differences.[7] The reactivity of small metal crystallites, with very clean, well-reduced surfaces, toward alkane cleavage has not been investigated due to the difficulty in preparing such surfaces.

Scheme I



There have been recent reports of C–H and C–C bond cleavages of alkanes at low temperatures by metal atoms[8,9] and dimers.[10] However, the possibility that these are all photoactivated reactions cannot be ruled out.[9] Activation of C–H bonds of alkanes by monometallic transition-metal complexes has been reported.[11a–d] No monometallic transition-metal complexes have been reported to be active in C–C bond activation of alkanes except for strained cyclic compounds such as cyclopropane.[11d] There has been a report of an unstrained C–C bond cleavage by a Ru_3 cluster compound ($Ru_3(CO)_{12}$).[12] There have been no reports of alkane cleavage (C–H or C–C bonds) by nickel in any form at very low tem-

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Table I. Effects of Deposition Parameters and Warm-Up Procedure on Magnetic Properties of Ni-Pentane Powders

sample no.	warm-up procedure[a]	wt. of Ni Vap, g	pentane/Ni[b]	ferromagnetic?
1	Ia	0.14	550	no
2	Ia	0.19	542	no
3	Ia	0.15	333	yes
4	Ia	0.18	243	yes
1s	Ib	0.26	147	no
2s	Ib	0.49	96	no
3s	Ib	0.81	41	no
4s	Ib	0.48	27	yes

[a] See Scheme I. [b] Cocondensation mole ratio.

peratures except for reports of hydrogen–deuterium exchange of propane on nickel films at −47 °C[13] and ethane adsorption (C–H bond cleavage) on nickel films at −78 to 70 °C.[4] Cleavage of C–C bonds of alkanes at low temperatures by nickel has not been reported.

Clustering of metal atoms in alkane media provides a route to formation of very small, clean crystallites whose interactions are exclusively with alkane molecules. We have recently reported some catalytic[14] and physical properties[14–16] of metal powders produced by clustering metal atoms in organic media. In this paper, we wish to report detailed studies of the clustering process of nickel atoms in alkane media and show that alkanes are cleaved by small nickel particles at low temperature (−130 °C).

Results

Magnetic Properties. One of the most noticeable features of Ni–alkane powders is their magnetic properties. Depending upon preparation conditions, Ni–alkane powders have magnetic properties ranging from completely nonferromagnetic (powder not attracted to a hand held bar magnet) to totally ferromagnetic. When nickel atoms are cocondensed with alkanes at −196 °C followed by gradual warm-up to room temperature and removal of excess alkane (Scheme Ia) fine black, pyrophoric powders are obtained. Nonferromagnetic powders could be produced with use of this procedure only if a large excess of alkane (>500:1) was present in the −196 °C matrix. In other experiments, Ni–alkane matrices were allowed to warm to −130 °C (pentane slush) and remain at this temperature for 2 h, followed by normal warm-up and workup (Scheme Ib). With use of this slow warm-up procedure, nonferromagnetic powders could be produced even when only a relatively small excess of alkane (∼40:1) was present in the matrix.

The influence of warm-up procedure and nickel dilution in the matrix upon the magnetic properties of Ni–pentane powders is illustrated in Table I. As can be seen, allowing a Ni–pentane matrix to remain at −130 °C for 2 h strongly favors the production of nonferromagnetic powders.

Crystallite Size, Thermal Stability, and Surface Area Determination. Table II lists the average sizes of crystallites of various Ni–alkane (and Co–pentane) powders as determined by X-ray diffraction line broadening with use of the Scherrer equation with the assumption of spherical geometry.[17] Since the sizes of the crystallites determined are at the lower limit of the sensitivity of the technique, we believe that the values listed in Table II represent maximum sizes. The samples shown in Table II were prepared with use of the slow warm-up procedure (Scheme Ib). Several unusual and unexpected results are shown in Table II. (1) *There are insignificant crystallite size differences between nonferromagnetic and ferromagnetic Ni–alkane powders.* (2) The ferromagnetic samples contain crystallites of sizes well below that of a ferromagnetic domain (100–300 Å).[18a–c] (3) No definitive trends can be found between crystallite size of the nickel and the alkane used. (4) No correlation exists between the magnetic properties of the various M–alkane powders and their crystallite sizes. (5) A correlation between preparation conditions (i.e., matrix concentration) is again seen in Table II as was shown in Table I. (6) Co–pentane samples are ferromagnetic when prepared under conditions in which Ni–pentane samples are always ferromagnetic.

