Sonochemical Coating of Nanosized Nickel on Alumina Submicrospheres and the Interaction between the Nickel and Nickel Oxide with the Substrate

Ziyi Zhong,† Yitzhak Mastai,‡ Yuri Koltypin,† Yanming Zhao,† and
Aharon Gedanken*,†

Department of Chemistry, Bar-Ilan University, Ramat-Gan, 52900 Israel, and Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot, 76100 Israel

Received October 8, 1998. Revised Manuscript Received May 27, 1999

The preparation and coating of nickel on amorphous and crystallized alumina were carried out by employing a sonochemical method. The interaction between the nickel as well as its oxide and the alumina core was then studied by TEM, XRD, DSC, DRS, FTIR, and magnetization measurements. The following were found: (1) Amorphous alumina can provide a great number of active sites for reaction with nickel and can yield a good coating effect in which most of nickel is adhered to the alumina surface tightly, while in the case of the crystallized alumina as substrate, most of nickel particles is distributed in the free space among the alumina submicrospheres. (2) As compared to the unadhered nickel, the adhered nickel has a strong interaction with the alumina core, which can retard the crystallization of elemental nickel and, conversely, promote the formation of the spinel phase $NiAl_2O_4$. (3) The first stage of the interaction between the nickel and the alumina may be through the isolated hydroxyl groups to form a kind of interface Ni−O−Al bond. The connection positions further become nucleation centers for elemental nickel. After the sample is heated to high temperatures, DRS and IR results showed the diffusion of nickel ions into the vacant tetrahedral sites in alumina. At higher temperature, an inversion process—the substitution of Ni^{2+} ions for part of Al^{3+} at octahedral sites has taken place, and it results in the final formation of the disordered spinel phase. (4) Magnetization measurements show that the as-prepared sonication products are superparamagnetic due to the ultrafine nature of nickel particles.

Introduction

Supported elemental nickel and nickel oxide catalysts on alumina have wide applications in important reactions, e.g., Ni/Al_2O_3 for methanation, hydrogenation, and hydrocracking,[1−4] and NiO/Al_2O_3 for CO oxidation[5] and N_2O decomposition.[6] In the past few decades, a flurry of effort has been directed toward the preparation of nanosized nickel and its oxide particles with a high degree of dispersion on alumina due to the fact that usually a fine, highly dispersed nickel phase can provide more active sites which are accessible to reactant molecules and available for catalysis. At the same time, it is aimed toward understanding the nature of the interactions between the metallic element as well as its oxide and the substrate because these interactions will directly influence their catalytic properties.[7,8] In most cases, the metallic nickel supported catalyst is obtained via the reduction of the deposited nickel oxide on substrate. Hercules et al.[9,10] found that there are two forms of nickel ions, namely the tetrahedrally and octahedrally coordinated nickel, presented on the surface of γ-alumina for low content of nickel loading. At the high nickel loading, a new nickel species characterized as bulk NiO appeared, due to the lack of interaction with the support. It was also found that only a part of the nickel supported on alumina was reducible. Burggraf et al.[3] believed that there is a strong interaction between the nickel oxide and the alumina support—nickel ions can incorporate into the surface and also into bulk cation vacancies of alumina to form octahedrally and tetrahedrally coordinated nickel at high temperatures. The octahedrally coordinated nickel ions are readily reducible to the metal, while the tetrahedrally coordinated nickel ions are not readily reducible to the metal and are catalytically inactive. The relative abundance and the distribution of these nickel species depend heavily on the preparation method and the heat-treatment temperature of catalyst.

---

* E-mail: Gedanken@mail.cc.biu.ac.il.
† Bar-Ilan University.
‡ Weizmann Institute of Science.

(1) Kruissink, E. C.; Reijen, V. L. L.; Ross, J. R. H. *J. Chem. Soc., Faraday Trans.* **1981**, *77*, 649.
(2) Alzamora, L. E.; Ross, J. R. H.; Kruissink, E. C.; Reijen, V. L. L. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 665.
(3) Burggraf, L. W.; Leyden, D. E.; Chin, R. L.; Hercules, D. M. *J. Catal.* **1982**, *78*, 360−379.
(4) Narayanan, S.; Vnnikrishnan, R. *J. Chem. Soc., Faraday Trans.* **1998**, *94* (8), 1123.
(5) Rymer, G. T.; Bridges, J. M.; Tomlinson, J. R. *J. Phys. Chem.* **1961**, *65*, 652.
(6) Schiavello, M.; Lojacono, M.; Cimino, A. *J. Phys. Chem.* **1971**, *75*, 1051.
(7) Rodeghiero, E. D.; Chisaki, J.; Giannelis, E. P. *Chem. Mater.* **1997**, *9*, 478.
(8) Davidson, A.; Tempere, J. F.; Che, M.; Roulet, H.; Dufour, G. *J. Phys. Chem.* **1996**, *100*, 4919.
(9) Wu, M.; Hercules, D. M. *J. Phys. Chem.* **1979**, *83*, 15, 2903.
(10) Ng, K. T.; Hercules, D. M. *J. Phys. Chem.* **1976**, *80*, 2094.

10.1021/cm981005m CCC: $18.00

Aside from catalysis, other research has focused on the potential application of nanosized nickel as magnetic materials in information industry. To date, the most-investigated systems are based on matrixes of Al_2O_3 and SiO_2 with particles of Ni, Fe, Co, FeNi, and FeCo.[11] However, it has been reported that SiO_2 readily forms the impurity phases with many of the magnetic materials,[11,12] so materials scientists have favored alumina as a matrix or support material.

In recent years, Suslick et al.[13] have developed an effective way to directly prepare nanophase amorphous metallic particles by using high-intensity ultrasound radiation. This method is based on the phenomena of acoustic cavitation—the formation, growth, and collapse of bubbles in liquid, in which the extreme conditions, such as the highest transient temperature, which exceeds 5000 K in localized hot spots, and the ultrafast cooling rate of $>10^{10}$ K s^{-1} that can be obtained and that are necessary to the formation of amorphous structure. In our lab, sonication has been further used as a tool to deposit the amorphous iron oxide, metallic nickel and cobalt on silica.[14,15] In this work, we aim to develop a straight and effective method to coat metallic nickel on an alumina surface. At the same time, the interaction between nickel oxide and alumina, which may provide insight into the nature of its catalysis, is studied.

Experimental Section

Preparation. Amorphous submicrospherical alumina was prepared by hydrolysis of aluminum *sec*-butoxide (ASB) in a dilute mixture solution of 1-octanol, 1-butanol, and acetonitrile, and in the preparation, hydroxypropylcellulose (HPC) was used as a dispersant.[16] The total initial mixed solution had a composition of approximately 59:1:40 1-octanol/1-butanol/acetonitrile in volume percent (vol %), and the aluminum alkoxide and water concentrations were 0.05 and 0.01 M, respectively. After precipitation, the precipitate was aged for 30 min and washed thoroughly with acetone and finally dried in a vacuum. Crystallized γ-Al_2O_3 was obtained when heated to 1000 °C.

