X-Ray Photoelectron Spectroscopic Study for the Reaction of Evaporated Iron with O₂ and H₂O

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Reactions of evaporated iron with O_2 and H_2O have been investigated by X-ray photoelectron spectroscopy. Binding energies of $Fe2p_{3/2}$ and $O1s$ electrons were measured during the course of reactions and their variation was discussed in terms of the positive and negative charges of the iron and oxygen of the surface oxide formed, respectively, assuming a simple charge-chemical shift relation. They are compared with the binding energies of the O1s in SiO_2, Al_2O_3, Fe_2O_3, $Cd(OH)_2$, KOH, and $Ni(OH)_2$ and those of $Fe2p_{3/2}$ in various iron compounds. High reactivity of the surface oxide with H_2O and the resulting hydroxyl group formation were observed. A rough estimation of the Fe to O atomic ratio of the surface oxide was also carried out from the ratio of the Fe and O peak areas.

Dissolution and corrosive reactions of metals are largely influenced by the presence of oxygen. In our UV absorption study[1] for acetylacetone adsorption on oxygen-treated metals, two or more chemical states have been observed for the oxygen on the metal surfaces.

X-Ray photoelectron spectroscopy,[2] giving information on the surface and semisurface of solids, seems to be useful for studying the variation in the charge of the atom in question and in the valence band during the course of surface reaction. Application of the spectroscopy for catalysis research has been reviewed recently.[3]

Two kinds of oxygen were observed for the surface oxide of nickel by X-ray photoelectron spectroscopy.[4] We report here on variations in the $2p_{3/2}$ binding energy of iron and the 1s of oxygen in an evaporated iron exposed to O_2 and H_2O. The core binding energy shifts were correlated to the charges of the atoms and compared with those of metal oxides, hydroxide and various iron compounds in order to investigate the chemical states and reactivity of the surface oxide.

Experimental

The apparatus for metal evaporation and reaction is illustrated in Fig. 1. Chamber (g) was evacuated for several hours at 10^{-6} Torr. The thin iron foil wound by tungsten filament (f) was then degassed by heating electrically and the metal was finally evaporated on copper plate (a). The iron sample was inserted (within 1 min) into chamber (c) for photoelectron measurement through a gate valve (d) without exposing the sample to air by use of rubber O-ring (e). The vacuum of (c) was 10^{-7} Torr. After recording the spectrum for the metal, the sample was pulled out to the reaction chamber and exposed to the gases to be studied. The sample plate was again inserted for spectral measurement on the surface species obtained.

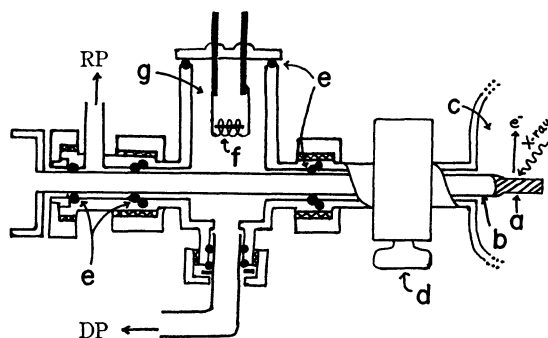Photoelectron spectra were measured with 0.1 eV step scan on a KEC-X2000 (Kokusai Electric Co.) electron

Fig. 1. Diagram of reaction chamber. (a): sample holder, (b): sample shaft, (c): photoemission chamber, (d): gate valve, (e): rubber O-ring, (f): tungsten filament, (g): reaction chamber.

spectrometer using $AlK\alpha_{1,2}$ X-ray line as an excitation source. The reproducibility of $Fe2p_{3/2}$ and $O1s$ peak positions was within 0.2 eV.

Water was distilled and degassed in a vacuum. Commercial oxygen was led into a vacuum system and was dried with liquid nitrogen cooled trap. The purity of iron was 99.99%.