Table II. Magnetic Properties and Average Crystallite Sizes of Various M-Alkane Powders

sample (no.)	av crystallite size, Å	ferromagnetic?	matrix alkane/metal mole/ratio[b]
Ni pentane (5s)	36	no	144:1
Ni pentane (6s)	25	no	138:1
Ni pentane (7s)	35	no	51:1
Ni pentane (8s)	36	yes	38:1
Co pentane (1s)	21	yes	58:1
Co pentane (2s)	18	yes	67:1
Co pentane (3s)	23	yes	221:1
Ni 2,2-DMB[a] (1s)	36	yes	35:1
Ni 2,3-DMB (1s)	25	yes	77:1
Ni 2,3-DMB (2s)	20	no	107:1
Ni cyclopentane (1s)	30	yes	123:1

[a] DMB = dimethylbutane. [b] Method 2 (Scheme Ib).

Table III. Surface Area and Particle Size of Ni-Alkane Powders and Raney Nickel

sample (no.)	surface area, $m^2\ g^{-1}$ [a]	av particle diameter, Å[b]
Ni pentane (6)	47	143
Ni hexane	70	96
Ni heptane (1)	37	182
Ni octane	53	127
Raney Ni[c]	52	129

[a] H_2 chemisorption at 25 °C. [b] Calculated from surface area. [c] Grace sample no. 28.

Ni–pentane powders can be heated to rather high temperatures before appreciable grain growth is noticed (nonferromagnetic 260–280 °C, ferromagnetic 220–240 °C).[14]

The surface areas of various ferromagnetic Ni–alkane powders were determined by H_2 chemisorption at 25 °C. Average particle diameters were calculated from surface area data with the assumption of spherical geometry.[19] The surface areas and average particle sizes of some Ni–alkane powders prepared by a rapid warm-up procedure (Scheme Ia) are given in Table III. The surface area of a Raney nickel sample is included for comparison. Nitrogen BET adsorption isotherms of ferromagnetic Ni–pentane powders at 77 K were obtained. Surface areas were calculated with use of 0.162 nm^2 $molecule^{-1}$ as the cross sectional area of N_2 and assuming liquid-like adsorption.[17] A Ni–pentane sample (no. 5) which had been degassed for 12 h in vacuo at 25 °C was found to have a surface area of <30 $m^2\ g^{-1}$. Upon further degassing for 9.5 h at 200 °C a surface area of 60 $m^2\ g^{-1}$ was measured which is in fair agreement with the value determined by H_2 chemisorption (47 $m^2\ g^{-1}$). The increase in apparent surface area upon sample heating may be due to an "unclogging" of pores by desorption of organic molecules.

Characterization of the Organic Component of Ni–Alkane Powders. We have carried out investigations to determine the amount of carbon and hydrogen present in Ni–alkane powders and identification of the surface hydrocarbon species.

Qualitative analysis of products desorbed from a nonferromagnetic Ni–pentane powder (sample no. 7) upon heating was

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Table IV. Elemental Analysis (C, H) of M-Alkane Powders[a]

sample[b] (no.)	at. % composition M	C	H	mole ratio N:C:H	[M],[e] at. %	ferromagnetic?
Ni pentane (8)[c]	40.4	18.7	40.9	2:1:2	0.7	no
Ni pentane (9s)[d]	34.1	18.0	47.9	2:1:3	1.1	no
Ni pentane (9)[c]	67.0	12.5	20.5	5:1:2	1.5	yes
Ni Cp (1s)[d]	50.8	13.6	35.6	4:1:3	1.5	yes
Ni 2,2-DMB (1s)[d]	48.2	17.9	33.9	3:1:2	2.8	yes
Ni 2,3-DMB (1s)[d]	48.5	12.8	38.7	4:1:3	3.2	yes
Ni heptane (1s)[d]	73.6	8.4	18.0	9:1:2	3.9	yes
Co pentane (4s)	55.1	14.9	30.0	4:1:2	1.4	yes

[a] These samples were degassed in vacuo at room temperature for several hours. Degassing at higher temperatures caused more carbonaceous material to be lost. The major species desorbed at 100 °C was CO_2 along with small amounts of C_1–C_4 alkanes. These results show that strongly adsorbed intact alkanes were not present in the samples after initial degassing at room temperature. The elemental analyses reflected the higher temperature treatments. For example the Ni:C:H ratio changed from approximately 2:1:2 to 6:1:1 for a nonferromagnetic Ni-pentane sample (nonferromagnetism remained, however). Other Ni-alkane samples showed similar behavior. [b] Cp = cyclopentane; DMB = dimethylbutane. [c] Analyzed by Spang Microanalytical Laboratory. [d] Analyzed by Schwarzkopf Microanalytical Laboratory. [e] Matrix concentration.

