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# The Catalysis of Maghemite and Hematite on the Aldol and the Retro-Aldol Condensation of Acetone

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The catalytic activities of maghemite on the aldol condensation of acetone and on the retro-aldol condensation of diacetone alcohol are found to be higher than those of hematite. Further, the catalytic activity of maghemite on the formation of mesityl oxide is significantly higher than that of hematite. The active sites are considered to be surface hydroxyl groups which behave as a Brϕnsted base and acid points. Maghemite has more basic surface hydroxyl groups than does hematite, and far more acidic surface hydroxyl groups than does hematite they are sufficiently strong to make its average surface acidity greater than that of hematite. The basic surface hydroxyl groups of maghemite are speculated to be those which bond to the iron ions of the octahedral sites the acidic ones are those of the tetrahedral sites of the spinel lattice of the surface.

Maghemite is a ferrimagnetic inverse-spinel type iron oxide, which is widely used for magnetic recording tapes. Its surface properties have a large influence on its dispersibility in paint and, thus, on the output and noise characteristics of tape. However, there have been relatively few studies on the surface properties of maghemite, compared to these of hematite.

In previous papers,[1–3] the nature of the surface hydroxyl groups of maghemite were examined by identifying either the PZC (Point of Zero Charge) or IEP (Isoelectric Point); the heat of formation of the surface hydroxyl groups was examined through measurements of the heat of immersion, compared with that of hematite. It was clarified that the surface hydroxyl groups of maghemite are more acidic than those of hematite, and that the heat of formation of the surface hydroxyl groups is lower than that for hematite. These differences between maghemite and hematite have been attributed to differences in the bulk crystal structure. However, these properties are related to the averaged parameters of the surface hydroxyl groups; more microscopic differences between maghemite and hematite are expected.

In the present work, the specific acidity and basicity of the surface hydroxyl groups of maghemite compared with those of hematite were studied using the Brϕnsted acid and base points as well as their effect on the catalysis of the aldol and the retro-aldol condensations of acetone. From the view point of heterogeneous catalysts for aldol or retro-aldol condensations, reports concerning iron oxides[4] have been fewer than those for aluminum oxides[5–8] or alkali earth metal oxides.[9–14]

## Experimental

**Samples.** The maghemite sample used in the present work was prepared from synthetic acicular $\alpha$-FeOOH (geothite) by sequential dehydration, reduction, and oxidation processes. The hematite sample was prepared by a heat treatment of the above-mentioned maghemite sample in air at 550 °C. In all cases, the samples were purified as follows: first, washing with an alkali solution, then distilled water and, finally, by electrodialysis. The samples were then filtered, dried at 100 °C for 24 h in an oven, and stored in a desiccator. The samples and purification procedure are the same as those reported previously.[1] The specific surface areas of the samples were 19 $m^2 g^{-1}$ for maghemite and 16 $m^2 g^{-1}$ for hematite, measured by using the BET method of nitrogen adsorption at liquid-nitrogen temperature, assuming the cross-sectional area of a nitrogen molecule to be 16.2 $Å^2$. The surface porosity of the samples was checked by a $t$-plot; the existance of surface pores less than 30 Å in diameter was confirmed to be negligible. The surface hydroxyl groups, which could behave as catalytic active sites, had densities of 11.8 groups $nm^{-2}$ for maghemite samples and 12.8 groups $nm^{-2}$ for hematite samples, as determined in a previous study.[2]

**Chemicals and Reactions.** The acetone used in the present work was of spectral grade, dehydrated with Drierite. Diacetone alcohol (4-hydroxyl-4-methyl-2-pentanone) was obtained from Wako Pure Chem. Ind. Ltd., and purified by vacuum distillation.

One-gram samples were ultrasonically dispersed in 40.0 g of acetone or diacetone alcohol in tightly stoppered 100 ml conical flasks; these were then placed in an incubator with water thermostated to an accuracy of less than ±0.05 °C. The products were analyzed by a gas chromatograph equipped with a 3 m column of PEG-20, and a detector for flame ionization, on the supernatant of the dispersion (sampled after a constant time and filtered by a membrane filter). The reaction times of both reaction systems were 15 h for the condensation of acetone and 10 h for the decomposition of diacetone alcohol.