Sonochemical coating of nanosized nickel particles on alumina spheres was carried out in the following way: 400 mg of appropriate alumina was added to 50 mL of Decalin in a sonication cell connected to the sonicator under flowing argon, and 4 mL of filtered nickel tetracarbonyl was then added. Prior to sonication, argon gas was bubbled for 0.5 h, preventing the possible oxidation of nickel from dissolved oxygen. The irradiation of nickel tetracarbonyl and alumina spheres was carried out by employing a high-intensity ultrasonic Ti-Horn (Vibracell, 20 kHz, 100W/cm^2, the diameter of Ti−Horn is 1 cm.) under argon at 0 °C for 1 h. (**Caution**: Due to the notorious toxicity of nickel tetracarbonyl, the above operation should be very carefully and processed in a good conditioned fume cupboard. The sonicator should not be started before making sure that the temperature in the sonicaton cell was cooled to 0 °C. In addition, carbon monoxide at the outlet must be collected in a liquid nitrogen bath to be safely disposed later.) The product was then washed thoroughly with hexane in a glovebox with a oxygen concentration less than 10 ppm. For comparison, two types of alumina were used in the sonication. They are as-prepared amorphous alumina and crystallized alumina. All samples were heated at different temperatures under argon or air.

Table 1. Composition Determined by EDX and Elemental Analyses for Sonication Products before and after Heating

substrate	Ni/(Ni + Al + O)^a (mol %)	C^b (wt %)	H^b
amorphous alumina	12.9	5.17	1.73
	13.9^c	1.73	0.69
crystallized alumina	23.0		
	25.5^c		

^{a} EDX results. ^{b}Elemental analyses results. ^{c}After heating at 400 °C in argon.

Characterization. X-ray diffraction(XRD) measurements were carried out on a Model 2028 (Rigaku) diffractometer (Cu Kα). The air-sensitive samples were covered with a layer of collodion in the inert atmosphere of a glovebox prior to XRD measurement to prevent their oxidation in air. The observation of particle morphology and their adherence to alumina was conducted on a JEOL-JEM 100SX microscope. Energy-dispersive X-ray analysis (EDX) was carried out on a JEOL JSM-840 electron microscope. Elemental analyses were carried out on an EA1110 CHNS-O analyzer. Differential scanning calorimetry (DSC) studies were carried out on a Mettler DSC 30 by using argon as a carrier gas. Infrared spectra were recorded employing a Nicolet 410 FTIR spectrometer by a KBr disk method. Magnetization measurements were conducted by employing a Quantum Design MPMS Squid magnetometer on accurately weighed samples packed in a gelatin capsule under argon. Diffuse reflectance spectroscopy (DRS) measurements were carried out on a Jasco (V-570) spectrophotometer equipped with an integrating sphere. Spectra were recorded at room temperature from 800 to 220 nm with a scanning speed of 100 nm/min. $MgCO_3$ was used as a reference. To measure the reflection quantitatively, 0.1 g of the sample was contained in a quartz cell (~10 mm). Bulk powder of $NiAl_2O_4$ was used as a comparison. (Nickel aluminate was prepared by coprecipitation of stoichiometric water solutions of Al and Ni nitrates with ammonium carbonate at pH 9. The precipitate was washed with water, dried, and finally heated at 1000 °C in air for 4h.[17]) The Kubelka−Munk[17,18] (KM) remission function was calculated from the recorded DRS. The KM value is equivalent to the absorption in transmission spectroscopy.

Results and Discussion

EDX, Elemental Analyses. EDX and elemental analyses results are listed in Table 1. It is indicated that for the as-prepared sonication products coated on amorphous and crystallized alumina, the nickel content is ~13 and 23 mol %, respectively. Elemental analyses results show that the sample coated on amorphous alumina has a relatively high content of carbon (~5 wt %).

TEM, DSC, and XRD Studies. TEM images of different samples for nickel coated on amorphous and crystallized alumina are shown in Figures 1 and 2, respectively. It is seen that for nickel coated on amorphous alumina, most of the nickel (elemental nickel or its oxide, which will be discussed later) forms loosely contacted small spherical particles with an average diameter of ~5−10 nm (Figure 1a). These small par-

---

(11) Dormann, J. I.; Djega-Mariadasson, C.; Jove, J. *J. Magn. Magn. Mater.* **1992**, *104*, 1576.

(12) Djega-Mariadasson, C.; Dormann, J. I.; Nogues, M.; Viller, G.; Sayouri, S. *IEEE Trans. Magn.* **1990**, *26*, 1819.

(13) (a) Suslick, K. S., Ed. *Ultrasound: Its chemical, Physical and Biological Effects*; VCH: Weinheim, 1988. (b) Suslick, K. S.; Choe, S. B.; Cichowlas, A. A.; Grinstaff, M. W. *Nature* **1991**, *353*, 414.

(14) Ramesh, S.; Prozorov, R.; Gedanken, A. *Chem. Mater.* **1997**, *9*, 2996.

(15) Ramesh, S.; Koltypin, Y.; Prozorov, R.; Gedanken, A. *Chem. Mater.* **1997**, *9*, 546.

(16) Ogihara, T.; Nakajima, H.; Yanagawa, T.; Ogata, N.; Yoshida, K.; Matsushita, N. *J. Chem. Ceram. Soc.* **1991**, *74*, 9, 2263.

(17) Busca, G.; Lorenzelli, V.; Escribano, V. S., Guidetti, R. *J. Catal.* **1991**, *131*, 167.

(18) Kubelka, D.; Munk, L. *J. Opt. Soc. Am.* **1948**, *38*, 448.