Table V. Carbon Removal from Ni–Alkane Powders

sample[a] (no.)	Ni:C[b]	H_2 treatment[c] % C removed	% C as C_1
Ni pentane (10s)	3.2:1	16	72 (71% CH_4 + 1% CO_2)
Ni MCp (1s)	6:1	21	84 (CH_4)
Ni MCp (3s)	6:1	27	92 (CH_4)
Ni Cp (2s)	24:1	34	74 (73% CH_4 + 1% CO_2)
Ni 2,3-DMB (1s)	32:1	44	69 (64% CH_4 + 5% CO_2)

[a] MCp = methylcyclopentane; Cp = cyclopentane, DMB = dimethylbutane. [b] Calculated from carbon evolved as hydrogenation products + CO_2 evolved from heating sample to >600 °C under O_2. [c] 200 torr H_2, 8 h at 100 °C + 4 h at 200 °C.

Table VI. Products Evolved during Hydrogenation of Ni Pentane[a]

product[c]	yield, μmol g^{-1} 100 °C, 8 h[b]	200 °C, 4 h[b]
CH_4	387	240
CO_2	3.7	1.3
C_2H_6	58.6	0.7
C_3H_8	9.2	3.2
i-C_4H_{10}	0.7	0.3
n-C_4H_{10}	3.2	0.9
i-C_5H_{12}	1.1	0.4
n-C_5H_{12}	2.8	0.4
2,3-DMB	2.6	0.3
2- or 3-MP	0.3	
n-C_6H_{14}	0.6	
MCp	1.0	0.2
c-Hx	0.3	0.2
n-C_7H_{16}	0.4	

[a] Ni pentane (sample no. 10s); under 200 torr H_2. [b] Experimental conditions. [c] DMB = dimethylbutane; MP = methylpentane; MCp = methylcyclopentane c-Hx = cyclohexane.

Table VII. Products Evolved during Hydrogenation of Ni MCp[a]

product[b]	yield, μmol g^{-1} 100 °C, 8 h[c]	200 °C, 4 h[c]
CH_4	376	294
CO_2	5.2	
C_2H_6	11.2	1.3
C_3H_8	1.8	0.4
i-C_4H_{10}		
n-C_4H_{10}	0.6	
i-C_5H_{12}	0.2	
n-C_5H_{12}	0.3	
2,3-DMB	0.3	
2- or 3-MP	0.1	
MCp	0.6	
c-Hx	1.6	
n-C_7H_{16}	0.5	

[a] Ni MCp (sample no. 3s); under 200 torr H_2. [b] Abbreviations same as Table VI. [c] Experimental condition.

Table VIII. Products Evolved during Hydrogenation of Ni Cyclopentane[a]

product[b]	yield, μmol g^{-1} 100 °C, 8 h[c]	200 °C, 4 h[c]
CH_4	461	136
CO_2	3.6	0.3
C_2H_6	19.4	0.9
C_3H_8	3.5	1.6
i-C_4H_{10}	0.2	0.1
n-C_4H_{10}	1.0	0.5
i-C_5H_{12}	0.2	0.1
n-C_5H_{12}	1.3	0.2
2,3-DMB	1.0	
2- or 3-MP	0.1	
n-C_6H_{14}	0.2	
MCp	0.3	
c-Hx	0.1	
n-C_7H_{16}	0.1	

[a] Ni cyclopentane (sample no. 2s); under 200 torr H_2. [b] Abbreviations same as Table VI. [c] Experimental conditions.

carried out. Only CO_2, CH_4, and H_2 were evolved upon heating the sample to 600 °C. No pentane was found in the desorption product mixture. During heating, CO_2 was evolved between 150 and 300 °C. Noncondensable gases (CH_4 and H_2) evolved from the sample only above 300 °C. From the amount of carbon evolved from the sample in the form of CO_2 and CH_4, a Ni:C mole ratio of 2.5:1 was calculated.

Elemental analysis (C, H) of a nonferromagnetic Ni–pentane powder gave a Ni:C:H mole ratio of 2.1:1:2 which agreed well with the ratio calculated from pyrolysis data. A ferromagnetic sample was analyzed to give a ratio of 5:1:2. In general, ferromagnetic Ni–alkane powders were found to contain less carbon than nonferromagnetic samples as shown in Table IV. All of the samples shown in Table IV were degassed by pumping to $<1 \times 10^{-3}$ torr for several hours prior to being sent out for analysis. As can be seen, all Ni–alkane powders contained large amounts of carbonaceous material. Furthermore, the choice of alkane used in the preparation had no major influence upon the amount of carbonaceous material incorporated into the sample. There are no smooth trends in the variation of carbon content with matrix concentration found in Table IV. However, it should be noted that the most concentrated matrix (3.9 at. % Ni) resulted in the lowest carbon content, and the most dilute matrix (0.7 at. % Ni) resulted in the highest amount of carbon incorporation. It can also be seen in Table IV that a large amount of carbonaceous material is present in Co–pentane powders.