## Results and Discussion

**Aldol Condensation of Acetone.** The aldol condensation of acetone to form diacetone alcohol (hereafter abbreviated to DAA) is known to be catalyzed by the Brϕnsted basic point of heterogeneous catalysts.[12] The following dehydration reaction of DAA to form mesityl oxide (4-methyl-3-penten-2-one (hereafter abbreviate MO)) is known to be catalyzed by the Brϕnsted acid.[15] A series of reactions is as follows:

$$2\,(CH_3)_2CO \xrightleftharpoons[\text{base point}]{} (CH_3)_2(OH)C\text{–}CH_2CO\text{–}CH_3$$

$$\xrightleftharpoons[\text{acid point}]{-H_2O} (CH_3)_2C{=}CH\text{–}CO\text{–}CH_3$$

In the present work, the catalytic activity of the aldol condensation (the catalytic activity of surface Brϕnsted base point) was measured on the samples as the conversion of acetone to the total products of DAA plus MO.

In all of these cases, the total conversions in the present reaction systems were less than 1.5%, which is far less than the reaction equilibrium;[16] no products excluding DAA or MO (such as the trimeric condensed product[17—19]) were detected in the present reaction systems. The rate of this reaction, even when it follows second-order kinetics, could be regarded as following zero-order kinetics and can be approximated by the following integrated form of the reaction rate formula:

$$kt = x/a(a-x) \fallingdotseq x/a^2 \ (x \ll a).$$

Here, $k$ is the reaction rate constant, $a$ the initial concentration of the reactant (i.e. acetone), and $x$ the concentration of products (i.e. DAA plus MO after a reaction time of $t$). Therefore, the conversions $x$ at a constant $t$ are proportional to the rates of reaction $k$. Figure 1 shows this total conversion per unit surface area of samples after a constant time of 15 h in an Arrhenius plot. These findings show that the catalytic activity of maghemite is slightly higher than that of hematite, and that the activation energies of both samples are of the same value, 70.6±0.5 kJ mol$^{-1}$ for maghemite and 67.3±0.5 kJ mol$^{-1}$ for hematite, respectively. Regarding the similar values for the activation energies of this reactions, it is considered that the rate-determining step does not depend on the activity of the samples. This consideration is well supported by the work of Zhang et al.,[13] which shows that the rate-determining step for C–C bond formation is the coupling of acetone and carbanion.

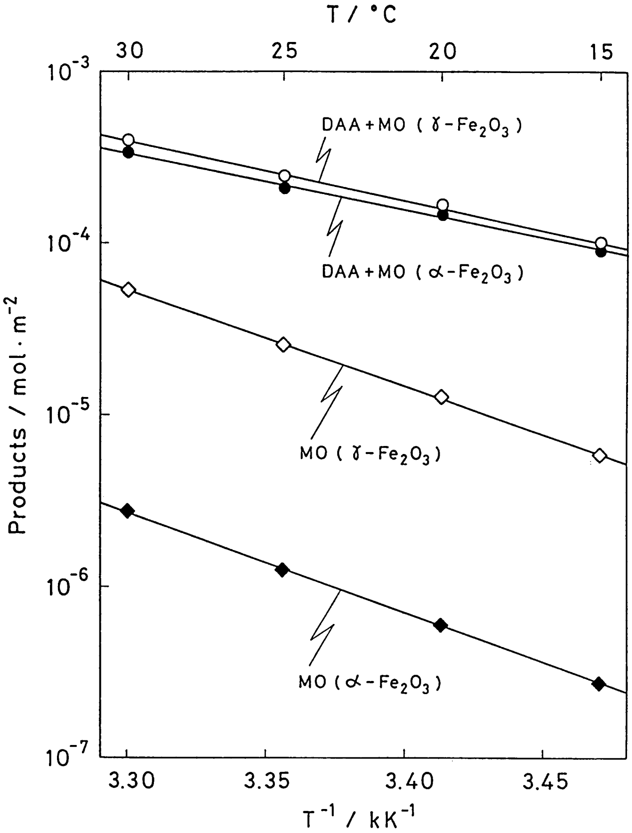

Fig. 1. Temperature dependences of the amounts of the reaction products of acetone after a reaction time of 15 h. Total amount of (DAA+MO) of maghemite ($\gamma$-Fe$_2$O$_3$): ○; total amount of (DAA+MO) of hematite ($\alpha$-Fe$_2$O$_3$): ●; amount of MO of maghemite ($\gamma$-Fe$_2$O$_3$): ◇; amount of MO of hematite ($\alpha$-Fe$_2$O$_3$): ◆.