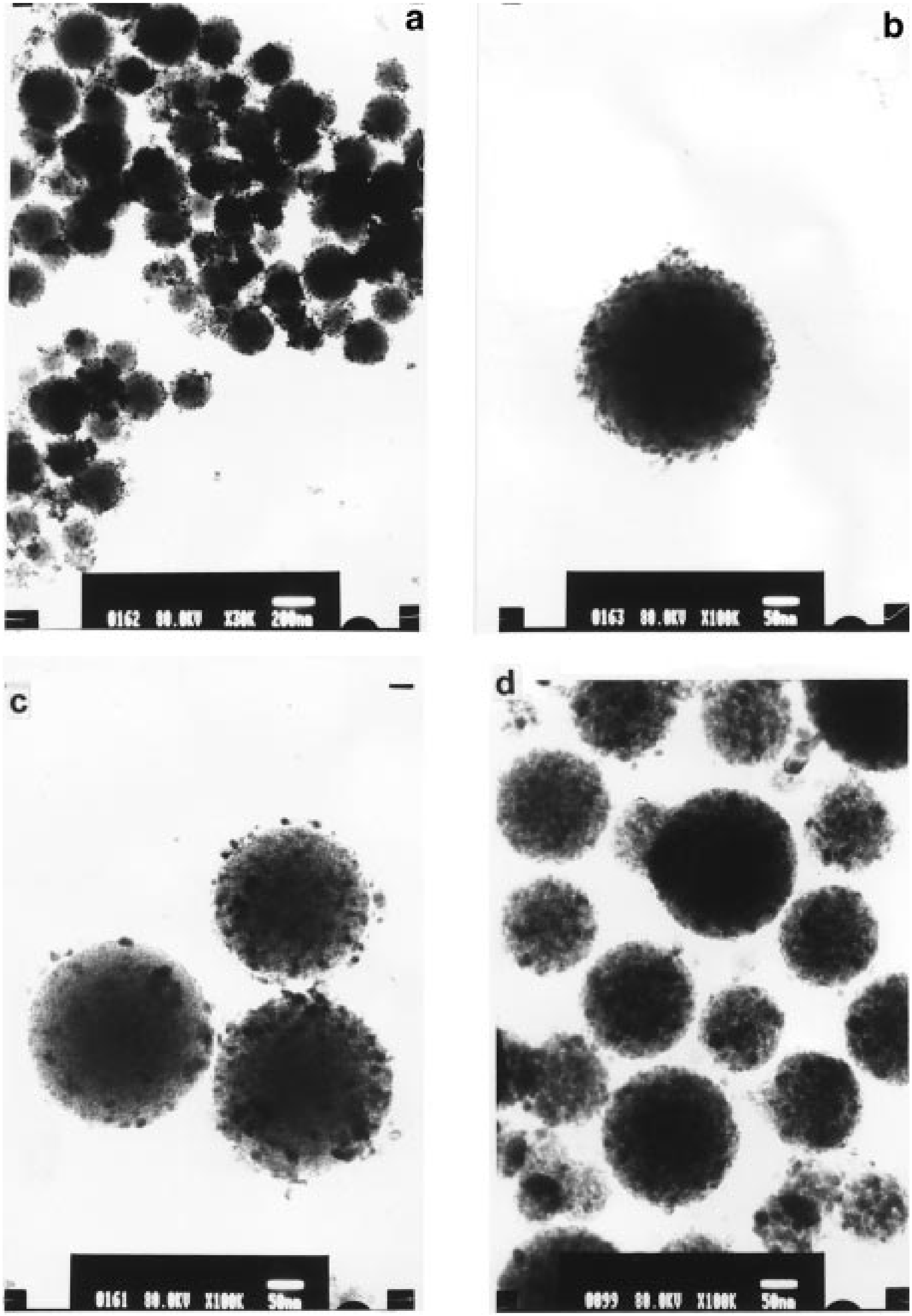

Figure 1. TEM micrographs of (a) as-prepared sample of nickel coated on amorphous alumina; (b) magnification image of micrograph a; (c) nickel coated on amorphous alumina and heated at 800 °C in air for 4h; and (d) nickel coated on amorphous alumina and heated at 1000 °C in air for 4h.

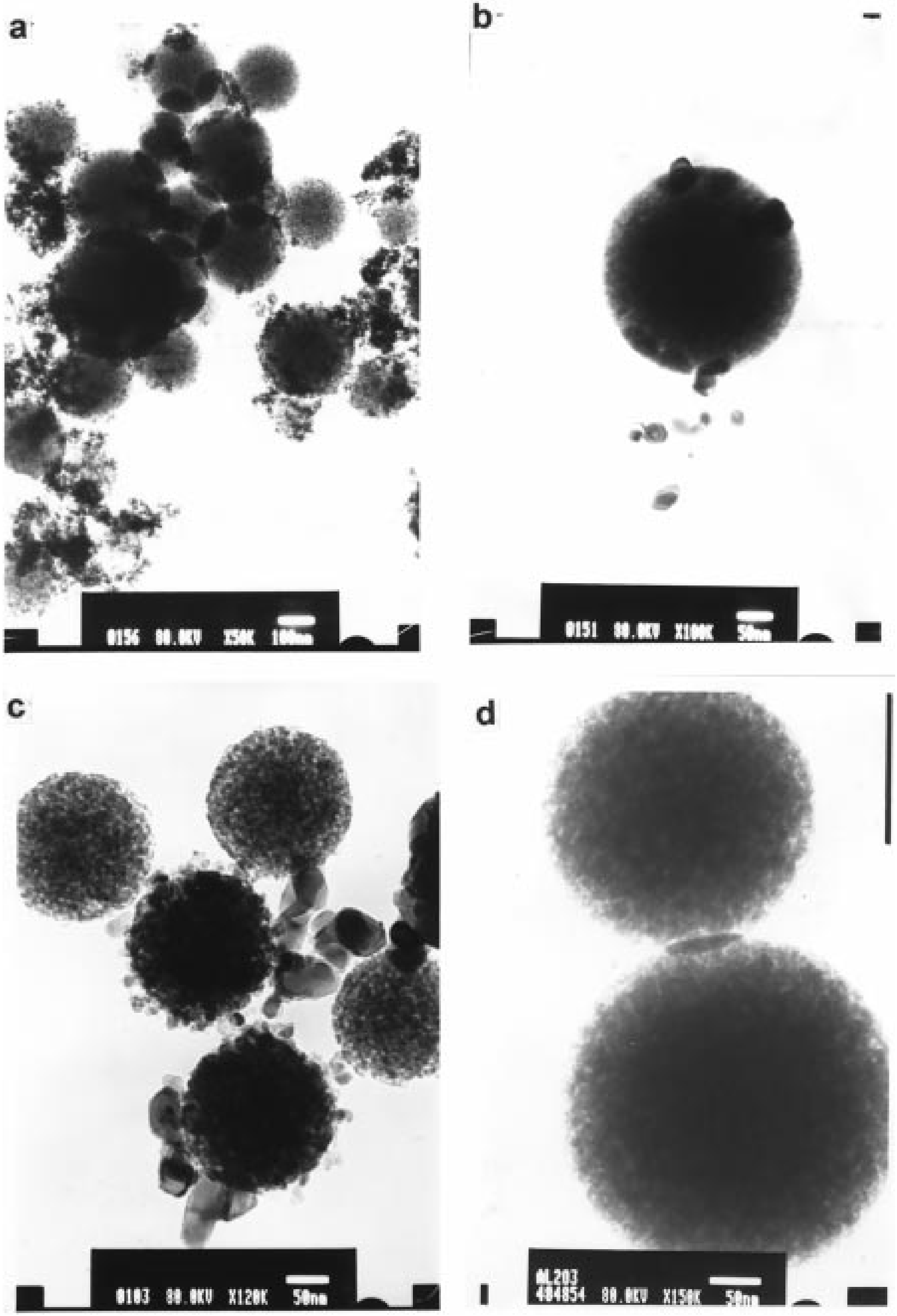

Figure 2. TEM micrographs of (a) as-prepared sample of nickel coated on crystallized alumina; (b) nickel coated on crystallized alumia and heated at 800 °C in air for 4 h; (c) nickel coated on crystallized alumina and heated at 1000 °C in air for 4 h; and (d) crystallized bare alumina (heated at 1000 °C in air for 4 h).

ticles are tightly adhered to the alumina spheres and separated from each other. Figure 1b is a magnified image of a single alumina sphere for the above sample. It is clearly shown that the surface of alumina sphere is almost fully covered by the small nickel particles. After heating to 800 °C in air, a growth of nickel particles up to 10−20 nm is observed (Figure 1c). Even after heating to 1000 °C, these nickel particles are still discernible (Figure 1d). In addition, TEM pictures show that for samples which have been heated to 800 and 1000 °C, it seems that more nickel particles are implanted deep into the alumina spheres instead of sticking to the surface of the alumina sphere, compared with the as-prepared sample. Hence the surface of the alumina spheres becomes smoother after heating to high temperatures (Figure 1c,d). This appearance can be seen more clearly by comparing the similarity of Figure 1d with the image of the bare alumina spheres (Figure 2d) and may be understood in terms of the occurrence of the incorporation of the nickel into the alumina spheres at high temperatures.

