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The surface chemical properties of cobalt-modified γ-Fe_2-O_3 magnetic particles

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The surface chemical properties of cobalt-modified γ-Fe_2O_3 (Co-γ-Fe_2O_3) magnetic particles were studied by adsorption isotherms, FT–i.r. spectroscopy and microcalorimetry. The monolayer-adsorption amount of water on Co-γ-Fe_2O_3 surfaces is 4.8 molecules per square nanometre, and the surface is considered to be covered with a thin water film in its normal environment. The surface hydrophilicity of Co-γ-Fe_2O_3 is comparable to that of TiO_2. The acidic carboxyl group shows the strongest interaction with Co-γ-Fe_2O_3, and a portion of this group chemically interacts. The basic amino group indicates stronger interaction with Co-γ-Fe_2O_3 than the neutral hydroxyl group. It is concluded that the Co-γ-Fe_2O_3 surface possesses a basic rather than an acidic character. This is interpreted in terms of the inherent nature of the adsorption site of Co-γ-Fe_2O_3. Furthermore, the Co-γ-Fe_2O_3 adsorption site appears to be energetically heterogeneous.

1. Introduction

The excellent dispersion of fine magnetic particles is of great practical importance in developing particulate magnetic recording media with higher storage densities [1, 2]. The subject of magnetic dispersion requires an understanding and a control of the interfaces between components such as magnetic particles, dispersants, binders or solvents. In particular, the adsorption behaviour of an organic adsorbate, dispersant or binder on magnetic particles has a definitive influence on the dispersibility of particles [3]. Adsorption is greatly dependent on the surface chemical properties of particles, that is, surface hydrophilicity or acid–base properties [4–9].

To date, in magnetic dispersion, the surface chemistry of γ-Fe_2O_3 magnetic particles has been investigated by a number of researchers [3, 10–12]. It was reported that, for γ-Fe_2O_3, the concentration of surface hydroxyl groups was 3 OH molecules per square nanometre, the adsorption site could react with either acidic or basic, or other molecules. However, very little work has been carried out on the surfaces chemical properties of cobalt-modified γ-Fe_2O_3 (Co-γ-Fe_2O_3) particles, which are the most widely used magnetic materials in recent magnetic recording media such as video tapes or floppy disks.

In this work, as a fundamental study of magnetic dispersion, the surface chemical properties of Co-γ-Fe_2O_3 (mainly the surface hydrophilicity and the acid–base properties) were studied by adsorption isotherms, FT–i.r. spectroscopy and microcalorimetry.

2. Experimental details

2.1. Materials

The magnetic particles used were acicular Co-γ-Fe_2O_3 [13] having a coercivity of 4.77×10^4 A m^{-1} (600 Oe) and a specific surface area of 39.5 m^2 g^{-1} (Fig. 1). After the epitaxial growth reaction of a cobalt–ferrite layer on the γ-Fe_2O_3 surface, the particles were washed with pure water by decantation until there was no further change in the electric conductivity in the supernatant water of the suspension. These particles have been widely used for video tapes.

An iron foil having an Fe purity of 99.99% and a thickness of 65 μm was also used in FT–i.r. spectroscopy. Electron spectroscopy for chemical analysis (ESCA) measurements revealed that the iron foil had an iron-oxide layer with a surface thickness of about 4.5 nm. Since the crystal structure of cobalt–ferrite is the same as that of iron oxide (γ-Fe_2O_3), and there is little difference between iron and cobalt in their electronegativity and ion radius, which greatly affect the nature of the surface-hydroxyl group, it is expected that the surface chemical property of the iron foil is very similar to that of Co-γ-Fe_2O_3. This iron foil has served as a model surface for Co-γ-Fe_2O_3 [14, 15].

Special-grade stearic acid ($C_{17}H_{35}$–COOH) and stearyl alcohol ($C_{18}H_{37}$–OH) and first-class-grade stearylamine ($C_{18}H_{37}$–NH_2, Nakarai Chemicals) were used without further purification. These monofunctional adsorbates, having a hydrophobic long chain, are a suitable probe molecule for characterizing the acid–base properties of particles. This is because they yield a measure of the specific interaction between the functional group and the particle surface. A special-grade toluene (Nakarai Chemicals) was used as a solvent.

