Self-Assembled Monolayer Coatings on Amorphous Iron and Iron Oxide Nanoparticles: Thermal Stability and Chemical Reactivity Studies

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Received September 23, 1996. In Final Form: July 3, 1997

Self-assembled coatings of long chain thiols on nanoparticles of amorphous iron as well as on amorphous Fe3O4 were formed. The thermal stability of these coatings was investigated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the particles and by mass spectrometric analysis of the molecules desorbed from the surface by heating the amorphous substrates. The results showed a sharp weight loss centered at about 200 °C for the thiol-coated particles. The mass spectrometric study of the molecules removed from the surface of the amorphous iron revealed the formation of a dialkyl thioether. For the amorphous Fe3O4 surfaces, a dialkyl disulfide was removed from the surface. The desorptions from the Fe3O4 surface occurred at higher temperatures than those for the amorphous iron. The different mechanisms responsible for these desorption reactions are discussed.

Introduction

The adsorption of alkanethiol molecules on metallic surfaces has been extensively studied in the past few years. Various experimental techniques have been applied in attempting to elucidate the nature of the metal–sulfur bonding. The adsorption of short alkanethiols having an appreciable vapor pressure could be carried out under UHV conditions, while for the long chain alkanethiols the metallic surface is immersed in a dilute solution of the thiol. The building of self-assembled monolayers was the focus of the investigation in both cases.

Temperature-programmed desorption (TPD) has been employed in various studies of thiol adsorption, and it has provided kinetic as well as thermodynamic data as to the nature of the metal–sulfur interactions. Nuzzo and co-workers have deposited methanethiol and dimethyl disulfide on Au(111) surfaces at various temperatures under UHV conditions. Their high-resolution electron energy loss spectrum showed the presence of the S–H stretching vibration at 2430 cm−1, suggesting that the adsorption of methanethiol does not involve the cleavage of the S–H bond. The TPD measurements for the methanethiol showed three desorption peaks at ~150, ~83, and ~45 °C. The first peak is associated with the desorption of multilayers which were formed on the surface. The binding energies of the two other peaks at ~83 and ~45 °C are 11.6 and 13.9 kcal/mol, respectively. These values reflect relatively modest heats of adsorption. The desorption in all cases is molecular, and there is no evidence for a chemisorbed thiolate in the methanethiol experiment.

Jaffey and Madix studied the adsorption and desorption of 1,1-dimethylethanol on Au(110) surfaces. The Au(110) induces an S–H bond cleavage in adsorbed 1,1-dimethylethanol. The tetbutyl thiolatethus formed is stable to about 400 K and decomposes to evolve isobutene, 1,1-dimethylethanol, and H2S. The TPD showed a huge desorption peak of the parent molecule at 160 K, which was attributed, as in Nuzzo’s case, to multilayer desorption.

In a similar study ethanethiol was adsorbed onto Au(110) and Ag(110) surfaces. Upon heating, the adsorbate decomposed to H2, H2S, C2H4, and C2H6 on both surfaces, while ethyl disulfide was detected from the Au surface.

Schlenoff and co-workers have incorporated an alkanethiol bearing a radioactive 35S isotope into self-assembled monolayer coatings on various substrates. Unlike the above-mentioned studies, which employed gas phase adsorption, Schlenoff’s coatings were done in solution. The clean surfaces of different metals were soaked in a 1 mM solution of the labeled octadecanethiol in hexane for 5 h. Desorption and thermal stability studies were among the many probes employed in their work. Water was found to be the best solvent for the octadecanethiol deposition, and THF the worst. When the various metals were compared, monolayers were least stable on copper and most stable on silver. Self-exchange and desorption experiments at room temperature demonstrated the presence of residual thiols at the surface which could not be exchanged and which were presumed to result from stronger binding at defect sites. Thermal stability measurements were carried out on a gold surface. They showed a complete loss of surface sulfur at 210 °C.
In a recent study by Nishida and co-workers on the desorption of an alkanethiol from a Au(111) surface by TPD, a dialkyl disulfide molecule was detected. From the desorption kinetics they calculated the desorption activation energy to be 32 kcal/mol. This result suggests that a chemically activated dimerization process is occurring on the gold surface.