Hydrogen was added to various Ni–alkane samples in order to displace any surface alkyl fragments by formation of the corresponding alkanes. For example, chemisorbed methyl or methylene species would desorb as methane. Ni–alkane hydrogenations were carried out at 100 and 200 °C for 8-h and 4-h periods, respectively. Following the hydrogenations the samples were oxidized with an excess of O_2 at temperatures $\gtrsim$600 °C. This was done to determine the amount of carbon in the samples that was not removed by the hydrogen treatments. All samples were thoroughly degassed in vacuo at 100 °C prior to the hydrogen treatments. The total amount of carbon removed from the samples was determined, and Ni:C ratios were calculated. Table V lists the Ni:C ratios obtained by the H_2/O_2 treatments, the percentage of carbon removed by hydrogen treatments only, and the percentage of carbon released by hydrogen treatments in the form of C_1 species (CH_4 and CO_2).

Table IX. Products Evolved during Hydrogenation of Ni 2,3-Dimethylbutane[a]

product[b]	yield, μmol g^{-1}	
	100 °C, 8 h[c]	200 °C, 4 h[c]
CH_4	135	11.0
CO_2	10.4	1.6
C_2H_6	0.9	0.5
C_3H_8	3.2	0.9
i-C_4H_{10}	0.4	0.1
n-C_4H_{10}	0.9	0.3
i-C_5H_{12}	1.1	0.1
n-C_5H_{12}	0.4	0.2
2,3-DMB	1.7	0.5
2- or 3-MP	0.1	
n-C_6H_{14}	0.1	0.1
MCp	0.2	0.1
c-Hx	0.9	0.1
n-C_7H_{16}	0.2	0.5
C_8H_{18}	0.9	1.3

[a] Ni 2,3-DMB (sample no. 1s); under 200 torr H_2. [b] Abbreviations same as Table VI. [c] Experimental conditions.

Table X. Products Evolved during Hydrogenation of Co Pentane[a]

product	mole %	product	mole %
CH_4	49	i-C_4H_{10}	2
CO_2	13	n-C_4H_{10}	9
C_2H_6	1	i-C_5H_{12}	8
C_3H_8	12	n-C_5H_{12}	6

[a] Co pentane (sample no. 3s); under 200 torr H_2, 6.5 h, 94 °C.

The total hydrogenation product analysis of Ni pentane, Ni methylcyclopentane (Ni MCp), Ni cyclopentane (Ni Cp), and Ni 2,3-dimethylbutane (Ni 2,3-DMB) are shown in Tables VI–IX. The predominance of methane is clearly seen. Also, the distribution of higher alkane products appears to be random with no significant influence of the original alkane. It can also be seen that both cyclic and branched alkanes were released upon hydrogenation of Ni pentane (Table XI) as well as very small amounts of alkanes containing more than five carbons.

The possibility that conditions used to displace the adsorbed hydrocarbons could have induced hydrogenolysis of the surface species was considered. Therefore, MCP was allowed to stand over a fresh Ni MCp (sample no. 2s) powder under 200 torr H_2 at 100 °C for 4 h. No hydrogenolysis of the MCp was detected, and the distribution of evolved products was the same as when the additional MCp was absent.

A Co–pentane powder was subjected to hydrogenation at 94 °C for 6.5 h under 60 torr H_2. The distribution of evolved products is shown in Table X. As can be seen, C_1 species (CH_4 and CO_2) were the major products evolved as was the case for Ni pentane.

An ESCA study was performed on an air exposed Ni–pentane powder (no. 10). Argon sputtering was used to expose the interior of the Ni–pentane pellet. The composition of the pellet at various depths (Ar^+ sputtering time) is shown in Figure 1. It can be seen that carbon is distributed throughout the sample. From the ESCA spectrum it was determined that the carbon was not in the form of carbides but rather sp^2- or sp^3-hybridized species.

Ni–alkane powders were subjected to hydrolysis by water at 100 °C for 8 h in order to hydrolyze Ni–C bonds and displace hydrocarbon fragments in the form of alkanes. Products evolved during hydrolysis of Ni pentane, Ni MCp, Ni 2,3-DMB, and Ni cyclopentane are given in Table XI. Although only a small fraction of the total carbonaceous material was displaced by hydrolysis (<5%), it can be seen that C_1 species predominate. Also, the amount of C_1 species evolved in the form of CO_2 is much larger in the hydrolyses than in the hydrogenations even when the water was thoroughly degassed.