Conversions to the MO per unit surface area of the samples are also shown in Fig. 1, and have a linear relationship in an Arrhenius-type plot. It is remarkable that the conversions of maghemite to MO are much higher than that of hematite. This is caused by the catalytic activities of the acidic points of the surface (surface hydroxyl groups) and are higher for maghemite compared to hematite.

Regarding the catalytic activity of maghemite, an identical magnitude of activity was confirmed for aldolization and dehydration with a commercially available maghemite sample. The sample has an acicular shape with a length of 0.2—0.4 μm and an acicular ratio of 8—10. The saturation magnetization is 73.0 emu g$^{-1}$ and the specific surface area is 24 m$^2$ g$^{-1}$. Purification of this sample was the same as that mentioned in the experimental section.

**Retro-Aldol Condensation of Diacetone Alcohol.** The retro-aldol condensation of DAA, which forms acetone, is known to be catalyzed by the Brϕnsted basic points of heterogeneous catalysts.[9,10] The MO is also formed (as mentioned above) in the presence of the Brϕnsted acid points. In the present work concerning this reaction system the products, except for acetone and MO, were negligibly small. The conversion of the retroaldolisation to acetone was less than 2%, which is also far less than equilibrium;[16] the rate of this reaction was reported to follow either zero-orders[6] or first-order kinetics.[9] The rate of this reaction, even when it follows the first-order kinetics, could be regarded as following zero-order kinetics, and can be approximated by the following integrated form of the reaction rate formula:

$$kt = \ln a/(a-x) \fallingdotseq x/a \ (x \ll a).$$

Then, conversions $x$ at a constant $t$ are proportional to the rates of reaction $k$. The conversions per unit surface area to acetone after a constant reaction time of 10 h are plotted in an Arrhenius plot in Fig. 2. The catalytic activity of acetone formation for maghemite is higher than that for hematite; this tendency does not change from the viewpoint of activity per hydroxyl group on the surface, considering the surface density of the hydroxyl groups. The activation energies for this reaction are 64.0±0.5 kJ mol$^{-1}$ for maghemite and 66.9±0.5 kJ mol$^{-1}$ for hematite. Both values are compatible with each other, and agree with the values reported in the literature.[9]