Unlike silver and gold, iron has not been a widely used substrate for thiol monolayer adsorption. Bernasek and co-workers carried out a comprehensive study on the interaction of alkanethiols with Fe(100) surfaces. They found that when adsorbed on the iron surface at 100 K, ethanethiol undergoes an S-H bond cleavage, forming a surface ethanethiolate (SC\(_2\)H\(_5\)). Full coverage of the iron surface by a thiol monolayer was observed at an exposure to 0.5 langmuir of ethanethiol. The formation of multilayers was observed at longer exposures of the surface to the ethanethiol, and a TPD desorption peak of the parent molecule (m/\(e\) 62) was seen at 136 K. At higher temperatures the dissociation of the ethanethiol is detected and a detailed mechanism is offered for the observed desorption pattern. In the course of the TPD experiment, the ethanethiol is completely decomposed. An Auger spectrum revealed sulfur atoms on the iron surface not at a trace of organic fragments.

Cheng et al. have also studied the effect of the hydrocarbon chain length on the thermal stability of alkanethiols on the iron surface. The experiments which included C1, C2, C4, C6, and C10 thiols resulted in the same decomposition temperature for all the thiols except the C1 thiol, methanethiol, which showed a much higher decomposition temperature. This is very different from what has been detected for gold surfaces.

The study of the longer alkyl chain thiols was later extended, and measurements such as Auger electron spectroscopy (AES), LEED, and HREELS were added as well. This work demonstrated that even longer chain alkanethiols are dissociatively adsorbed on iron at 100 K (S-H cleavage). Saturation coverage corresponds to 0.5 monolayer. Higher exposures lead to the formation of multilayers. The removal of the multilayers of butanethiol, hexanethiol, and decanethiol from the iron surface appears at 150, 140, and 175 K, respectively. Alkenes were found as a major thermal decomposition product, via C-S bond cleavage and \(\beta\)-hydrogen elimination. Due to the strong interaction between the substrate and the alkanethiol, as well as the \(\beta\)-elimination process, longer hydrocarbon chains do not enhance the stability of the alkanethiol on the iron surface, unlike what has been proposed for gold.

In another study by the same group, ethanethiol was coadsorbed with sulfur, oxygen, and water on an Fe(100) surface. Preadsorbed sulfur, and to a lesser extent oxygen, showed a site-blocking effect for the ethanethiol adsorption.

In a very detailed study, the bond formation between iron and decanethiol has been probed by surface-sensitive techniques such as XPS and AES as well as cyclic voltammetry. Chemisorption bonds between the iron and the thiol could be formed by cleavage of the S-H bond only if the metal surface is free of any oxide layer.

In other recent reports, Stratmann has formed Langmuir-Blodgett films of X\(_2\)SiC\(_2\)H\(_{2n+1}\) (X = Cl and n = 16, 18) on water and transferred the film to metal substrates like Cr, Fe, and Ni. Coverage of the metals was assayed by using SEM and scanning Auger microscopy. Angle dependent XPS investigations suggested a perpendicular orientation of the silane molecules with respect to the metal surface.

The weak bonding between iron oxide and a hydroxamic acid functional group has been studied by Folkers et al. According to their listing, the order of the affinity for iron oxide is RCONHOH > RPO\(_2\)H\(_2\) > ROOH.

Finally, Liu and Xu have demonstrated that when a bolamphiphile, 16-mercaptohexadecanoic acid, is deposited on nanosized particles of \(\gamma\)-Fe\(_2\)O\(_3\), it anchors through the bonding to the carboxylate head group, leaving the thiol chromophore reactive. This is an unexpected result, since the carboxylic acid head group is the weakest bonding group to iron oxide, according to the above-mentioned list.