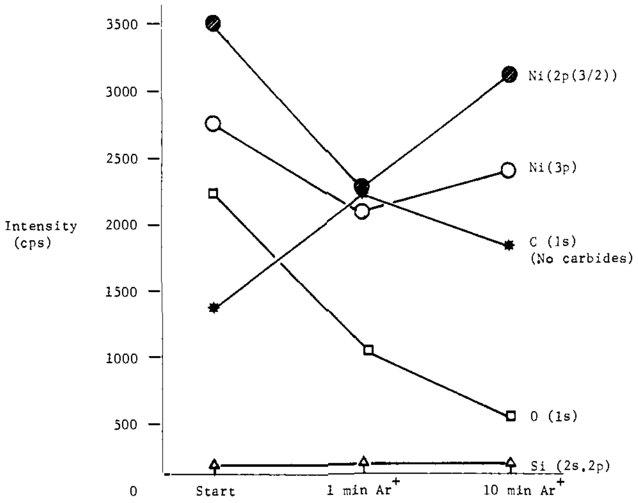
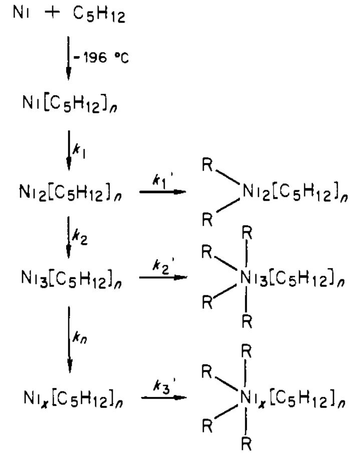


Figure 1. Elemental analysis of Ni pentane by ESCA.

Scheme II



Discussion

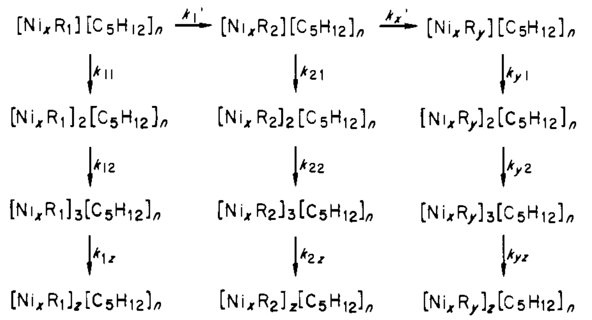
It can be seen from Table I that the formation of nonferromagnetic Ni–pentane powders is favored when the matrix is allowed to warm-up via a 2-h residence time at −130 °C (Scheme Ib) rather than a rapid warm-up (Scheme Ia). Also, nonferromagnetic Ni–alkane powders contain an significantly larger amount of carbonaceous materials (C, H) than ferromagnetic samples as can be seen in Table IV. Pyrolysis, hydrogenation, and hydrolysis of Ni–alkane powders (c.f. Tables VI–IX and XI) indicate that the carbonaceous material is not simply excess alkane adsorbed to the powders but rather *fragments of the original alkane*. It is also clearly seen that the fragmentation has been extensive with C_1 surface species predominating. These obser-

Table XI. Products Evolved during Hydrolysis of Ni–Alkane Powders[a]

sample[b] (no.)	product yield, μmol g^{-1}								
	CH_4	CO_2	C_2H_6	C_3H_8	i-C_4H_{10}	n-C_4H_{10}	i-C_5H_{12}	n-C_5H_{12}	Cp
Ni pentane (11s)	27.8	43	0.6	1.4	0.1	0.7	0.3	2.6	
Ni MCp (4s)	8.2	16.3	0.2	0.1					
Ni 2,3-DMB (3s)	12.2	31.7	0.4	0.2					
Ni Cp (3s)	17.7	11.8	1.2	4.3	0.6	2.1	0.3	0.7	2.1

[a] 0.05 mL of H_2O, 100 °C, 8 h. [b] Cp = cyclopentane; MCp = methylcyclopentane; DMB = dimethylbutane.

Scheme III



[a] R = carbonaceous residue from pentane dehydrogenation and fragmentation on crystallite, Ni$_x$, surface.

vations show that when a Ni–alkane matrix is allowed to remain at −130 °C there is an accumulation of carbonaceous material, which is a result of cleavage of the alkane medium by nickel. The black appearance of the Ni–alkane matrices at −196 °C and the results of a study of V atom clustering in alkane matrices by Ozin and co-workers[20] strongly suggest that Ni particles and not atoms are responsible for the alkane cleavage at $\lesssim$−130 °C. Ozin observed no cleavage of alkanes by V or V$_2$ up to −130 °C (cyclooctane) or $^1/_2$ the melting point of an alkane. Furthermore, Hauge[9] observed photoactivated insertion of Fe and Co atoms into C–H bonds of methane at 12 K, but Ni atoms failed to react. It can be seen from Table II that the crystallites of Ni–alkane powders are very small (<36 Å). Since the size range of the crystallites is at the lower limit of resolution of the X-ray diffraction technique, we believe that the values listed in Table II are size maxima. The extremely small crystallite sizes produced by clustering nickel atoms in alkane media combined with the observation of alkane cleavage by nickel at $\leq$−130 °C strongly suggests the presence of a competition between nickel particle growth (k) and reaction of nickel particles with the alkane medium (k'). This type of competition, illustrated in Scheme II for Ni–pentane powders, serves to stabilize the nickel particles at very small sizes.