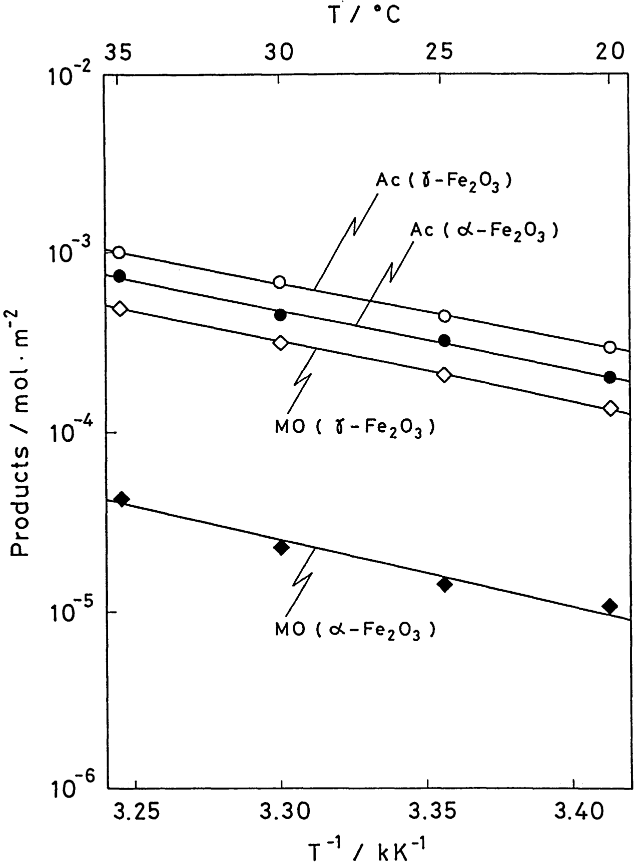

Fig. 2. Temperature dependences of the amounts of the reaction products of DAA after a reaction time of 10 h. Amount of acetone of maghemite (γ-$Fe_2O_3$): ○; amount of acetone of hematite (α-$Fe_2O_3$): ●; amount of MO of maghemite (γ-$Fe_2O_3$): ◇; amount of MO of hematite (α-$Fe_2O_3$): ◆.

Regarding the dehydration to MO, the conversion was less than 2%, which is far less than equilibrium; the rates of this reaction, reported to follow first-order kinetics,[15] could be approximated as mentioned before to be proportional to the conversions. The conversions per unit surface area of the samples after a constant reaction time of 10 h are plotted in an Arrhenius plot in Fig. 2. The catalytic activity of maghemite for the dehydration of DAA to MO has been found to be much higher than that of hematite. However, the activation energies of this reaction are almost the same (66.5±0.5 kJ $mol^{-1}$ for maghemite and 71.9±0.5 kJ $mol^{-1}$ for hematite), and almost equal to the value reported in the literature.[15]

**Acidity and Basicity of the Surface Hydroxyl Groups.** The catalysis used in the present work, originated from the acidic or basic nature of the surface hydroxyl groups, and could be explained from the view point of the Brϕnsted acid and base.

For acidic catalysis (that is, the dehydration reaction of DAA to MO) the catalytic activity of maghemite is higher than that of hematite. The fact that the acidity of maghemite is higher than that of hematite is well supported by the following view points. Concerning the enthalpy of formation of a bulk crystal, of which maghemite is higher than that of hematite,[20] the partial charges of the oxygen atoms of maghemite should be less than those of hematite, causing a higher acidity of maghemite than that of hematite.[21] This is well confirmed by the chemical shift of O(1s) of XPS[3,22] as well as the point of the PZC (Point of Zero Charge), of which the value for maghemite is lower than that for hematite.[1] Regarding for the dissociation and association of the proton of the surface hydroxyl groups, the equilibrium constants were determined in a previous study;[3] the chemical reactions and those values are as follows:

$$FeOH_2^+ \overset{K_{a1}^{int}}{\rightleftarrows} FeOH + H^+, \quad FeOH \overset{K_{a2}^{int}}{\rightleftarrows} FeO^- + H^+.$$

$$\text{Maghemite: } pK_{a1}^{int} = 2.7, \quad pK_{a2}^{int} = 8.3$$

$$\text{Hematite : } pK_{a1}^{int} = 3.2, \quad pK_{a2}^{int} = 10.2$$

The Brϕnsted acidity of maghemite is higher by a factor of 2 orders of magnitude than that of hematite, considering the values of $pK_{a2}^{int}$. According to the above-mentioned points, the results of the present work indicate that the acidic catalytic activity of maghemite is higher than that of hematite, which is reasonable in view of these acidities of the surface hydroxyl groups.

Regarding the basic catalysis (that is, the aldolization or retro-aldolization between acetone and DAA) the catalytic activity of maghemite is higher than that of hematite. This result is in contradiction to the fact that the Brϕnsted basicity of maghemite is lower than that of hematite, e.g. these values for PZC and the values for $pK_{a1}^{int}$. Concerning this point, further discussion is necessary, and the average basicity is not available. Especially the surface hydroxyl groups on maghemite are not more uniform than are those of hematite, since the crystal structure of maghemite is an inverse-spinel type which has iron ions in the tetrahedral coordination sites (the coordination number (CN) is 4) and in the octahedral coordination sites (the coordintion number (CN) is 6), whereas the crystal structure of hematite is the corundum type, which only has iron ions at the octahedral coordination sites.