2.2. Measurement of the surface hydrophilicity of Co-γ-Fe_2O_3

In order to quantitatively evaluate the surface hydrophilicity of Co-γ-Fe_2O_3, the adsorption isotherm of

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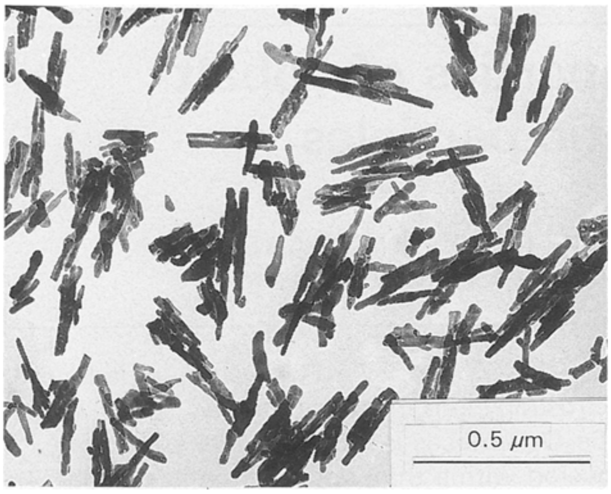

Figure 1 Transmission-electron-microscopy image of the Co-γ-Fe_2O_3 magnetic particles.

water and the heat of immersion in water were measured. The amount of water adsorption on a Co-γ-Fe_2O_3 surface was measured gravimetrically with a precise electrical balance (Cahn 2000). First, Co-γ-Fe_2O_3 was evacuated at room temperature to remove physi-sorbed water until there was no further reduction in the particle weight. Next, water vapour was adsorbed on Co-γ-Fe_2O_3 at 20 °C. During this process, the particle weight and the water vapour pressure, measured by a Baratron pressure gauge, were recorded automatically to determine the adsorption isotherm of water. The monolayer-adsorption amount of water was calculated by applying the Brunauer–Emmett–Teller (BET) equation to the adsorption isotherm obtained.

The heat of immersion of Co-γ-Fe_2O_3 in water was measured by using a highly sensitive conduction-type microcalorimeter (Tokyo Riko MMC-5113). Before thermal equilibrium at 30 °C, the Co-γ-Fe_2O_3 was evacuated for 2 h at different temperatures under a pressure of 10^{-2} Pa to remove adsorbed water and impurities. Multiple measurements were performed to allow data averaging.

2.3. Characterization of the acid–base property of Co-γ-Fe_2O_3

The acid–base property of the Co-γ-Fe_2O_3 surface was characterized by the interaction between the monofunctional adsorbates given above and Co-γ-Fe_2O_3, and the interaction was evaluated by adsorption isotherms, FT–i.r.–ATR (attenuated total reflection) and the heat of adsorption.

The procedure for the adsorption isotherms of the adsorbates on Co-γ-Fe_2O_3 was as follows: 1 g of Co-γ-Fe_2O_3 dried in vacuum was dispersed in 20 cm^3 of adsorbate solution for three days at 30 °C. The adsorption amount of adsorbate was obtained by measuring the adsorbate concentration in the solution before and after the dispersion of Co-γ-Fe_2O_3. The adsorbate concentration was determined gravimetrically by evaporating the solvent in the supernatant solution of adsorbate. Adsorption amounts were reproducible to about $\pm 3\%$ in this method.

The FT–i.r.–ATR (Nicolet 7199) method was used to analyse the adsorption state of the adsorbates on the iron-oxide surface. The oxidized iron foil was dipped in 0.1% adsorbate solution for 1 h, and the foil adsorbed with the adsorbate was placed at a 45° angle with a germanium plate in dry air to obtain ATR spectra. Each spectrum was recorded at a resolution of 4 cm^{-1} with a total of 300 scans.

Integral heats of adsorption of the adsorbates on Co-γ-Fe_2O_3 from toluene were directly measured by using the above microcalorimeter. In practice, the heat of adsorption, Q, was calculated from the heat of immersion of Co-γ-Fe_2O_3 in the solution Q_1, in the solvent, Q_2, and the amount of adsorption on Co-γ-Fe_2O_3, $A (Q = (Q_1 - Q_2)/A)$ [16]. The outgassing temperature of Co-γ-Fe_2O_3 was 150 °C. The toluene was dried before use with freshly activated molecular sieves to a water content of less than 10 p.p.m (parts per million).