SiO_2(Mallinckrodt Chemical Works) and Al_2O_3(alumina activated for chromatography, Nakarai Pure Chemicals) were heated in a crucible at 600°C for 2 hr and after being left standing for 15 hr in the air, their photoelectron spectra were measured for the powder sample pressed on an adhesive aluminum tape. Fe_2O_3 was obtained in two ways, by heating ferric oxalate in a crucible at 500°C for 5 hr or at 700°C for 3 hr. $Ni(OH)_2$ and $Cd(OH)_2$ were produced by the reaction of $Ni(NO_3)_2$ and $CdCl_2$, respectively, with aq. KOH solution. Photoelectron spectra of $K_4Fe(CN)_6$, $K_3Fe(CN)_6$, $Fe_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$, and KOH(Nakarai Pure Chemicals) were measured in powder without further purification.

Results

The $Fe2p_{3/2}$ and $O1s$ photoelectron lines from the evaporated iron exposed to O_2 are shown in Fig. 2. Binding energies have been calculated using the value of 285.0 eV for C1s line of a contaminant observed in the background spectrum of evaporated fresh iron. For the fresh iron, the $Fe2p_{3/2}$ peak is located at 708.2 eV and the O1s at 532.4 and 530.6 eV (case a). The metal was then exposed to O_2 in succession (b, 0.01

1) K. Kishi, S. Ikeda, and K. Hirota, *J. Phys. Chem.*, **71**, 4384 (1967); K. Kishi and S. Ikeda. *ibid.*, **73**, 729 (1969).

2) K. Siegbahn, *et al.*, "ESCA; Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almqvist and Wiksells, Uppsala, 1967.

3) W. Delgass, T. R. Hughes, and C. S. Fadley, *Data Rev.*, **4**, 179 (1970).

4) K. Kishi and S. Ikeda, *Chem. Lett.*, **1972**, 245.

TABLE 1. BINDING ENERGIES AND INTENSITIES[a] OF $Fe2p_{3/2}$ AND O1s LINE FROM EVAPORATED IRON EXPOSED TO O_2

| Oxidation condition | $Fe2p_{3/2}$ | | O1s | |
	Binding energy (eV)	Intensity	Binding energy (eV)	Intensity
Fresh iron	708.2	100	530.7	4
		0	532.4	6
0.01 Torr O_2	708.2	42	530.7	19
1 min	711.4(3.2)[b]	34	532.7	10
0.5 Torr O_2	708.2	32	530.7	26
1 min	711.4(3.2)	35	532.7	11
10 Torr O_2	708.2	18	530.7	34
5 min	711.9(3.7)	36	532.7	12
100 Torr O_2	708.2	9	530.7	35
30 min	712.2(4.0)	37	532.7	13
$K_4Fe(CN)_6$	710.2(2.0)			
$K_3Fe(CN)_6$	711.6(3.4)			
Fe_2O_3	712.4(4.2)			
$Fe_2(C_2O_4)_3 \cdot 6H_2O$	713.8(5.6)			
$Fe_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$	714.4(6.2)			
SiO_2			534.5	
Al_2O_3			532.5	
Fe_2O_3			530.4	
$Cd(OH)_2$			532.7	
KOH			531.9	
$Ni(OH)_2$			531.9	

a) The intensities are obtained from the respective peak areas and normalized with respect to the area of $Fe2p_{3/2}$ in fresh iron (100).

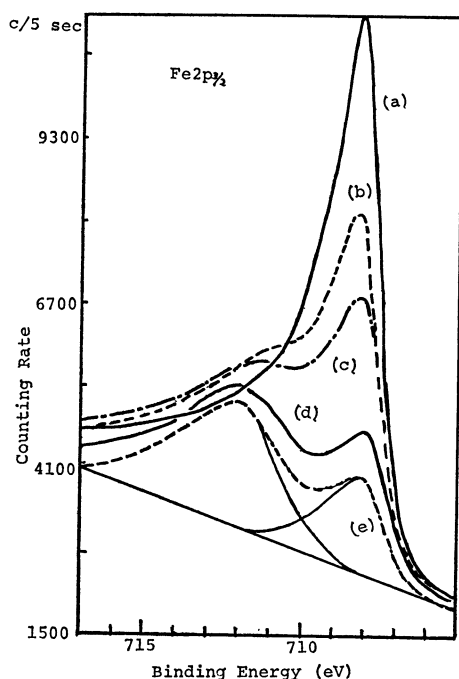b) Chemical shifts from genuine Fe are given in parentheses.