**Specific Acidity and Basicity of the Surface Hydroxyl Groups.** Regarding the acidity or basicity of the surface hydroxyl groups as as a function of the value of PZC, Parks[23] again showed that the surface hydroxyl groups bonding to the metal ions of the tetrahedral coordination sites show a lower value of 2.4 pH units, compared with those of octahedral coordination sites. For an evaluation of PZC, maghemite can be treated as being a complex oxide comprising iron oxide in the tetrahedral coordination as well as the octahedral coordination. For the PZC of a complex oxide containing $n$ distinct component oxides, Parks[24] also showed that

$$PZC = \sum_{i=1}^{n} f_i \, PZC_i,$$

in which $PZC_i$ is the PZC of the component oxides ($i$), and $f_i$ is the atomic fraction on the surface. On the other hand, PZC has the following relations with $K_{a1}^{int}$ and $K_{a2}^{int}$:

$$PZC = 1/2\,(pK_{a1}^{int} + pK_{a2}^{int}).$$

The PZC of a complex oxide can thus be written as

$$PZC = 1/2\left(\sum_{i=1}^{n} f_i\, pK_{a1}^{int}{}_i + \sum_{i=1}^{n} f_i\, pK_{a2}^{int}{}_i\right),$$

where $K_{a1}^{int}{}_i$ and $K_{a2}^{int}{}_i$ are the $K_{a1}^{int}$ and $K_{a2}^{int}$ of the component oxides ($i$). To examine the specific basicity of the surface hydroxyl groups, the component values of $K_{a1}^{int}{}_i$ as well as those of the fraction of $f_i$ are more important than the average value of $K_{a1}^{int}$. It is still difficult to evaluate or determine the values of $K_{a1}^{int}{}_i$. The $K_{a1}^{int}{}_i$ are related, as mentioned above, with the $PZC_i$ as follows:

$$PZC_i = 1/2\,(pK_{a1}^{int}{}_i + pK_{a2}^{int}{}_i).$$

The values of $PZC_i$ correspond with those of the $K_{a1}^{int}{}_i$. Yoon et al.[25] have proposed improvements to Parks' semiempirical equation for PZC in the following manner; for a complex oxide, when the correction of the crystal field stabilization energy of the metal ion by the hydroxide ion is not required, as in the case of $Fe^{3+}$ ion with the tetrahedral or octahedral coordination,[26]

$$\begin{aligned} PZC &= \sum_{i=1}^{n} f_i\, PZC_i \\ &= 18.43 - 53.12 \sum_{i=1}^{n} f_i\,(v/L_s)_i - 0.5 \sum_{i=1}^{n} f_i \log((2-v)/v)_i. \end{aligned}$$

Here, $v$ is the bond valence, i.e., the valency of the metal ion per coordination number, and $L_s$ ($=L+r$) is the sum of the mean M–O bond length ($L$) and the O–H distance ($r$), taken to be 1.01 Å. According to the above equation, the component values of $PZC_i$ and those of the fraction of $f_i$ are calculated using the parameters of $Fe^{3+}$ ions and the Fe–O bonds, referring to crystallographic data for maghemite[27] and hematite.[28]

These numerical parameters and values are listed in Table 1. The $Fe^{3+}$ ions of maghemite are arranged in a spinel-type crystal lattice, and are divided into 4 classes as $Fe^{3+}$ (1), $Fe^{3+}$ (2), $Fe^{3+}$ (3), and $Fe^{3+}$ (4), respectively. The $Fe^{3+}$ ions of hematite are entirely equivalent to $Fe^{3+}$ (5) in Table 1. These $Fe^{3+}$ ions are arranged in a corundum-type crystal lattice.

The values of the PZC, i.e. the summation of the $f_i$ $PZC_i$, according to the above equation, are higher than those values determined by measurements carried out in a previous paper,[1] i.e. 5.5 for maghemite and 6.7 for hematite. The semiempirical equations by Parks and Yoon et al., in which the constants are defined using the PZG values of the hydrated samples, show higher values than do those for the unhydrated samples, as used in the present work and the previous paper.[1] The differences between the values of the PZC for maghemite and hematite are 1.2 pH units by measurement and 1.3 pH units by using the above-mentioned calculation, and are almost the same in value. This fact well supports the validity of the application of the above equations to the present work.