### Design of Current Study

Suslick and co-workers have demonstrated that sonication of Fe(CO)\(_5\) as a neat liquid or as a solution in decane or decalin yields a powder which was identified as amorphous iron particles having nanometer-sized diameter. The size of these nanoparticles can be controlled by varying the concentration of the Fe(CO)\(_5\) in the decal solvent. Amorphous cobalt and amorphous nickel were also prepared by a similar method from Co(CO)\(_5\)NO and Ni(CO)\(_5\), respectively. When the Fe(CO)\(_5\) solution is ultrasonically irradiated in air, amorphous Fe\(_2\)O\(_3\) nanoparticles are obtained. The amorphous Fe nanoparticles, and later the Fe\(_2\)O\(_3\) ones, were subjected to self-assembled monolayer coatings by surfactants such as octadecyltrichlorosilane (OTS), sodium dodecyl sulfate (SDS), and long chain alkanethiols. In this report we will present the results of thermal stability studies based on TGA (thermogravimetric analysis) and DSC (differential scanning calorimetry) measurements, as well as the mass-resolved analysis of the thiol-coated amorphous Fe and amorphous Fe\(_2\)O\(_3\) nanoparticles. The different bonding interactions of the thiol to the two surfaces is manifested in the products of the thermal desorption. While the amorphous Fe releases a dialkyl thioether (R\(_2\)S) from its surface, a dialkyl disulfide (R\(_2\)S\(_2\)) is the main product of the thermolysis at the amorphous Fe\(_2\)O\(_3\) surface.

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**Experimental Section**

A 1 M solution of Fe(CO)$_3$ (Aldrich) in decalin (Aldrich, dried over 4 Å size molecular sieves) is sonicated (Sonics and Materials, VC-600, Ti horn, 20 kHz, 100 W cm$^{-2}$) under argon for 3 h. The powder obtained is centrifuged, washed five times with dry pentane, and dried in vacuum for 2 h. The coating process is performed on iron that has been accumulated from 2–3 sonication cycles, and the total amount of iron is divided into samples of equal weight. The samples are exposed to different concentrations of the alkanethiol solution. Heptanethiol (Aldrich), dodecanethiol, decanethiol (Aldrich), and octadecanethiol (Aldrich) were used without further purification. The mixture of the iron and the alkanethiol solution is stirred for 30 min in an ultrasonic bath and then is further shaken for 22 h. The coated particles are centrifuged, washed repeatedly in ethanol (8–10 times) in a glovebox, and dried in vacuum for 2 h. A similar process is repeated for the Fe$_2$O$_3$ particles, the difference being that the coating process is identical to that of the iron, except that, as was the case for particle formation, coating of the iron oxide is carried out in air, while the iron is coated in a glovebox.

The TGA analysis is done using a Mettler TG-50, and the DSC measurements are carried out on a Mettler DSC-30 (Mettler TC11 TA processor). Mass spectrometer measurements are carried out on a VG Instrument (Autospec CI).

The XPS analysis was performed on a Kratos Analytical AXIS-HS instrument using a monochromatized Al Kα source ($h\nu = 1486$ eV). Charging during the measurement was neutralized by an e-gun, and final calibration of the energy scale was done using the C(1s) line.

**Results**

A. Amorphous Iron Coated by Alkanethiol. The TGA and DSC spectra of amorphous iron coated with octadecanethiol are presented in Figures 1 and 2, respectively. Almost the same curves are obtained for dodecanethiol, decanethiol, and heptanethiol. The DSC spectrum of the amorphous iron coated with octadecanethiol reveals a sharp endothermic peak at 60 °C. The mass spectrum of the coated particles heated to 100 °C showed a peak at 286 amu which corresponds to the octadecanethiol mass. At higher temperatures DSC reveals an exothermic peak at 330 °C. The main features of the DSC spectrum are presented in Table 1 and compared with the main peaks observed for the coated Fe$_2$O$_3$ particles.

The TGA shows its first sharp drop in the weight of the coated particles at about 200 °C. At almost the same temperature a corresponding peak is observed in the DSC spectrum. The TGA shows that the coated particles continue to lose weight in the 300–800 °C range but with a less steep slope.