Fig. 2-(i). $Fe2p_{3/2}$ photoelectron lines from evaporated iron exposed to O_2 in succession. (a): fresh iron, (b): 0.01 Torr O_2; 1 min, (c): 0.5 Torr; 1 min, (d): 10 Torr; 5 min, (e): 100 Torr; 30 min.

Torr, 1 min; c, 0.5 Torr, 1 min; d, 10 Torr, 5 min; e, 100 Torr, 30 min). The genuine Fe peak was depressed and another peak appeared at high energy
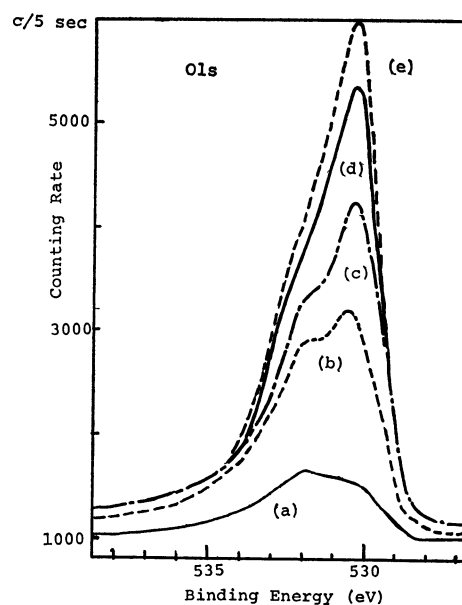

Fig. 2-(ii). O1s photoelectron lines from evaporated iron exposed to O_2 in succession.

side. The chemical shift of this peak from the genuine one varied from +3.2 eV in case b to +4.0 eV in case e. With O peak, two peaks were observed and the low energy one increased mainly in intensity after oxidation, showing no shift in binding energy. These results of chemical shift and intensity are summarized in Table 1, with the corresponding chemical shifts

of various compounds for comparison. Each peak area was estimated by resolving roughly the two peaks graphically as exemplified by case e. In the case of $Fe2p_{3/2}$ peaks, the two peaks were resolved on considering the shape of fresh metal and bulk oxide peaks. However, the maximum peak positions and the peak area of the surface oxide could not be accurately determined, especially in the case of (b), because of their unsymmetrical profiles. Approximate values for Fe peaks are listed in Table 1.

Figure 3 shows the $Fe2p_{3/2}$ and the Ols peaks from the evaporated iron exposed to H_2O in succession (a, fresh iron; b, 1 Torr, 1 min; c, 15 Torr, 30 min; d, 15 Torr, 2 hr). As an example, the second Fe appeared at +3.2 eV from the genuine Fe in case d. With Ols, the high energy peak is larger in intensity than the other, unlike the cases for oxidation with O_2.
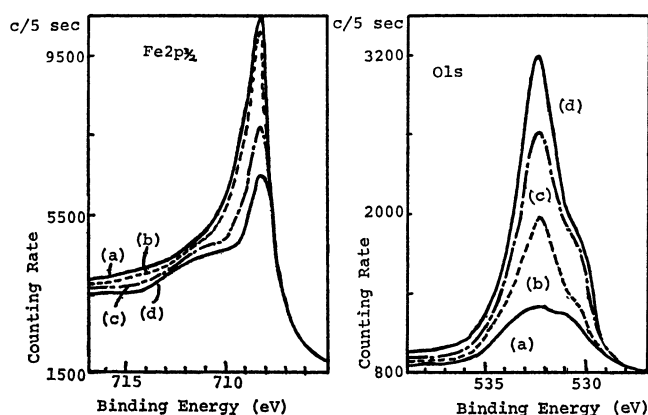

Fig. 3. $Fe2p_{3/2}$ and Ols photoelectron lines from evaporated iron exposed to H_2O in succession. (a): fresh iron, (b): 1 Torr H_2O; 1 min, (c): 15 Torr; 30 min, (d): 15 Torr; 2 hr.