Although Scheme II can account for the extremely small sizes of the crystallites present in Ni–alkane powders, it does not explain their magnetic properties. It was previously assumed[16] that nonferromagnetic Ni–pentane powders contained smaller crystallites than ferromagnetic samples and Scheme II could account for the magnetic properties. However, detailed X-ray diffraction studies reveal that there is no significant crystallite size difference between ferromagnetic and nonferromagnetic Ni–alkane powders (Table II). Since the crystallite sizes of ferromagnetic Ni–alkane powders are much below that of a ferromagnetic domain, ferromagnetism is an unusual property. In light of recent work by Scott and co-workers,[21] the ferromagnetism that we observed can be explained by assuming the presence of magnetic coupling between crystallites. The particle sizes of ferromagnetic Ni–alkane powders (Table III), calculated from surface areas, are much larger than crystallite sizes determined by X-ray diffraction. This lack of accessibility of gases (H$_2$ or N$_2$) which results in large apparent particle sizes (96–143 Å) of Ni–alkane powders can be interpreted as an indication of crystallite aggregation. Since the particle sizes determined from surface area are below a ferromagnetic domain, loose aggregation of particles is probably present.[21,22] The difference in carbon content of ferromagnetic and nonferromagnetic Ni–alkane powders can be explained by the presence of a competition between accumulation of carbonaceous material (hydrocarbon fragments) on the surfaces of small crystallites ($\lesssim$35 Å) (k') and aggregation of crystallites (k_{ij}) to form particles as illustrated in Scheme III for Ni–pentane powders. Particles composed of crystallites covered with a thin carbonaceous layer (R$_1$) display ferromagnetism due to magnetic coupling. If thick carbonaceous layers (R$_y$) are present on the crystallites at the time of aggregation, magnetic coupling is inhibited and nonferromagnetic properties are observed. A thick carbonaceous layer is favored by allowing the Ni–alkane matrix to remain at −130 °C prior to warm-up to room temperature.

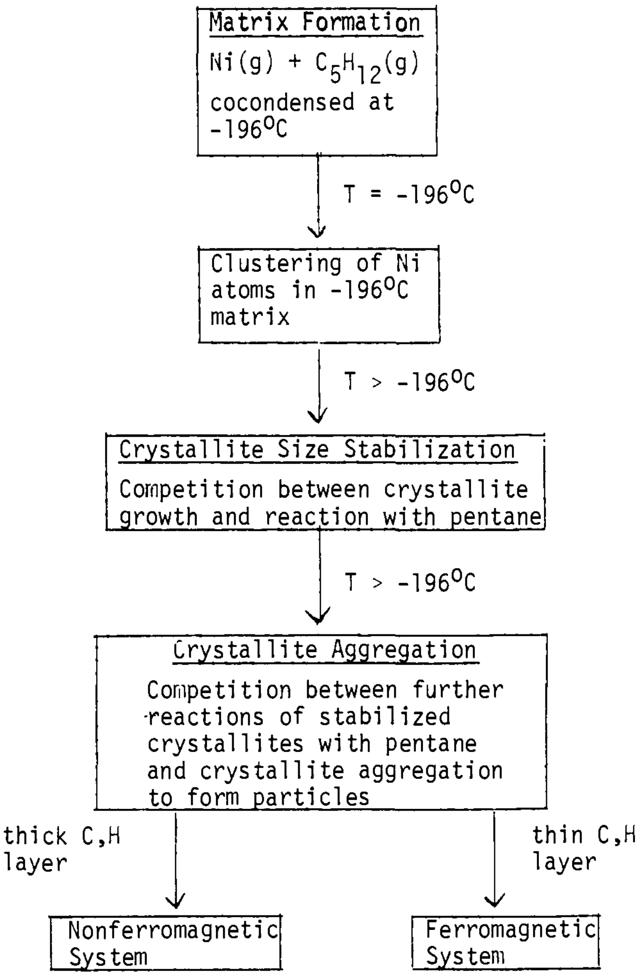


Figure 2. Formation of Ni pentane particles.