To determine the nature of the desorbing molecules, a sample of octadecanethiol-coated iron particles was placed at the inlet of an analytical mass spectrometer, and the sample was heated to 240 °C. This procedure was repeated for all four thiols with comparable results. The results for the octadecanethiol are presented in Figure 3. A relatively large peak is observed at 539 amu, followed by those of some other fragmentation species such as the largest peak at 253 amu corresponding to an octadecyl fragment. The peak at 539 is the protonated form of a CH$_3$-(CH$_2$)$_7$S-(CH$_2$)$_7$CH$_3$ (538 amu) species, evaporated from the surface area of the amorphous iron, suggesting that the cleavage of a C–S bond occurs at the surface upon heating.

An XRD (X-ray diffraction) spectrum of the coated sample heated to 240 °C in vacuum did not show any diffraction pattern, indicating that the removal of the coating and the chemical reaction that took place for the formation of the R–S species have not altered the organization of the iron atoms. We have also examined by elemental analysis measurements the carbon and sulfur content before and after the heating. The measured C/S molar ratio before the heating treatment is much higher, for all the four thiols used in our experiments, than the theoretical value. This is accounted for as originating from the 3–4% of carbon atoms that can be found on the amorphous iron or amorphous iron oxide at the end of the sonication process. It was however found that the C/S ratio is reduced after the heating of the particles to 240 °C. The reduction in the C/S ratio after the heating varied from a factor of 2 for heptanethiol to 4.5 in the case of octadecanethiol. This finding is in accordance with mass spectrometric results, indicating that the loss of sulfur also involves the loss of the long hydrocarbon chains. Assuming that the heating is not rupturing a C–S bond, the change (decrease) in the C/S molar ratio before and after the heating could be related to the evaporation of dialkyl sulfide, which depletes the surface of carbon atoms, while leaving S-containing material on the surface.

We have recently reported the FTIR, Mössbauer, and XANES spectra of the octadecanethiol-coated iron particles. These data provide further support for the existence of chemical bonding between the thiol and the amorphous iron; coatingsolution contained a 12:1 iron–thiol molar ratio. The heating rate is 10 °C/min. The carrier gas is 99.999% N$_2$.

### Table 1. Comparison between the Main Features of the DSC Spectra of Fe and Fe$_2$O$_3$ Coated with Octadecanethiol

<table>
<thead>
<tr>
<th>Compound</th>
<th>Endothermic Peak (°C)</th>
<th>Exothermic Peak (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>57</td>
<td>313</td>
</tr>
</tbody>
</table>

Figure 1. TGA spectrum of octadecanethiol-coated amorphous iron particles; coating solution contained a 12:1 iron–thiol molar ratio. The heating rate is 10 °C/min. The carrier gas is 99.999% N$_2$.

Figure 2. DSC spectrum of octadecanethiol-coated amorphous iron particles; coating solution contained a 12:1 iron–thiol molar ratio. The heating rate is 10 °C/min. The carrier gas is 99.999% N$_2$.
iron substrate. For the 2850 and 2920 cm\(^{-1}\) CH\(_2\) stretching bands, the exact position of the peak and the half-width are indicative of the degree of order of the coating.\(^{34,35}\) The width of the 2920 cm\(^{-1}\) band suggested a less ordered coating than the corresponding OTS and SDS coatings on amorphous iron.\(^9\) A 7.5 cm\(^{-1}\) shift to lower frequency was detected for the 2920 cm\(^{-1}\) peak when compared with its frequency in a CCl\(_4\) solution (2927.5 cm\(^{-1}\)).

A slight drop in weight is also observed in the TGA at around the crystallization temperature (320 °C). We could not identify the desorbed compound by mass spectrometric measurements, due to the small amount of material coming off the surface and the lack of sensitivity in the mass spectrometer. However, it is reasonable that the changes that the iron undergoes upon crystallization would reduce its surface area and cause a reduction in the number of alkanethiol molecules which remain on the surface at 320 °C. For the same reasons we could not characterize the species evaporated from the surface area in the temperature range 400–800 °C. We do, however, relate these molecules to the surfactant residues and not to an evaporation of the amorphous iron, although due to the small size of the iron particles this possibility cannot be ruled out.