3. Results and discussion

3.1. Surface hydrophilicity

Fig. 2 shows the adsorption isotherm of water vapour on Co-γ-Fe_2O_3 at 20 °C. As can be seen from the shape of isotherm, the adsorption of water is a typical multilayer adsorption. The monolayer-adsorption amount of water molecules on the Co-γ-Fe_2O_3 surface was 4.8 molecules per square nanometre, as determined from the BET equation. The isotherm also indicates that the adsorption amount of water in a relative humidity of 60% at 20 °C, found in a normal environment, is approximately 10 molecules per square nanometre, more than two layers of water molecules being adsorbed. Assuming the area occupied by a water molecule is 0.108 nm^2 [17], the monolayer adsorption amount is 9.3 molecules per square nanometre for closest packing of water molecules. From these results, it is inferred that, microscopically, only water molecules are exposed on the

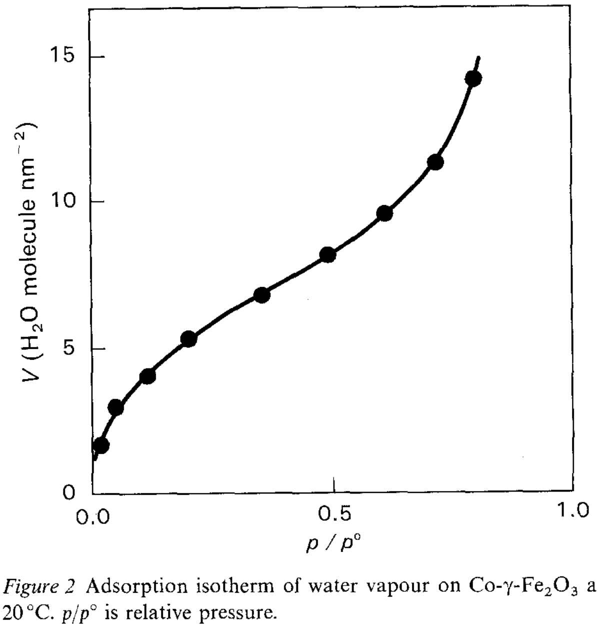

Figure 2 Adsorption isotherm of water vapour on Co-γ-Fe_2O_3 at 20 °C. p/p° is relative pressure.

outermost surface of Co-γ-Fe_2O_3 at normal temperatures and humidities, and the particle surface is covered with a very thin water film.

Fig. 3 shows the dependence on outgassing temperature of the heat of immersion of Co-γ-Fe_2O_3 in water. The heat of immersion increases from 300 to 725 mJ m^{-2} with an increase of the outgassing temperature in the range of the measurement. Such a tendency has been reported on metal-oxide particles like SiO_2, Al_2O_3 or TiO_2 [18–20]. It is said that the surface hydroxyl group, namely the adsorption site M–OH (where M is a metal element), is transformed into a M–O–M bond by dehydration on heating, and a large amount of heat is generated by cleavage of the M–O–M bond in the immersion into the water.

The value of the heat of immersion in water is one of the quantitative measures of surface hydrophilicity of a particle. From the comparison with the heats of immersion of metal-oxide particles in water reported previously (at an outgassing temperature of 200 °C) [21], the surface hydrophilicity of Co-γ-Fe_2O_3 (560 mJ m^{-2}) is comparable to that of TiO_2 (rutile, 540 mJ m^{-2}).

3.2. Acid–base properties

Fig. 4 shows the adsorption isotherms of stearic acid, stearylamine and stearyl alcohol on Co-γ-Fe_2O_3 from toluene solutions at 30 °C. All adsorbates fit the following Langmuir equation.

$$A = \frac{A_s KC}{1 + KC}$$

Here, A is the adsorption amount at the equilibrium concentration C, and A_s is the saturated adsorption amount. Since the constant K is related to the energy of adsorption [22], an increase in K indicates a stronger interaction between the adsorbate and the adsorbent. The saturated adsorption amount and the value of the K calculated by using the Langmuir equation are listed in Table I. As shown in Table I, the saturated adsorption amount and the constant K increase in the following order: stearyl alcohol, stearylamine and stearic acid. Consequently, the data obtained mean that the interaction strength of functional groups with Co-γ-Fe_2O_3 increases the hydroxyl, amino and carboxyl groups, in this order.