The competitive processes proposed above are summarized in Figure 2 for the formation of Ni–pentane particles. Cobalt appears to behave in a similar manner although nonferromagnetic samples could not be produced, presumably due to the much higher magnetic moment of Co than Ni.[23]

Conclusions

We have shown that upon clustering nickel atoms at low temperatures in alkane media, small crystallites are formed which have sufficient reactivity to cleave alkane molecules. The alkane cleavage occurs at $\leq$−130 °C and results in the formation of a carbonaceous deposit consisting, predominantly, of C$_1$ species. The alkane fragmentation serves to halt the growth of nickel particles and provide thermal stability to the Ni–alkane powders. Another result of the alkane fragmentation is a reduction in the degree of ferromagnetism displayed by the nickel particles due to an inhibition of magnetic coupling between crystallites, which is due to the formation of an organic layer on the cluster surfaces. The

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[20] Klotzbucher, W. E.; Mitchell, S. A.; Ozin, G. A. *Inorg. Chem.* **1977**, *16*, 3063.

[21] Scott, B. A.; Plecenik, R. M.; Cargill, G. S. III; McGuire, T. R.; Herd, S. R. *Inorg. Chem.* **1980**, *19*, 1252.

[22] Scott and co-workers[21] studied nickel powders prepared by clustering of metal atoms in toluene and did not observe superparamagnetism in the samples although the crystallite sizes were well below those in a ferromagnetic domain. Ferromagnetism was observed to a greater or lesser extent but generally well below that of bulk nickel. A comparison of their work with ours thus suggests that the nonferromagnetism that we observe (no attraction to a bar magnet) does not necessarily imply the presence of superparamagnetism.

[23] "Handbook of Chemistry and Physics", 56th ed.; Weast, R. C., Ed.; Chemical Rubber Co., Cleveland, 1968; p E-120.

Table XII. Preparation of Ni-Alkane Powders by Method 1[a]

sample (no.)	[Ni vapor], g	[alkane], mL	alkane/Ni mole ratio
Ni pentane (1)	0.141	150	550
Ni pentane (2)	0.191	200	542
Ni pentane (3)	0.155	100	333
Ni pentane (4)	0.179	84	243
Ni pentane (5)	0.209	60	146
Ni pentane (6)	0.180	80	230
Ni pentane (7)	0.063	96	779
Ni pentane (8)	0.159	100	324
Ni pentane (9)	0.784	100	66
Ni pentane (10)	0.208	72	175
Ni hexane	0.312	60	86
Ni heptane (1)	0.363	60	67
Ni octane	1.128	100	32

[a] See text (Scheme Ia).

unusually high reactivity of the nickel particles toward alkanes is probably a result of two factors: (1) very clean surfaces and (2) special surface features present on the growing crystallites. Since the metal crystallites formed during the preparation of Ni–alkane powders are "solvated" by the alkane they remain very clean until reaction with the alkane occurs. Furthermore, as the crystallites grow, their surfaces continually change to attain spherical shape. As this occurs, special surface sites may be formed which are very reactive. Single crystal studies have suggested that active sites for C–H bond cleavage may be at "step" sites and C–C bonds cleave at "kink" sites.[24]

Experimental Section

The metal atom–vapor reactor used for the preparation of Ni–alkane- and Co–pentane powders has been described previously.[25a] Also, detailed descriptions of the technique and methodology involved have been published.[25b,c]

M–Alkane Powder Preparation. The following alkanes were purified prior to use by refluxing over benzophenone ketyl under a nitrogen atmosphere: pentane, hexane, heptane, octane (mixture of isomers), cyclopentane (Cp), methylcyclopentane (MCp), 2,2-dimethylbutane (2,2-DMB), and 2,3-dimethylbutane (2,3-DMB). Prior to drying and distillation, the alkanes were stirred over concentrated sulfuric acid to remove any olefinic impurities. The purified alkanes were analyzed by GC to check their purity. The alkanes were placed in a solvent flask and degassed by freeze–thaw cycles immediately prior to their use.

Two methods were used in the preparation of nonferromagnetic and ferromagnetic Ni–alkane powders. The preparation of nonferromagnetic Ni–pentane powders by method 1 (Scheme Ia) and by method 2 (Scheme Ib) will serve as examples for the preparation and workup of Ni–alkane powders. Specific deposition parameters are given in Tables XII and XIII.