In contrast to the samples coated on amorphous alumina, the TEM image shows that for samples of nickel coated on crystallized alumina, most of the nickel particles are not anchored to the alumina substrate (Figure 2a), but form a kind of aggregate in the interparticle space of the alumina spheres. After heating to 800 °C (Figure 2b), it is found that some nickel particles have grown in size and developed toward the inside of alumina spheres. Figure 2c is the image for the sample of nickel on crystallized alumina that has been heated to 1000 °C. The unadhered nickel particles in the interparticle space of alumina have grown to ∼50−100 nm in size, while the nickel particles that have adhered to alumina spheres remain an average size of ∼10−20 nm. This is very similar to the behavior of nickel coated on amorphous spheres, thus it is reasonable to divide the state of nickel into two parts: (1) the adhered nickel, which is connected tightly to alumina core and which should have a strong interaction with the alumina core; and (2) the unadhered nickel, which is concentrated in the free space among the alumina spheres and which should have a weak interaction with alumina. From the TEM results we can conclude that the coating effects are strongly dependent on the nature and structure of the substrate. The amorphous alumina possesses a great number of active sites which can react with the nickel tetracarbonyl to form a highly dispersed nickel when promoted by the promotion of sonication, while crystallized alumina can only provide a limited number of active sites for the reaction and lead most of the nickel to form unadhered nickel.

First, the influence of the interaction between the alumina substrate and the coated nickel on the crystallization behavior of nickel was checked by DSC measurements, and these DSC curves are shown in Figure 3. Figure 3a presents the DSC curve of as-prepared nickel coated on amorphous alumina, Figure 3b on crystallized alumina, and Figure 3c for bulk elemental nickel prepared by the sonication of nickel tetracarbonyl under argon.[19] The large exothermic peak between 200 and 400 °C corresponds to the crystallization of amorphous nickel, as confirmed by our previous results[19] and XRD results in the following. It was found that the crystallization peak for nickel coated on amorphous alumina appeared at 353 °C, while the sample coated on crystallized alumina appeared at 305 °C, and for pure nickel, at ∼260 °C. In the above three samples, besides the slight change of nickel particle size, the main difference is the connection extent of nickel particle to the substrate alumina. For bulk nickel sample, there is no interaction between the nickel and alumina because of the absence of substrate. So the crystallization behavior of nickel is strongly influenced by the presence of substrate and its nature. In other words, the crystallization temperature increases with the increase of interaction between nickel and alumina. The sample of nickel coated on amorphous alumina exhibits the highest crystallization temperature among the above three samples, because most of nickel exists in the form of adhered nickel.

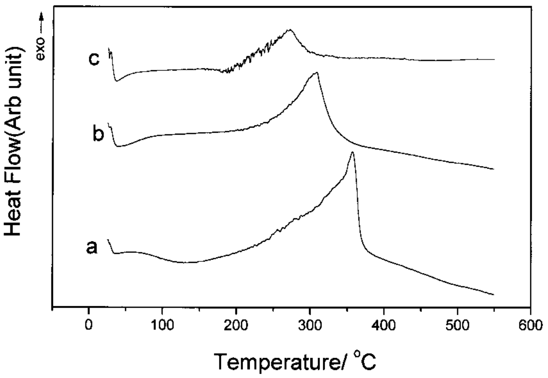

Figure 3. DSC curves of (a) as-prepared nickel coated on amorphous alumina; (b) as-prepared nickel on crystallized alumina; and (c) bulk nickel prepared by the sonication of Ni(CO)$_4$ in argon.

Figure 4 shows the XRD patterns for samples of nickel coated on amorphous alumina. The as-prepared alumina and its as-prepared sonication product possess an amorphous nature (Figure 4a). The sample heated at 400 °C under argon exhibits the feature peaks of metallic Ni (Figure 4b). After the sample is heated to 550 and 700 °C in air, the formation of NiO is observed. However, the sample heated at 800 °C develops two peaks at $2\theta = 45.1°$ and $65.8°$ (marked with an asterisk in Figure 4e), apart from the diffraction peaks of NiO, characteristic of the formation of the nickel aluminate spinel phase ($NiAl_2O_4$). The sample heated at 1000 °C (Figure 4f) exhibits only the feature peaks of $NiAl_2O_4$ (compared with the ASTM card 10-339, and the XRD pattern of bulk $NiAl_2O_4$ in Figure 4g which was prepared by the coprecipitaton method, as mentioned above), indicating the thorough diffusion of nickel into the alumina lattice. The XRD patterns for the sample of nickel coated on crystallized alumina are displayed in Figure 5. It was found that γ-Al_2O_3 was formed after bare alumina was heated to 1000 °C (Figure 5a). For all samples after coating, a weakening of γ-Al_2O_3 feature peaks is observed, which can be attributed to the covering of nickel on the surface of alumina core. For the as-prepared sample of coating (Figure 5b), a very broad and low peak centered at $2\theta = 44.6°$ is observed, indicating the formation of metallic nickel and its ultrafine nature in size, or crystallization of part of the

---

(19) Kolltypin, Y.; Katabi, G.; Cao. X.; Prozorov, R.; Gedanken, A. J. *Non-Cryst.Solids* **1996**, *201*, 159.

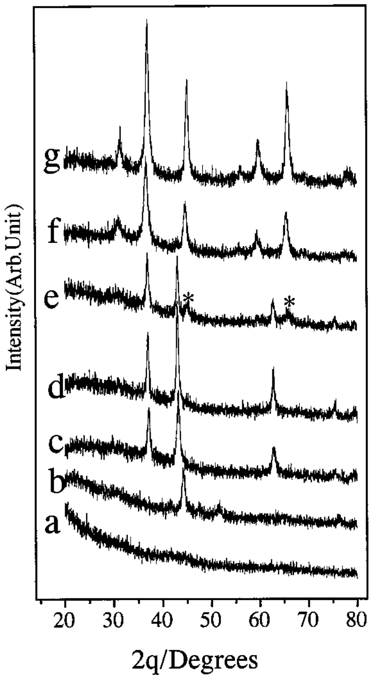

Figure 4. XRD patterns of (a) as-prepared sample of nickel coated on amorphous alumina; (b) nickel coated on amorphous alumina and heated to 400 °C under argon for 4 h; (c) nickel coated on amorphous alumina and heated to 550 °C in air for 4 h; (d) nickel coated on amorphous alumina and heated to 700 °C in air for 4 h; (e) nickel coated on amorphous alumina and heated to 800 °C in air for 4 h; (f) nickel coated on amorphous alumina and heated to 1000 °C in air for 4 h; and (g) reference sample $NiAl_2O_4$ prepared by precipitation method and heated at 1000 °C in air for 4 h.