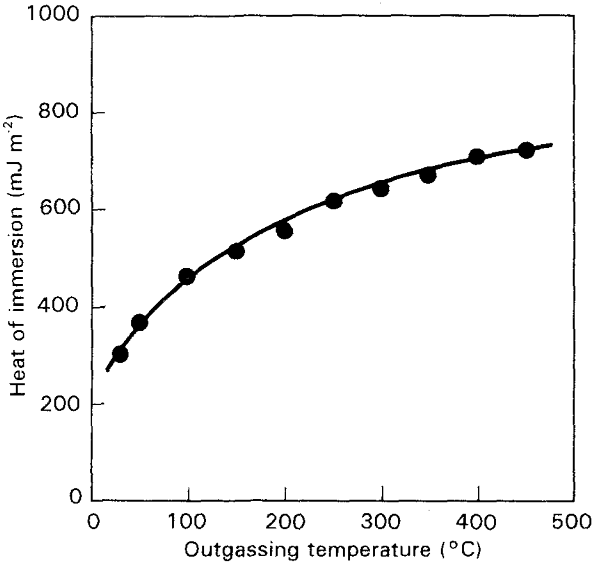

Figure 3 Dependence of the heat of immersion of Co-γ-Fe_2O_3 in water on outgassing temperature.

Figs 5, 6 and 7 show FT–i.r.–ATR spectra before and after adsorption on the oxidized iron foil for stearic acid, stearylamine and stearyl alcohol, respectively. Assignments of the main peaks are designated in each figure. In both stearylamine and stearyl alcohol, no significant differences are observed between the spectra before and after the adsorption onto the iron-oxide surface. This result clearly indicates that the chemical structure of the functional groups of the two adsorbates does not change during the adsorption. Hence, the adsorptions of the amino group and hydroxyl group on Co-γ-Fe_2O_3 are shown to be physical.

In stearic acid, however, there are two new weak peaks, at 1540 and 1430 cm^{-1}, after the adsorption onto the iron-oxide surface. These new peaks reveal the existence of stearate species [23]. Moreover, the strong peak at 1700 cm^{-1} assigned to the C = O stretching vibration of the free carboxyl group is also observed in this spectrum. Thus, a portion of the carboxyl group has chemically interacted with the iron-oxide surface.

Heats of adsorption (per molar adsorption amount of the adsorbates) on Co-γ-Fe_2O_3 as a function of the

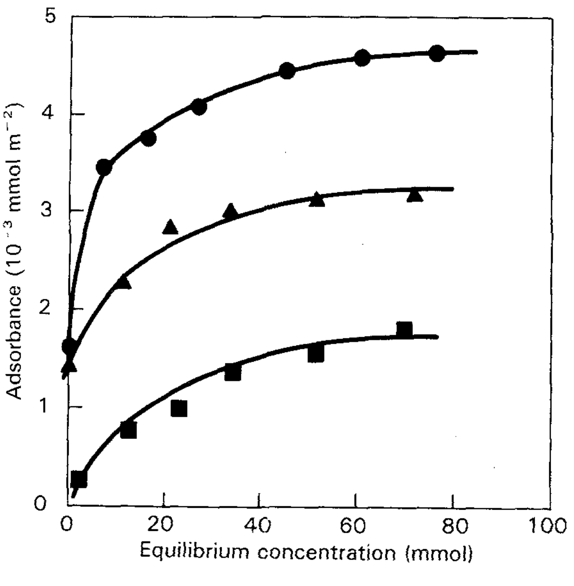

Figure 4 Adsorption isotherms of: (●) stearic acid, (▲) stearylamine and (■) stearyl alcohol, on Co-γ-Fe_2O_3 from toluene solutions at 30 °C.

TABLE I Saturated absorption amounts and K constants of adsorbates in the adsorption on Co-γ-Fe_2O_3 from toluene solution at 30 °C

Adsorbate	Saturated adsorption amount (mmol m^{-2})	Constant K
Stearic acid	4.66×10^{-3}	0.36
Stearylamine	3.25×10^{-3}	0.22
Stearyl alcohol	1.76×10^{-3}	0.07