**B. Amorphous Iron Oxide Coated by Alkanethiols.** The TGA of the Fe\(_2\)O\(_3\) particles coated with octadecane thiol is depicted in Figure 4. It reveals a different pattern from that observed for the Fe particles. Unlike the coated Fe particles, which showed a rapid drop in weight at about 200 °C, followed by a gradual monotonic decrease in weight at higher temperatures, the TGA curve of the coated Fe\(_2\)O\(_3\) particles shows weight loss activity only in one temperature range. This temperature range in Figure 4 is 250–450 °C, with an inflection point at 293 °C. This inflection point shows a strong dependence on the octadecane thiol–Fe\(_2\)O\(_3\) molar ratio. When this concentration ratio is increased, the inflection point is shifted to higher temperatures.

The DSC spectrum reveals (Figure 5) an endothermic peak at 57 °C, almost the same temperature where the corresponding peak for the coated iron particles is detected. The DSC spectrum also reveals a rich exothermic structure comprised of three bands, the strongest peaking at 327 °C. The temperature of the strongest exothermic peak is also dependent on the octadecane thiol–Fe\(_2\)O\(_3\) molar ratio, and for lower mass ratios than depicted in Figure 5, it was detected at 280 °C. For the uncoated Fe\(_2\)O\(_3\) particles an exothermic peak is observed at 268 °C;\(^31\) it is attributed to the conversion of the amorphous iron oxide to the crystalline form.


Comparison of the TGA data for Fe$_2$O$_3$ and Fe particles makes it clear that the removal of the alkanethiol molecules occurs at higher temperatures for the iron oxide than for the iron particles; the chemical bonds formed between the octadecanethiol and the iron oxide substrate are stronger than those formed between the thiol and the iron particles. A temperature dependent mass spectrometric measurement, similar to those carried out for the iron particles, was also performed for the Fe$_2$O$_3$-coated octadecanethiol particles (Figure 6). The largest peak is observed at 570 amu with a much weaker peak at 285 amu. The 570 band is assigned as corresponding to the disulfide CH$_3$-(CH$_2$)$_{17}$-S-S-(CH$_2$)$_{17}$-CH$_3$. This result differs dramatically from the observed ion of a dialkyl sulfide, R$_2$S, as the leaving species from the iron particle surface. As a control, the mass spectrum of the octadecanethiol was also measured. A completely different fragmentation pattern was observed, with the strongest peak detected at 285 amu and a very weak feature at 572 amu. This supports our mass spectrometric assignment and rules out the possibility that the 570 amu peak is a weak van der Waals dimer of the octadecanethiol. When the total ion current in the mass spectrometer was measured as a function of temperature, ions began to appear at 240 °C and the total current reached its maximum at 400 °C. This also substantiates the claim that the thiols are bonded more strongly to Fe$_2$O$_3$ than to Fe.

Parts a and b of Figure 7 present the XPS spectra of the Fe(2p) photoelectrons of the bare amorphous Fe$_2$O$_3$ and the thiol-coated Fe$_2$O$_3$ particles, respectively. The energies of the Fe(2p) doublet in the amorphous Fe$_2$O$_3$ match those reported by Liu$^{24}$ for the crystalline γ-Fe$_2$O$_3$ (710.7 and 724.3 eV). They report that coating the γ-Fe$_2$O$_3$ with stearic acid or with 16-mercaptododecanoic acid did not produce energetic changes or half-width changes in the Fe XPS spectra. On the other hand, they observe a clear change in line shape upon coating, as is the case for our coated particles. The thiol-coated Fe(2p) line shows a significantly larger intensity at 712 eV, confirming the chemical bonding to the sulfur atom.

The sulfur 2p doublet is depicted in Figure 8. Its spectral position indicates a direct bonding to the Fe atom. Note that no signal reflecting an oxidized sulfur (S-O) is detected. The observed energy is in good agreement with that seen for the sulfur in FeS, 161.04 eV.