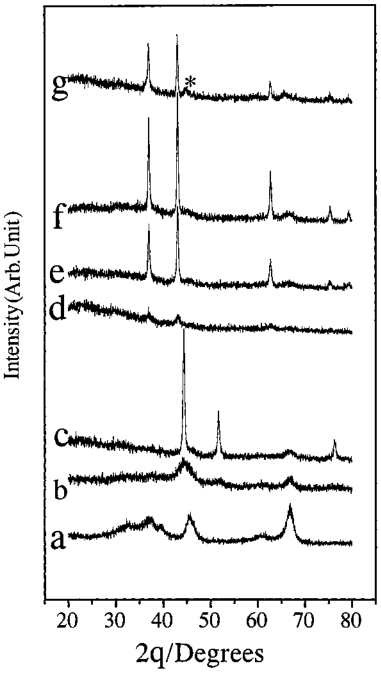

Figure 5. XRD patterns of (a) crystallized alumina heated at 1000 °C in air for 4 h; (b) as-prepared sample of nickel on crystallized alumina; (c) nickel on crystallized alumina and heated to 400 °C under argon for 4 h; (d) nickel coated on crystallized alumina and heated to 550 °C in air for 4 h; (e) nickel coated on crystallized alumina and heated to 700 °C in air for 4 h; (f) nickel coated on crystallized alumina and heated to 800 °C in air for 4 h; and (g) nickel coated on crystallized alummina and heated to 1000 °C in air gfor 4 h.

nickel. But these particles are not small enough to be amorphous to X-ray diffraction. As mentioned in TEM studies, it may be attributed to a weak interaction of nickel with alumina core, which leads the nickel particles to aggregate easily. In contrast to the samples coated on amorphous alumina, the samples coated on crystallized alumina exhibit a small feature peak of spinel phase at $2\theta = 45.1°$ only after the sample is heated to 1000 °C (Figure 5g). So the formation temperature of the spinel phase for a sample of nickel coated on crystallized alumina is much higher than that of its counterpart, coated on amorphous alumina. Obviously, as observed by TEM and discussed above, the relative easiness of the formation of spinel phase in the sample coated on amorphous alumina is owing to the strong interaction of the tightly adhered nickel with alumina.

DRS and FTIR Measurements. It was found that the color of all samples containing nickel oxide changed markedly with changes in the heating temperatures. To our knowledge, the color of nickel oxide is closely related to its electronic structure, e.g., the coordination state of Ni. In NiO, all nickel ions are octahedrally coordinated. In aluminas, except for the thermodynamically stable α-Al_2O_3, in which all Al cations are octahedrally coordinated, Al cations can occupy both tetrahedral and octahedral sites. For example, the γ-Al_2O_3 has a structure almost identical with that of a spinel, and one-third of the Al cations are missing. The Al ion vacancies render it very susceptible to cation diffusion and compound formation.[20] In the heating process, Ni ions can occupy the octahedral and tetrahedral sites in γ-Al_2O_3 to form octahedrally and tetrahedrally coordinated Ni (Ni(O) and Ni(T)). It has also been reported that in spinel $NiAl_2O_4$, the ratio Ni(O)/Ni(T) depends on the temperatures at which it is prepared.[21,22] Hence it is expected that DRS study can directly provide information about the interaction between nickel and the substrate alumina.

DRS spectra for nickel oxide coated on amorphous and crystallized alumina are shown in Figures 6 and 7, respectively. According to the literature,[23] the Ni(O) exhibits three absorbance bands at ~715, 377, and/or 410 nm, while Ni(T) has absorbance bands at ~645 nm. From Figure 6f, it is seen there are two intense peaks at 600 and 640 nm for the prepared reference sample of $NiAl_2O_4$, indicating the formation of the spinel structure, as observed by XRD experiments (Figure 4g). For samples with amorphous alumina as support, it was found that after heating to 400 °C in argon (Figure 6a), there is a very small broad peak centered ~720 nm, revealing the existence of traces of NiO. This small peak can be seen more clearly in Figure 7a for as-prepared samples of nickel coated on crystallized alumina. After the sample is heated to 550 °C in air, a small but somewhat higher peak centered at ~710 nm is resolved, suggesting the oxidation of more elemental nickel. This

---

(20) Pott, G. T.; Stork, W. H. J. *Preparation of Catalysts*; Delmon, B., Jacobs, P. A., Poncelet, G., Eds.; Elsevier: Amsterdam, 1976; p 537.

(21) Schmalzried, H. *Z. Phys. Chem.* **1961**, *28*, 203.

(22) Reinen, D. *In structure and Bonding*; Hemmerich, P., Jorgensen, K. C. K., Neilands, J. B., Nyholm, R. S., Reinen, D., Williams, R, J. P., Eds.; Springer: Berlin, 1970; Vol. 7.

(23) Scheffer. B.; Heijeinga. J. J.; Moulijn, J. A. *J. Phys. Chem.* **1987**, *91*, 4752.

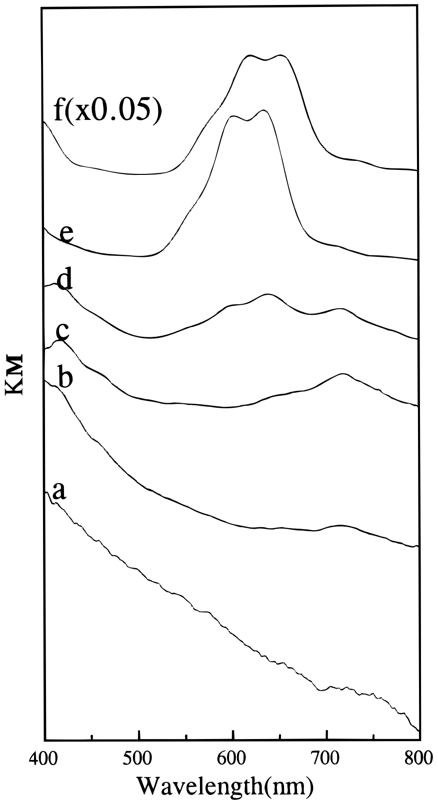

Figure 6. DRS spectra (KM remission function) of (a) nickel coated on amorphous alumina and heated at 400 °C in argon for 4 h; (b) nickel coated on amorphous alumina and heated at 550 °C in air for 4 h; (c) nickel coated on amorphous alumina and heated at 700 °C in air for 4 h; (d) nickel coated on amorphous alumina and heated at 800 °C in air for 4 h; (e) nickel coated on amorphous alumina and heated at 1000 °C in air for 4 h; and (f) reference sample of $NiAl_2O_4$ heated at 1000 °C in air for 4 h.

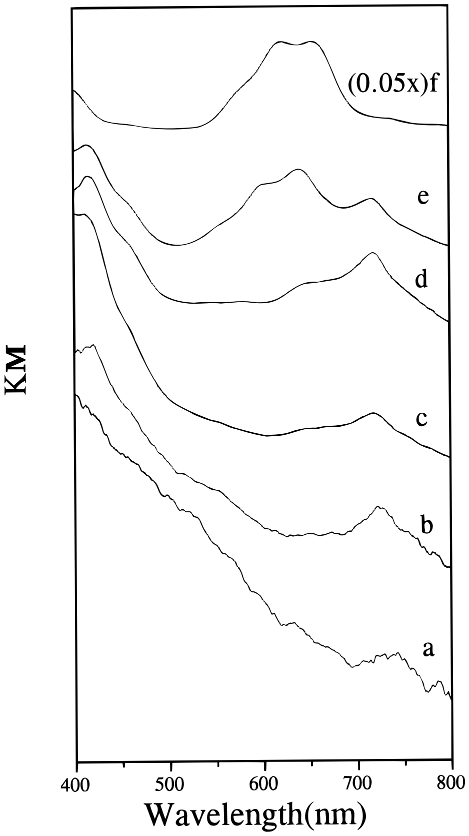

Figure 7. DRS spectra(KM remission function) of (a) nickel coated on crytallized alumina and heated at 400 °C in argon for 4 h; (b) nickel coated on crystallized alumina and heated at 550 °C in air for 4 h; (c) nickel coated on crystallized alumina and heated at 700 °C in air for 4 h; (d) nickel coated on crystallized alumina and heated at 800 °C in air for 4 h; (e) nickel coated on crystallized alumina and heated at 1000 °C in air for 4 h; and (f) reference sample of $NiAl_2O_4$ prepared by precipitation method.

is also confirmed by the above XRD results (Figure 4c). The peak intensity at 710 nm increases with the heating temperature, but as the temperature exceeds 700 °C, a decrease in its intensity is observed, which coincides with the formation of the spinel phase at this temperature, as confirmed by XRD (Figure 4e). Obviously, the depletion of NiO, after the sample is heated to 700 °C, is mainly due to the diffusion of nickel into the alumina and the further formation of the spinel phase.