Method 1 (Ni Pentane, Sample No. 1). A piece of Ni shot (ca. 2 g) was loaded into a Sylvania Emmissive Products Integral WAl_2O_3 crucible (CS-1008), weighed, and placed in the proper position in a metal atom reactor.[25] The reactor was assembled and evacuated down to $<10^{-3}$ torr during which time the crucible was degassed by resistive heating to a dull red heat. The reactor vessel was cooled to −196 °C with liquid nitrogen, and then the inflow of pentane vapor was started. After about 10 mL of pentane was inletted, Ni vaporization was started. For about 2 h, Ni vapor (0.141 g) and pentane vapor (150 mL) were cocondensed at −196 °C. Once the codeposition was completed, the reactor was isolated from the vacuum system, the liquid nitrogen source was removed, and the black matrix was allowed to melt down. Vigorous magnetic stirring was commenced and continued as the black Ni–pentane slurry warmed. Small flocculent Ni particle aggregates were formed and suspended in the pentane. Once the reactor reached room temperature, it was vented to prepurified N_2. This N_2 was prepurified by passing the gas over a Chem. Dyn. Cat. R3-11 deoxygenation catalyst at 110 °C just prior to use. A stopper to the reactor was removed with a good flush of N_2. The slurry was removed by siphoning into a preflushed Schlenk tube through a Teflon hose. Excess pentane was then removed under vacuum. The resultant dry, black Ni–pentane powder was transferred in a Vacuum Atmospheres inert-atmosphere box (<5 ppm of O_2).

Table XIII. Preparation of Ni-Alkane and Co-Alkane Powders by Method 2[a]

sample (no.)	[Ni vapor], g	[alkane], mL	t, min[b]	alkane/Ni mole ratio
Ni pentane (1s)	0.259	75	120	147
Ni pentane (2s)	0.488	92	120	96
Ni pentane (3s)	0.807	65	170	41
Ni pentane (4s)	0.485	25	160	27
Ni pentane (5s)	0.349	98	120	144
Ni pentane (6s)	0.323	87	120	138
Ni pentane (7s)	0.981	97	127	51
Ni pentane (8s)	1.173	88	115	38
Ni pentane (9s)	0.624	95	160	78
Ni pentane (10s)	0.901	110	125	62
Ni pentane (11s)	0.752	120	120	80
Co pentane (1s)	0.591	67	110	58
Co pentane (2s)	0.533	70	100	67
Co pentane (3s)	0.581	250	200	221
Co pentane (4s)	0.546	73	120	69
Ni heptane (1s)	0.820	63	120	31
Ni MCp (1s)	0.706	94	200	70
Ni MCp (2s)	0.740	45	135	32
Ni MCp (3s)	0.455	65	120	75
Ni MCp (4s)	1.577	128	230	42
Ni 2,2-DMB	0.954	76	120	35
Ni 2,3-DMB (1s)	0.285	50	120	77
Ni 2,3-DMB (2s)	0.571	135	120	107
Ni Cp (1s)	1.018	200	110	123
Ni Cp (2s)	0.671	65	110	61

[a] See text (Scheme Ib). [b] At 130 °C.

Method 2 (Ni Pentane, Sample No. 1s). The above procedure was used except that 0.259 g of Ni was vaporized and cocondensed with 75 mL of pentane. Also, once the codeposition was completed and the reactor isolated from the vacuum system, the liquid-nitrogen source was removed and replaced with a pentane slush bath (−130 °C). The matrix was then allowed to remain at −130 °C for 2 h. After 2 h, the pentane slush bath was removed and the Ni–pentane slurry was allowed to warm to room temperature while stirring magnetically. Work-up of the Ni–pentane slurry was then carried out with use of the above procedure.

Co Pentane. The procedure described above for method 2 was employed except Co was used instead of Ni. The reaction parameters are given in Table XIII.

Crystallite Size Determination. Quantitative crystallite size determinations of M–alkane powders were obtained by X-ray diffraction with use of a recording diffractometer (Picker FACS-1 single crystal diffractometer). Capillary tubes (0.5 mm) were packed with sample in a drybox, mounted on the diffractometer, and irradiated with Mo Kα X-radiation filtered with a 1-mil Zr filter. The samples were scanned from 4° to 60° (2θ) at a rate of 2° min^{-1}.

Surface Area Determination. Normal BET-H_2 chemisorption (25 °C) and N_2 physical adsorption (−196 °C) methods were used.[4,17,18]

Pyrolysis, Hydrogenation, and Hydrolysis of M-Alkane Powders. The apparatus used for carrying out pyrolysis, hydrogenation, and hydrolysis of Ni–alkane and Co–pentane powders is described elsewhere.[26] Noncondensable products (H_2, O_2, CH_4, CO) were collected with a Toepler pump and analyzed by GC by using a 10 ft × $^1/_4$ in., 5-Å molecular sieve column at 25 °C. Separation of the condensable and noncondensable product fractions was achieved by passing the product mixture through three U-tube traps at −196 °C before the Toepler pump. The condensable fraction was collected in a 6.7-mL glass sample tube,[25] $BrCCl_3$ added as an internal standard, and the mixture analyzed by GC by using a 15 ft × $^1/_4$ in., SE-30 (25%)/Chromosorb W column with a 50-cc min^{-1} flow of He carrier gas. A 0–200 °C nonlinear temperature program was used which enabled separation of C_2–C_8 normal alkanes and most isomers.

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