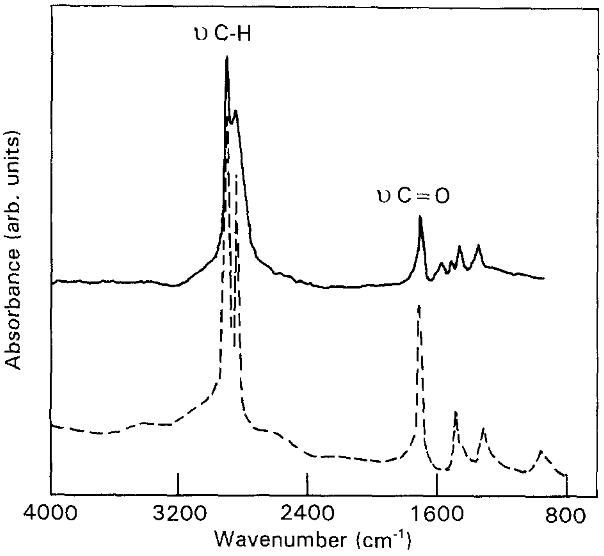

Figure 5 FT–i.r.–ATR spectra of stearic acid on the oxidized iron foil: (– – –) the spectra before adsorption, and (——) after the spectra adsorption.

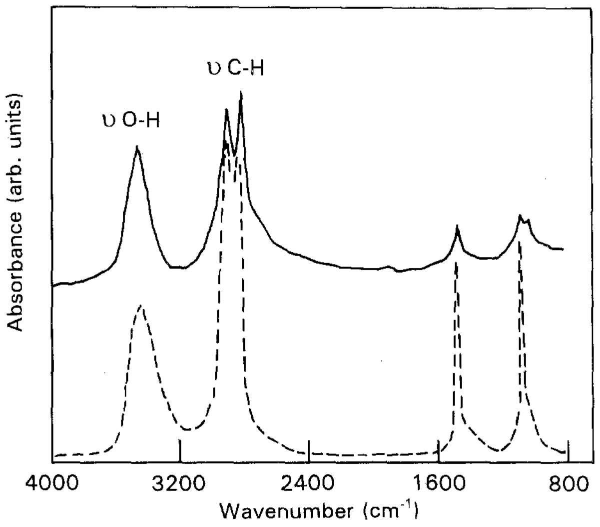

Figure 7 FT–i.r.–ATR spectra of stearyl alcohol on the oxidized iron foil: (– – –) the spectra before adsorption, foil: and (——) the spectra after adsorption.

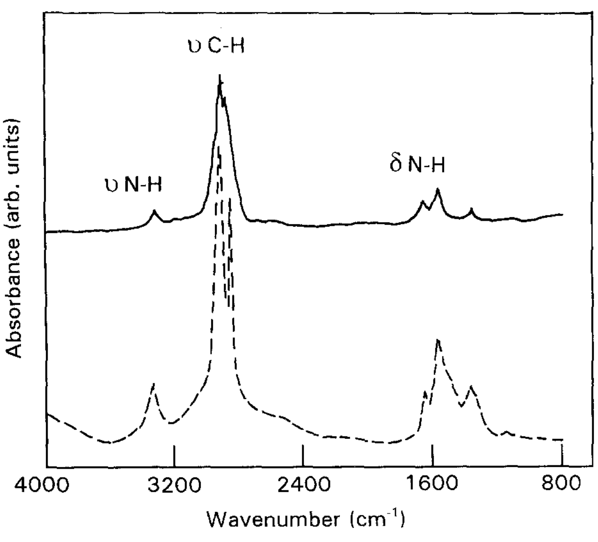

Figure 6 FT–i.r.–ATR spectra of stearylamine on the oxidized iron foil: (– – –) the spectra before adsorption, and (——) the spectra after adsorption.

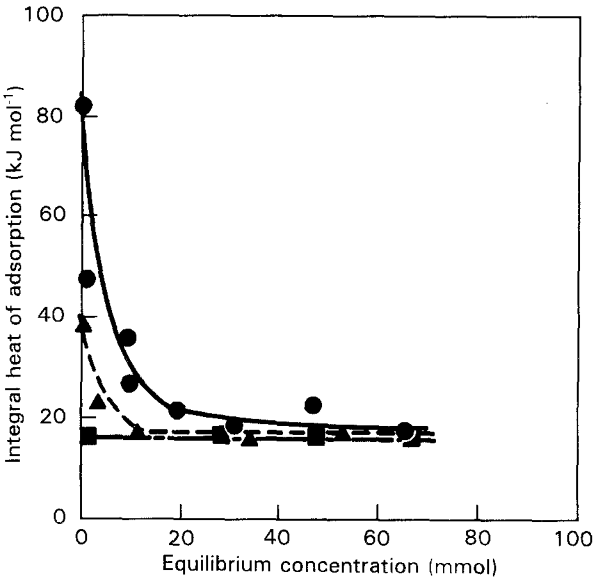

Figure 8 Integral heats of adsorption of (●) stearic acid, (▲) stearylamine, and (■) stearyl alcohol, on Co-γ-Fe_2O_3 at 30 °C.