The sample heated at 700 °C begins to develop a small broad peak at ~650 nm, besides the peak at 710 nm (Figure 6c). As mentioned above, the peak at 650 nm can be ascribed to the absorbance of Ni(T). But the XRD (Figure 4d) pattern did not show any feature diffraction peaks of the spinel phase $NiAl_2O_4$ for this sample, so the diffusion of Ni^{2+} is only limited into the tetrahedral vacancies in alumina at this temperature. After the above sample is heated to 800 °C, two peaks in the middle of spectrum, featuring the formation of $NiAl_2O_4$, are observed (Figure 6d). For the sample heated at 1000 °C (Figure 6e), only the feature peaks of the spinel phase are observed, indicating that NiO has completely diffused into the alumina matrix to form the spinel phase. According to the literature,[24,25] the peak near 590 nm is assigned to the absorbance of Ni^{2+} in octahedral symmetry. Combining this with the XRD results, it is easy to deduce that the absorbance at ~590 nm only relates to the Ni ions with octahedral symmetry in the spinel structure. So the diffusion of Ni^{2+} into the alumina lattice occurs at a relatively low temperature, but the formation of the spinel phase requires a higher temperature. Scheffer et al.[23] also reported that the diffusion of Ni^{2+} started at about 500 °C for the Ni/Al_2O_3 system, and Linder et al.[26,27] reported that the formation of $NiAl_2O_4$ is a slower process than the diffusion of Ni^{2+} in Al_2O_3. That the formation of Ni(T) and Ni(O) in alumina is not synchronous will be further discussed below.

For samples coated on crystallized alumina, a similar result is obtained, except that the feature peak of the spinel phase is observed only after heating at 1000 °C (Figure 7e). We also found that there is a shift for the position of double feature peaks in the range of 500−650 nm for coated samples compared to that of the reference $NiAl_2O_4$, which may be related to the difference in ratio of Ni(O)/Ni(T) in the two types of samples.

The IR absorbances below 1000 cm^{-1} usually reflect the vibration of the M−O bond (here M represents a

---

(24) Jacono, M. L.; Schiavello, M.; Cimino, A. *J. Phys. Chem.* **1971**, *75* (8), 1044.

(25) Mont. D. S. D.; Lule, A.; Reinen, D.; Bunsenges, B. *Phys. Cem.* **1965**, *69*, 76.

(26) Linder, R.; Akerstrom, A. *Z. Phys. Chem (Munich)* **1958**, *18*, 303.

(27) Pettit, F. S.; Randklev, F. E.; Felten, E. J. *J. Am. Ceram. Soc.* **1966**, *49*, 199.

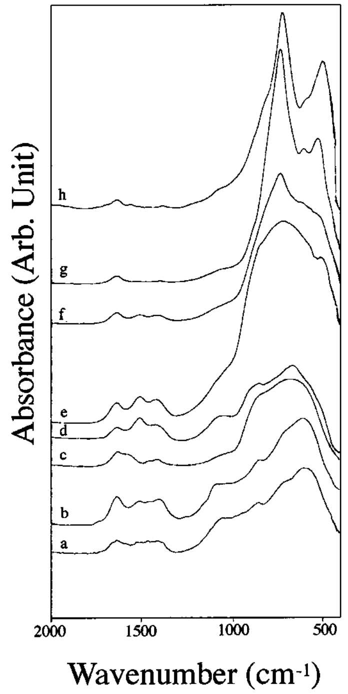

Figure 8. Infrared spectra of (a) as-prepared amorphous alumina; (b) as-prepared sample of nickel coated on amorphous alumina; (c) nickel coated on amorphous alumina and heated to 400 °C in air for 4 h; (d) nickel coated on amorphous alumina and heated to 550 °C in air for 4 h; (e) nickel coated on amorphous alumina and heated to 700 °C in air for 4 h; (f) nickel coated on amorphous alumina and heated to 800 °C in air for 4 h; (g) nickel coated on amorphous alumina and heated to 1000 °C in air for 4 h; and (h) reference sample of $NiAl_2O_4$ prepared by precipitation method.

metallic element). It is expected that the IR spectra can provide deep insight into the interaction between the nickel oxide and the alumina, as well as the structure evolution in the heating process. The spectra for nickel coated on the amorphous and the crystallized alumina are shown in Figures 8 and 9, respectively, and the peak positions are listed in Table 2. For the convenience of analyses, the IR spectra of amorphous and crystallized alumina, self-prepared $NiAl_2O_4$, and NiO are also listed.

It is seen from Figure 8a, that amorphous alumina possesses three peaks centered at ~608, 729, and 857 cm^{-1}. As reviewed by Morterra,[28] the absorbance at 608 cm^{-1} can be assigned to the stretching vibration mode of Al−O for the octahedrally coordinated Al ions, while the peak at 729 cm^{-1} can be attributed to the Al−O vibration mode for tetrahedrally coordinated Al ions, and the peak near 857 cm^{-1} to the Al−O vibrational mode localized in the surface layer, and most likely involving deformation of surface OH groups. It is found that after coating (Figure 8b), the above three absorbance peaks have not been perturbed markedly, indicating that no very extensive interaction between the nickel and the substrate occurred at this stage or the interaction was limited only to a small number of active sites. However, after heating the sample to above 400 °C, we can observe a series of changes in intensity and position in IR spectra. First, the surface Al−O vibration peak near 850 cm^{-1} disappears after the sample is heated to 800 °C (Figure 8f), and second, the absorbance intensity of the Al−O vibrational mode for octahedrally coordinated Al ions decreases with an increase of heat-treatment temperature. Meanwhile, the relative intensity of Al−O vibration for tetrahedrally coordinated Al ions increases dramatically with an increase of heating temperature. After the sample is heated at 1000 °C, a very sharp absorbance peak at 735 cm^{-1} for tetrahe-

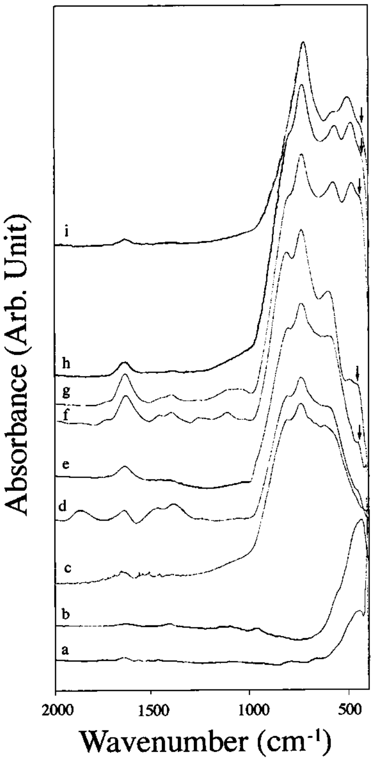

Figure 9. Infrared spectra of (a) bulk nickel heated at 500 °C in air for 2 h; (b) commercial NiO(Aldrich); (c) crystallized alumina heated at 1000 °C for 4 h; (d) as-prepared sample of nickel coated on crystallized alumina; (e) nickel coated on crystallized alumina and heated to 400 °C in air for 4 h; (f) nickel coated on crystallized alumina and heated to 550 °C in air for 4 h; (g) nickel coated on crystallized alumina and heated to 700 °C in air for 4 h; (h) nickel coated on crystallized alumina and heated to 800 °C in air for 4 h; (i) nickel coated on crystallized alumina and heated to 1000 °C in air for 4 h. The peak at ~474 cm^{-1}, an indication of bulk Ni−O, has been marked with an asterisk.