On the basis of an analysis of the line shape of the Fe signal of our amorphous Fe$_2$O$_3$ particles, comparing coated and uncoated materials (Figure 7a and b), we estimate the contribution of the sulfur-bonded Fe(2p) signal as 20–
40% of the overall intensity. In agreement with this, the ratio of the concentration of Fe to the concentration of oxygen bonded to iron was found to increase by a similar percentage, suggesting that part of the oxygen atoms were replaced by sulfurs. Finally, this value (20%) nicely corresponds to the fraction of atoms on the surface of a 20 nm spherical particle (the average size of our particles based on TEM measurements). This too is consistent with the replacement of Fe–O bonds by Fe–S bonds upon coating.

**Discussion**

DSC of the coated iron and the coated Fe₂O₃ particles showed an endothermic peak at around 60 °C. This peak is attributed to the removal of multilayers of octadecanethiol by breaking the van der Waals bonds. This result is comparable to the desorption of methanethiol reported to occur at ~150 °C and that of 1,1-dimethylethanethiol at ~113 °C. For octadecanethiol, +60 °C is a reasonable temperature for this process, given the ability of normal alkyl chains to form close-packed lamellar structures, with a van der Waals interaction energy of 0.8 kcal/mol per CH₂ group at room temperature. Furthermore, the observation of an endothermic peak at the same temperature for both the iron and iron oxide substrates indicates that this desorption temperature is independent of the nature of the substrate and is related only to the alkanethiol. Furthermore, the mass spectrum of the iron-coated particles heated to 100 °C, which revealed the appearance of the octadecane thiol mass, also substantiates this interpretation.

The endothermic DSC band at 200 °C for the iron coated with octadecanethiol is related to the sharp drop in weight observed in the TGA spectrum at almost the same temperature. This peak, unlike the 60 °C band, does not have a corresponding band in the coated Fe₂O₃ TGA spectrum. It is attributed to the desorption of the dialkyl thioether, which is observed in the mass spectrum of the molecules removed from the iron at this temperature. The 200 °C endothermic peak does not appear for the coated Fe₂O₃ particles, since the bonds between the oxide and the alkanethiol are cleaved only at higher temperatures.

It is important to compare the desorption of alkanethiol molecules that we have observed to occur at ~200 °C with the results obtained by Cheng et al., where decanethiol molecules dissociatively desorbed from the iron surface and decene is detected at 260 K (~13 °C). Cheng did not report any dependence on the length of the alkyl chain: the same decomposition temperature was observed for ethanethiol and decanethiol. This would therefore also be expected for octadecanethiol. We suggest that our observed higher temperature desorption is related to the amorphous nature of our iron. When we compare crystalline iron, where each of the iron atoms is bonded to other irons (whether to 12 nearest neighbors, as in a bulk bcc iron, or less, because of being surface irons, is immaterial), to the amorphous iron of a nanoparticle where a large portion of the atoms are surface atoms, it is clear that the bonding of this less coordinatively saturated iron atom to an amphiphile should be much stronger. This explanation is supported by our observation that octadecanethiol did not form a coating on commercial (Aldrich) submicron iron particles or on the crystalline nanoparticles obtained by heating the amorphous iron to 350 °C under vacuum for 3–4 h.

The assertion that amorphous nanocrystals should be more reactive (i.e. more strongly bind thiols) than the corresponding crystalline material is well supported in the literature. Suslick et al. compare the catalytic activity of amorphous Fe on SiO₂ vs that of crystalline Fe on SiO₂ and show the amorphous material to be dramatically more reactive. Similarly, the behavior of amorphous and crystalline alloys and oxides have also been compared with the amorphous materials having substantially enhanced reactivity.

DSC of the coated iron particles also reveals an exothermic peak at 330 °C, with a correspondingly more complex DSC structure in the same temperature range for the coated Fe₂O₃. This peak is assigned in both cases to the phase transition of amorphous iron to crystalline iron. This assignment is based on previous measurements...