Figure 4 shows the spectra of $Fe2p_{3/2}$, and Ols electrons. The $Fe2p_{3/2}$ for the surface oxide (case a, after exposing the metal to 200 Torr O_2 for 30 min) shifted 0.6 eV to low energy after the reaction with H_2O (15 Torr) for 1 hr (case b). The low energy Ols was depressed and the high energy one enhanced.
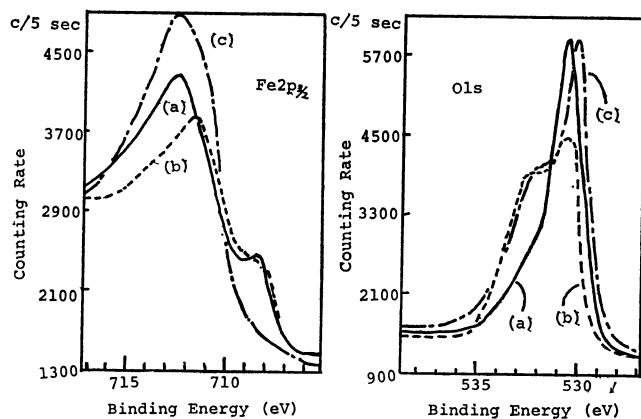

Fig. 4. Reaction of surface oxide with H_2O. $Fe2p_{3/2}$ and Ols photoelectron lines from, (a): iron metal exposed to 200 Torr O_2 for 30 min, (b): the surface oxide exposed to 15 Torr H_2O for 1 hr, (c): Fe_2O_3. (Counting rate unit for Fe_2O_3 is arbitrary.)

When Fe_2O_3 (case c, obtained by heating ferric oxalate at 700°C for 3 hr) was treated with H_2O for 2 hr, only a slight change was observed for the Ols peaks and none at all for the $Fe2p_{3/2}$.

Discussion

The high energy Ols peak for fresh iron is likely to be assigned to a contaminant or absorbed species except for the oxide since the low energy peak increased mainly in intensity (after exposing the metal to O_2). Measurable carbon and oxygen peaks due to a contaminant were also reported for prereduced Pt foil.[3] The peak area ratio of the high energy Ols to the Cls due to a contaminant, however, differs from that of fresh iron and gold, the ratio being larger considerably for iron. This suggests that on iron surface the active gases such as CO, CO_2, H_2O adsorbed with strong chemical force and hydrocarbons predominate on gold.