Table 2. Positions of Absorption in IR Spectra below 1000 cm^{-1}

heating temp (°C)	positions of absorption[a] (cm^{-1})				
Al_2O_3[b]	857	729	608		
no-heating	870	733	614		
400	850	688			
550	850	667			
700	853	715		514	
800		735	614	527	
1000		735	601	527	
$NiAl_2O_4$ (R)[c]		735	608	520	
NiO[d]					460
NiO[e]					450
Al_2O_3[f]	816	749	635		
no-heating	816	749	635		
400	816	749	601		467
550	829	749	608	500	474
700	823	749	588	494	474
800	829	742	588	507	474
1000		735	588	520	474

[a] Coated on amorphous alumina. [b] Bulk Ni prepared by sonication and heated at 500 °C in air. [c] Crystallized alumina. [d] Commercial NiO. [e] $NiAl_2O_4$ prepared by precipitation method.

---

(28) Morterra, C.; Magnacca, G. *Catal. Today* **1996**, *7*, 497.

drally coordinated Al−O is observed (Figure 8g). It is known that Al ions prefer to occupy octahedral sites after high-temperature treatments. For example, α-Al_2O_3 is the most thermodynamically stable form of alumina and in which Al ions possess an octahedral coordination. In our previous IR study[29] for iron coated on alumina, we also observed the gradual depletion of tetrahedrally coordinated Al ions and the formation of more and more octahedrally coordinated Al^{3+} ions at higher temperatures. As reported in the literature,[23] the Ni^{2+} favors occupation of the octahedrally coordinated sites. So in the process of heat-treatment, a substitution of Ni ions for Al at octahedral sites has taken place and is confirmed by our IR study.

The mixed spinel-structured oxides, $M^{II}Al_2O_4$, have three forms of spinel structure, namely the normal spinel structure, in which the M^{II} ions occupy the tetrahedrally coordinated sites, the inverse spinel structure, in which the M ions occupy octahedral sites, and the third, disordered spinel, which can be regarded as a partially inverted spinel. The three types of spinels can be designated as $M^{II}[Al_2]O_4$, $Al[M^{II}Al]O_4$, and $M^{II}_{1-x}Al_x[M^{II}_xAl_{2-x}]O_4$, respectively, where the square brackets enclose the ions which occupy octahedral sites.

γ-Al_2O_3 has a spinel structure, and its vacancies are mainly distributed over the tetrahedral sites.[3,24] (In this work, the crystallized alumina has a structure of γ-Al_2O_3. Its precursor—amorphous alumina should possess a close coordination state for Al ions, so we use γ-Al_2O_3 as a model structure in this discussion.) The formation of Ni(T) in the γ-Al_2O_3 lattice can be represented by the diffusion of Ni^{2+} ions:

$$Ni^{2+} + 3Al_{2/3}\square_{1/3}[Al_2]O_4 \rightarrow 3Al_{2/3}Ni_{1/3}[Al_2]O_4$$

As represented in the following, the formation of Ni(O) in the alumina lattice can be considered as an inversion process of the Ni(T):

$$3Al_{2/3}Ni^{II}_{1/3}[Al_2]O_4 \rightarrow 3Al[Ni_{1/3}Al_{5/3}]O_4$$

So the formation of Ni(O) in the alumina lattice needs a net exchange of an Al^{3+} from an octahedral position to a tetrahedral position, and it is expected to need a much higher activation energy than is needed for the formation of Ni(T). In other words, the formation of the disordered $NiAl_2O_4$ needs heating to a higher temperature. As revealed by XRD and DRS results, we only observed the formation of spinel phase $NiAl_2O_4$ for nickel coated on the amorphous alumina after the sample is heated to 800 °C; IR results also confirmed the occurrence of the above inversion process.

The IR spectra for nickel coated on crystallized alumina are shown in Figure 9. It can be seen that the alumina heated at 1000 °C shows three absorbance peaks at 635, 749, and 816 cm^{-1}, indicating the presence of octahedrally and tetrahedrally coordinated Al ions and surface Al−O groups. This is in good agreement with its γ-Al_2O_3 structure, as confirmed by XRD study (Figure 5a). Before heating to 550 °C, almost no change is observed for the above three peaks, revealing that the interaction between nickel and alumina is not extensively or mainly related to some surface hydroxyl groups at this stage, as will be discussed below. For samples heated to 1000 °C, an increase in absorbance intensity of the Al−O bond vibration for tetrahedrally coordinated Al ions and a weakening for that of octahedrally coordinated Al ions are also observed, similar to that of samples for nickel coated on amorphous alumina.

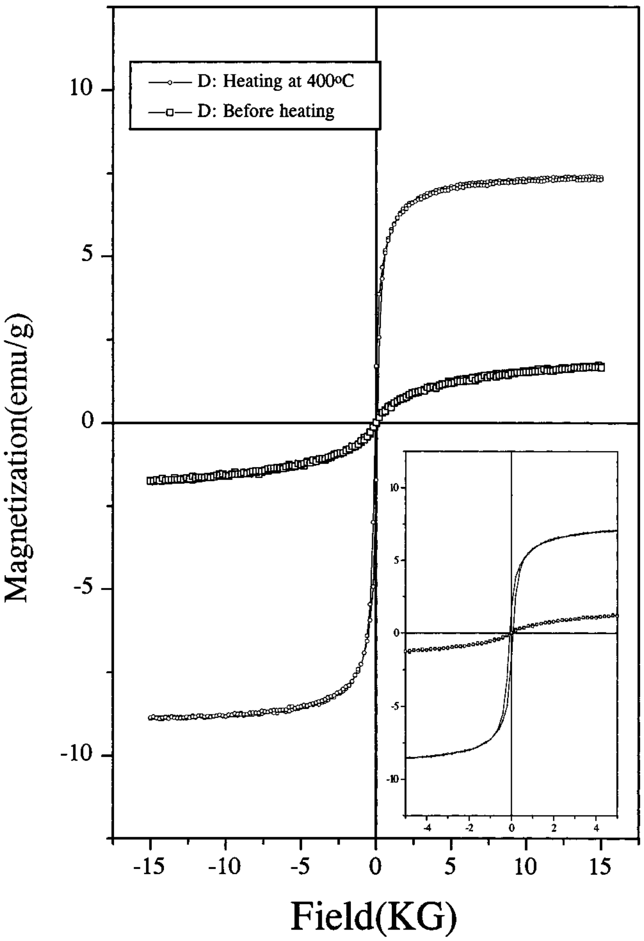

Figure 10. Magnetic curves of samples coated on amorphous alumina: (□) as-prepared sample and (○) heated at 400 °C under argon. Inset in the figure shows the M−H behavior in the lower magnetic field range.