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of the DSC of amorphous iron, showing such an exothermic peak at this temperature.

In the low-temperature range, the DSC spectrum of the Fe$_2$O$_3$ particles coated with octadecanethiol is almost identical to that of the coated Fe particles (discussed above). The high-temperature range shows a rich exothermic structure with its strongest peak at 327 °C. The temperature of the strongest exothermic peak was found to be dependent on the octadecanethiol–Fe$_2$O$_3$ molar ratio. For example, for molar ratios lower than that depicted in Figure 5 (1:1), it was shifted toward lower temperatures and was detected at 280 °C. For the uncoated Fe$_2$O$_3$ particles an exothermic peak is observed at 268 °C and is attributed to the transition from amorphous iron oxide to the crystalline form. Therefore we assign the exothermic peak in the 280–330 °C range to the crystallization temperature. We suggest the following explanation for the temperature dependence of this peak on the thiol: Fe$_2$O$_3$ ratio. We have demonstrated that the amorphous to crystalline transition temperature of the amorphous Fe$_2$O$_3$ is dependent on the particle size. For the particles obtained from the sonication of pure Fe(CO)$_5$ (under air) the crystallization temperature was lower than that for particles obtained from the sonication of a 0.25 M solution of Fe(CO)$_5$ in decalin. In fact, a gradual change of the crystallization temperature as a function of Fe(CO)$_5$ concentration during sonication was observed (pure < 4 M < 1 M < 0.25 M). For the octadecanethiol-coated Fe$_2$O$_3$ particles the crystallization temperature varied as follows. For the molar ratio of thiol–Fe$_2$O$_3$ = 0.3, the measured crystallization temperature is 280 °C; for thiol–Fe$_2$O$_3$ = 1.0, the observed temperature is 327 °C. In Table 2 we present the temperature dependence of the exothermic peak on the octadecanethiol–Fe$_2$O$_3$ molar ratio. We interpret this observation as a result of the surfactant influence on the aggregation form of the iron oxide. For the lower thiol–Fe$_2$O$_3$ molar ratio a more dense agglomerated structure is formed, while for the higher molar ratio a more porous Fe$_2$O$_3$ is formed, resulting in a higher crystallization temperature.

The comparison between the DSC data of the coated Fe and the coated Fe$_2$O$_3$ particles, which is presented in Table 1, reveals that while similar features are observed at 60 and 320 °C, the endothermic peak which appears at 200 °C in the coated Fe spectrum does not have a corresponding feature in the coated Fe$_2$O$_3$ spectrum. We attributed this peak to the desorption of the dialkyldisulfide from the iron surface. The corresponding desorption of dialkyldisulfide, which is removed from the Fe$_2$O$_3$ surface, occurs at much higher temperatures. Its TGA is dependent on the thiol–Fe$_2$O$_3$ molar ratio but appears consistently in the 290–350 °C temperature range, consistent with the rich structure in the DSC spectrum around the 300 °C range. We explain the spectrum as being composed of the exothermic crystallization peak and the endothermic desorption peak. The combination of a maximum (exothermic) and a trough (endothermic) is the reason for the complexity of the DSC spectrum.

The DSC and TGA spectra of the octadecanethiol adsorbed on Fe and Fe$_2$O$_3$ show several differences. The major part of the octadecanethiol on amorphous Fe particles is removed at temperatures < 200 °C (66%); the corresponding evaporation from the Fe$_2$O$_3$ occurs at higher temperatures (the inflection points are 208 °C for coated iron particles vs 293–370 °C for the Fe$_2$O$_3$ particles). The differences are also reflected in the shape of the TGA curves for the two substrates. In the iron case, the removal of these molecules is evident via DSC as an endothermic peak whose $\Delta H$ of desorption is 42.6 J/g. The corresponding endothermic peak, in the coated Fe$_2$O$_3$, is less distinct and overlaps the exothermic peak associated with the crystallization of the particles.