equilibrium concentration of the solutions are shown in Fig. 8. The heat of adsorption of stearic acid decreases from more than 80 kJ mol $^{-1}$ to less than 20 kJ mol^{-1} as the equilibrium concentration increases. When the concentration is greater than about 40 m mol (when the adsorption monolayer of stearic acid is complete), the heat of adsorption remains constant at about 19 kJ mol^{-1}. Stearylamine shows similar behaviour to stearic acid, except for a smaller evolution of heat at low concentrations. In stearyl alcohol, the heat of adsorption is almost independent of the concentration having a constant value which is less than 18 kJ mol^{-1}

The energy generated in bond formation is known to be about 4–20 kJ mol^{-1} for van der Waals bonds, about 20–40 kJ mol^{-1} for hydrogen bonds and more than about 80 kJ mol^{-1} for chemical bonds [16, 24]. Therefore, it is readily understood from Fig. 8 that almost all the carboxyl group is adsorbed onto Co-γ-Fe_2O_3 with a greater interaction strength than hydrogen bonds, and at very low concentrations a portion of the carboxyl group is chemically adsorbed. Moreover, it is obvious that most amino groups and all hydroxyl groups are physically adsorbed on Co-γ-Fe_2O_3 with an interaction strength corresponding to either hydrogen bonds or van der Waals bonds.

These results are consistent with those obtained by the adsorption isotherms and FT–i.r.–ATR. It is therefore concluded that the surface of Co-γ-Fe_2O_3 has a basic character rather than an acidic character. The dispersibility of Co-γ-Fe_2O_3 is expected to improve by using acidic polymers like vinyl-chloride copolymers or poly(vinyl butyral) [8].

In the adsorption sites of Co-γ-Fe_2O_3 (–FeOH or –CoOH), the difference in electronegativity [25] between Fe (or Co) and O is 1.7 and that between O and

H is 1.4. Thus, the Fe ··· OH structure is normally chosen in preference to the FeO ··· H structure [26] when an adsorbate molecule approaches the Co-γ-Fe_2O_3 surface. This inherent nature of the adsorption site is believed to be responsible for the basic surface of Co-γ-Fe_2O_3. In this study, the basic character of the solvent (toluene) is considered to provide the strong interaction between the carboxyl group and Co-γ-Fe_2O_3.

Most adsorbents, including metal-oxide fine particles, are heterogeneous, in the surface-chemical sense, in that they contain a wide range of high-to-low-energy adsorption sites because of surface imperfections or organic and inorganic contaminations [22, 24]. In such particles, preferential adsorption of an adsorbate molecule should take place onto adsorption sites having higher energy during the initial adsorption. Hence, the large evolution of heat observed in carboxyl and amino groups during the initial adsorption is probably due to preferential adsorption of these groups onto the higher-energy adsorption site of Co-γ-Fe_2O_3.

4. Conclusion

The surface chemical properties of Co-γ-Fe_2O_3 particles, the most widely used magnetic materials in magnetic recording media, were studied by adsorption isotherms, heats of immersion, FT–i.r.–ATR and heats of adsorption. The monolayer-adsorption amount of water on the surface of Co-γ-Fe_2O_3 was 4.8 molecules per square nanometre, and the surface was inferred to be covered with a thin water film at normal temperatures and humidity. The heat of immersion of Co-γ-Fe_2O_3 in water increased with increasing outgassing temperatures in the same manner as the other metal oxides. The surface hydrophilicity of Co-γ-Fe_2O_3 was shown to be close to that of TiO_2. The strength of the interaction with Co-γ-Fe_2O_3 increased in the order of hydroxyl, amino and carboxyl groups. A portion of the carboxyl group chemically interacted with Co-γ-Fe_2O_3. The Co-γ-Fe_2O_3 surface was believed to be basic rather than acidic. The adsorption site on the Co-γ-Fe_2O_3 surface was considered to be energetically heterogeneous.

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