Figures 10 and 11 show the results of magnetization measurements for samples of nickel coated on the amorphous and crystallized alumina before and after heating at 400 °C in argon. The magnetization is only relative to the unit mass of composite materials. It is seen from the magnetization curves that the heated samples exhibit a narrow hysteresis loop and always show a higher magnetization at a given magnetic field than their corresponding as-prepared samples. As discussed above, this can be understood in terms of the crystalline nature and growth of particle size after heating. On the other hand, it also reflects the ultrafine nature for nickel particles in as-prepared sonication products. This is in agreement with the above DSC results, which showed that nickel was crystallized below 400 °C.

It is known that NiO is an antiferromagnetic material, whereas elemental nickel is a ferromagnetic material. The exhibition of medium magnetization for the as-prepared samples coated on the two types of alumina

---

(29) Zhong, Z. Y.; Prozorov, T.; Zhao, M. Y.; Felner, I.; Gedanken, A. *J. Phys. Chem. B* **1999**, *103*, 944.

(30) Hucul, D. A.; Brener, A. *J. Phys. Chem.* **1981**, *85*, 496.

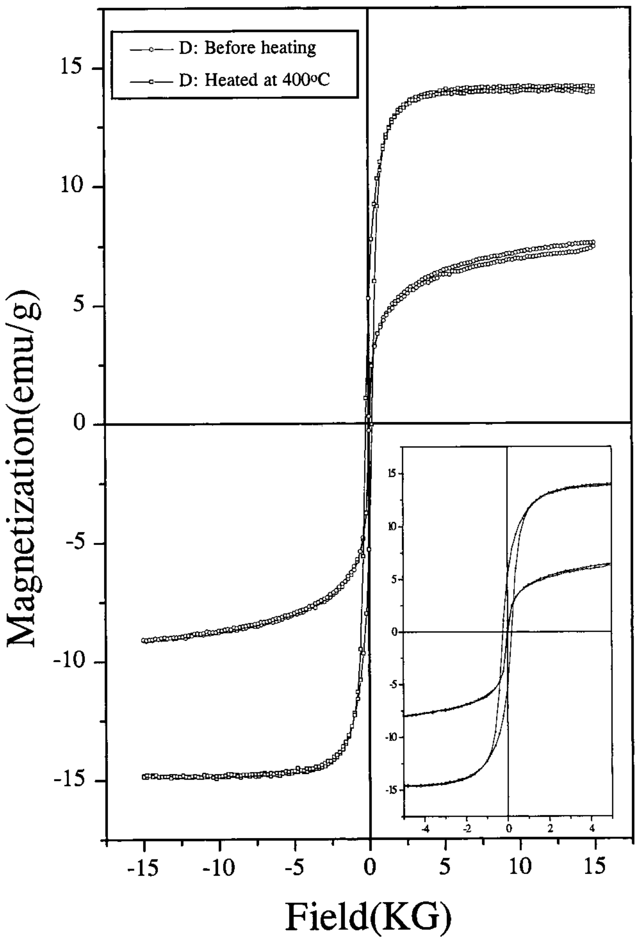

Figure 11. Magnetic curves of samples coated on crystallized alumina: (○) as-prepared sample and (□) heated at 400 °C under argon. Inset in the figure shows the M−H behavior in the lower magnetic field range.

suggests that most of nickel exists in the form of elemental nickel, not in the form of oxide. The above XRD results also show a broad peak centered at approximately $2\theta = 44.6°$ (Figure 4b and 5b), which is characteristic of the elemental nature of the sample heated at 400 °C in argon.

However, we indeed observe the presence of trace nickel oxide in DRS spectra (Figure 6a,b) for samples heated at 400 °C in argon. Brenner et al.[30] once carried out an investigation on the reaction between Al_2O_3 surface hydroxyls and zerovalent transition metals formed by the thermal decomposition of various adsorbed metal carbonyls. They suggested that the reaction can be described by the following equation:

$$M(CO)_j + n(\sigma\text{-OH}) \rightarrow (\sigma\text{-O-})_n M^{n+} + (n/2)H_2 + jCO$$

This means that the interaction between the transition metal elements and the Al_2O_3 substrate is through the hydroxyl groups on the surface. Our previous studies[29] have shown that the OH groups on the alumina surface reacted with iron pentacarbonyl to form iron oxide, a process promoted by sonication. In this work, the different coating effects for nickel on the amorphous and crystallized alumina also demonstrate that the hydroxyl groups on the alumina surface have taken part in the reaction with nickel. So, with respect to nickel coated on alumina, it is most probable that the nickel first reacted with surface hydroxyl groups to form a kind of interlayer bond Ni−O−Al and that then the connection position further became a nucleation center for elemental nickel. The existence of trace nickel oxide may be mainly located at the interlayer between the nickel and the alumina substrate. (We cannot completely rule out the possibility that part of the nickel oxide may be formed on the surface of coated nickel particles in the sample-handling process, due to their sensitivity to air.)

Conclusions

In this work, the samples of nickel coated on amorphous and crystallized alumina have been prepared by the sonochemical method. The sonication products before and after heat treatment at different temperatures are characterized by TEM, XRD, DSC, DRS, FTIR, and magnetization measurements. It is found that the coating effect is influenced markedly by the properties of the substrates. The amorphous alumina, which possesses a great number of isolated hydroxyl groups on the surface, can connect to the nickel tightly with the promotion of sonication, while the crystallized alumina cannot provide enough reaction sites to cause the nickel to adhere. Therefore, we can reasonably divide the state of the coated nickel into two parts: (1) the adhered nickel, which is connected to alumina core tightly and has a strong interaction with the alumina core; and (2) the unadhered nickel, which is concentrated in the free space among the alumina spheres and has a weak interaction with alumina. The strong interaction between the adhered nickel and alumina core can retard the crystallization of elemental nickel and, conversely, promote the formation of the spinel phase $NiAl_2O_4$. For nickel coated on amorphous alumina, DSC and XRD results showed that the nickel was crystallized at 353 °C, and the spinel phase $NiAl_2O_4$ was observed after the sample is heated to 800 °C, while for nickel coated on crystallized alumina, the corresponding temperatures are 305 and 1000 °C, respectively.

The coating and interaction between nickel and its oxide and alumina may occur first through the isolated hydroxyl groups to form interface bond Ni−O−Al, and then the connection positions further become a nucleation center for elemental nickel. After heat-treatment, the Ni^{2+} diffuses into the vacant tetrahedral sites. At higher temperatures, an inversion process—the substitution of Ni^{2+} ions for part of Al^{3+} at octahedral sites—occurs. Apart from the XRD patterns, the DRS spectra and FTIR can be used as a tool to monitor the evolution of the above process. Magnetization measurements show that the as-prepared sonication products are superparamagnetic, due to the ultrafine nature of nickel particles.

Acknowledgment. A. Gedanken thanks the Ministry of Science and Technology for supporting this research through a grant for infrastructure. Dr. Ziyi Zhong thanks the Kort Scholarship Foundation for supporting his postdoctoral fellowship. The authors thank Professor M. Deutsch, Department of Physics, for extending the XRD facility, and Dr. Shifra Hochberg for editorial assistance. The support of the NEDO International Joint Research Grant and that of the German Ministry of Science through the Deutche−Israeli program DIP is also acknowledged.

CM981005M