It is interesting to reconcile these results with those of Folkers and of Liu regarding the affinity of various ligands to iron oxide. Folkers$^{23}$ reports that carboxylic acid is a weak ligand toward iron oxide as a substrate. On the other hand, Liu$^{24}$ reports that a carboxylic acid can anchor to an iron oxide substrate. The Liu result seems to be attributable to the high surface area and reactivity of his nanocrystalline iron oxide. Similarly, we contend that the binding of our thiol ligands to iron oxide is greatly enhanced by our having high surface area nanoparticles. The amorphous nature of our nanoparticles should, if anything, make the binding even stronger (as explained above).

We suggest that this can be attributed to the nanometer size of Liu’s particles$^{24}$ and the huge surface area of the iron oxide substrate. Similarly, in understanding how a thiol (which forms weaker bonds with iron oxides than a carboxylic acid) desorbs off the iron oxide surface at such a high temperature, the amorphous nature of the material is again implicated.

The molar differences between the desorption products of the thiol coated iron and the thiol coated iron oxide are related to the valency of the iron atom bonded to the thiolate group. The octadecanethiol in the amorphous iron coating is assumed to be bonded to an Fe(II), while in the Fe$_2$O$_3$ it is bonded to an Fe(III). This explains why the desorption in the former case occurs at 200 °C and that in the latter case occurs at 300 °C. Once the thiolate bond is cleaved, two different reactions take place. For the desorption from the amorphous iron, the nucleophilic attack of the sulfur is on the adjacent CH$_2$ group. This is because the Fe=S is a good leaving group and the reaction will require a relatively low activation energy. The possibility that the nucleophilic attack would be directed toward the adjacent sulfur atom is disfavored because this will result in an unstable Fe(I) species. In the desorption from Fe$_2$O$_3$, the sulfur is more electrophilic due to its bonding to the Fe(II) and the effect of the electronegativity of the oxygen atoms. Hence, the reaction to form R$_2$S$_2$ has a lower activation energy. The attack on the adjacent sulfur atom results in the formal reduction of the Fe(III) to Fe(II). This would explain the aforementioned experimental observations. We cannot rule out, however, without further experimentation, the possibility that the bonding scheme for the iron oxide involves Fe–O=S bonds. We prefer the Fe=S scheme because the O=S is a weak bond of only 68 kcal/mol$^{18}$ as opposed to the Fe=S bond, which is stronger. This is consistent with the XPS data (Figures 7 and 8), which clearly show direct bonding of the Fe to the sulfur.

The molar desorption heat of the removal of the R$_2$S molecule from the iron surface is calculated from DSC as +5.5 kcal/mol. This rather small heat of reaction can be understood as follows. The heat of the reaction

$$2\text{C}_{18}\text{H}_{37}S-\text{Fe} \rightarrow \text{Fe} + \text{C}_{18}\text{H}_{37}S-\text{Fe}$$

is $\Delta H = 0$ kcal/mol (as computed by subtracting the enthalpies of the new bonds formed from the enthalpies of the bonds cleaved). This is a very crude approximation.
for the heat of the reaction, since the bond energies used are defined for the gas phase. This computation also assumes that the energies of the breaking and the formation of the C–S and Fe–S bonds are constant regardless of the alkyl group bonded to the sulfur atom. It also assumes comparable energetics for formation of the Fe=S bond and for breaking an Fe–S bond. However, it is clear that a very small $\Delta H$ for this process is reasonable.

In both systems studies herein, the determination of the species that is left after the desorption of the thioether or the disulfide is under further investigation.

Acknowledgment. This research was supported by grant No. 94-00230 from the U.S.–Israel Binational Science Foundation (BSF), Jerusalem, Israel. Y.K. thanks the Ministry of Absorption for their financial support (Giladi scholarship). A.G. is grateful to Bar-Ilan Research Authorities for supporting this project. The XRD measurements were carried out on an instrument belonging to Prof. M. Deutsch; we thank him for his assistance and advice. T.P. thanks the Ministry of the Sciences and the Arts for an Eshkol scholarship.