The results from the above calculations can be used to understand the catalytic activities of maghemite and hematite, that the $PZC_i$ values of octahedral sites of maghemite are higher than those of hematite. This fact indicates that the values of $pK_{a1}^{int}{}_i$ of the surface hydroxyl groups bonding to the surface iron ions of octahedral sites of maghemite ($Fe^{3+}$ (2), (3), (4)) are higher than those of hematite ($Fe^{3+}$ (5)). In other words, the Brϕnsted basicity of the surface hydroxyl groups bonding to the iron ions of the octahedral sites of maghemite is higher than that of hematite. This consideration leads to a reasonable explanation that the basic catalytic activity of the aldolization or the retro-aldolization of acetone of maghemite is higher than that of hematite.

It is also worthwhile noting from the above calculations that the value of $PZC_i$ of the tetrahedral sites $Fe^{3+}$ (1) of maghemite is far lower than that of the octahedral sites ($Fe^{3+}$ (2), $Fe^{3+}$ (3), and $Fe^{3+}$ (4)) compared with the

Table 1. Parameters of $Fe^{3+}$ Ions and Fe–O Bonds, and Component Values of $PZC_i$ for Maghemite ($\gamma$-$Fe_2O_3$) and Hematite ($\alpha$-$Fe_2O_3$)

| | Fe³⁺ ions | | | Fe–O bonds | | | | $PZC_i$ | PZC |
|---|---|---|---|---|---|---|---|---|---|
| | | CN[a] | $N_m$[b] | $v$ | $L_s$/Å | $N_b$[c] | $f_i$ | | $\sum_{i=1}^{n} f_i PZC_i$ |
| Maghemite ($\gamma$-$Fe_2O_3$) | $Fe^{3+}$(1) | 4 | 8 | 3/4 | 1.88 | 32 | 0.286 | 4.53 | |
| | $Fe^{3+}$(2) | 6 | 4 | 1/2 | 2.03 | 24 | 0.214 | 9.45 | |
| | $Fe^{3+}$(3) | 6 | 8 | 1/2 | 2.02 | 48 | 0.429 | 9.42 | |
| | $Fe^{3+}$(4) | 6 | 4/3 | 1/2 | 2.13 | 8 | 0.071 | 9.73 | |
| | | | | | | | | | 8.05 |
| Hematite ($\alpha$-$Fe_2O_3$) | $Fe^{3+}$(5) | 6 | 36[d] | 1/2 | 1.99 | 216 | 1.000 | 9.34 | |
| | | | | | | | | | 9.34 |

a) CN is the coordination number. b) $N_m$ is the number of $Fe^{3+}$ ions per unit cell. c) $N_b$ is the number of Fe–O bonds per unit cell. d) In the hexagonal unit cell.

value given in Parks' review,[23)] in which a difference between the values of 2.4 pH units is reported. More than double the value of the difference is derived from a calculation. This also suggests that the value of $\mathrm{p}K_{\mathrm{a2}}^{\mathrm{int}}{}_{i}$ is far lower than the average value of $\mathrm{p}K_{\mathrm{a2}}^{\mathrm{int}}$ of 8.3 for maghemite. These sites would show strong Brϕnsted acidity and promote the acidic catalysis of the dehydration reaction to MO.

## Conclusion

(1) The catalytic activities of maghemite on the aldol condensation of acetone and the retro-aldol condensation of diacetone alcohol are higher than those of hematite.

(2) The catalytic activity of maghemite for the formation of mesityl oxide is significantly higher than that of hematite.

(3) Maghemite has the more basic surface hydroxyl groups than hematite and far more acidic surface hydroxyl groups than hematite, which are strong enough to make the average surface acidity higher than hematite.

(4) The basic surface hydroxyl groups of maghemite are bonded to the iron ions of the octahedral sites, and the acidic ones are of the tetrahedral sites of the spinel lattice of the surface.

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