The low energy Ols for fresh iron can be assigned to the oxygen on the metal with a small amount of surface oxide under the pressure of 10^{-6}—10^{-7} Torr. The corresponding $Fe2p_{3/2}$ peak, however, could not be detected because of the broad tailing of the peak of high energy side. After reaction of the fresh iron with O_2, the second $Fe2p_{3/2}$ peak appeared, followed by the enhancement of the low energy Ols being shifted +3.2 eV (case b, c), +3.7 eV (d), and +4.0 eV (e) to high energy from the genuine Fe, as shown in Fig. 2. When the fresh iron was exposed immediately to 200 Torr O_2 for 30 min, the Fe shifted +4.2 eV, the same binding energy as for Fe_2O_3. The chemical shifts of Fe3p electrons of various iron compounds have been reported;[5] K_2FeO_4 (+5.3 eV from Fe metal), K_3FeF_6 (+5.3 eV), $K_3Fe(CN)_6$ (+2.6 eV) and Fe_2O_3 (+2.5 eV). If we assume that the localized positive charges on iron atoms are 3 and 0 in K_3FeF_6 and Fe metal, respectively, and that the Fe3p binding energies reflect only the charge of the metal and have a linear dependence on the charge, the positive charge of Fe in Fe_2O_3 is estimated to be 1.4.[6] In our results with $Fe2p_{3/2}$, the corresponding chemical shifts for all compounds measured are larger than those with the above 3p electrons (Table 1) and the shift of Fe_2O_3 is larger than that of $K_3Fe(CN)_6$. Assuming the positive charge of 1.5 for Fe_2O_3 giving the 4.2 eV shift of $Fe2p_{3/2}$, the iron atom in the surface oxide is considered to transfer, on the average, about 1.1 and 1.5 electrons to oxygen atoms when the chemical shift of the iron atom is +3.2 eV and +4.2 eV, respectively, after exposure to O_2. The localized charges

5) L. N. Kramer and M. P. Klein, *J. Chem. Phys.*, **51**, 3618 (1969).

6) In order to treat the relation of charge-chemical shift more strictly, a correction due to crystal potential effect should be included. However, there are several findings indicating that the expected differences in crystal potentials do not appear in the measured values. For example, the observed Nls binding energies are almost the same for the nitrates, $NaNO_3$ (407.4 eV), NH_4NO_3 (407.2 eV), and $[Rh(NH_3)_6](NO_3)_3$ (407.3 eV) (W. L. Jolly, *et al.*, *Inorg. Chem.* **8**, 2642 (1969). There are also no differences in the Al2p spectra for kaolinite (Al: 6-coordinate), microcline (4-coordinate), and sillimanite (half, 4-coordinate; half, 6-coordinate).[3]

on Fe in these oxides are not so large as in $Fe_2(C_2O_4)_3 \cdot 6H_2O$ (estimated charge, $+2.0$) and $Fe_2(SO_4)_3(NH_4)_2\text{-}SO_4 \cdot 24H_2O$ ($+2.2$). In the latter, the number of H_2O is uncertain because of release of H_2O on evacuation. As an example, the dark green $[Cr(H_2O)_4Cl_2]Cl$ turned purple-red after photoelectron measurement, the coloration being immediately restored after exposure to air. This indicates that the H_2O is released from the complex on evacuation.

The Fe to O atomic ratio of the surface oxide was estimated roughly as follows. The peak area ratio of low energy Ols to $Fe2p_{3/2}$ and to Fe3p in Fe_2O_3 were approximately 1.3 and 1.9, respectively. These values, however, can not be used directly for the estimation of the Fe to O ratio of the surface oxide since electrons of low kinetic energy can only escape from near the surface, whereas electrons of high kinetic energy can escape from deeper inside the material, as illustrated in Figure 5. The kinetic
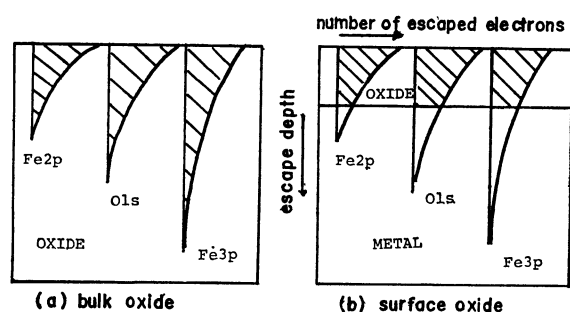

Fig. 5. Intensity-oxide depth relation for $Fe2p_{3/2}$, Ols, and Fe3p lines from surface oxide.

energy of electrons ejected from the Ols orbital (ca. 950 eV) is larger than that from the $Fe2p_{3/2}$ (ca. 770 eV), the escape depth thus being deeper for the former. Therefore, for the surface oxide where the genuine metal peak remains, the apparent peak area ratio (Ols/$Fe2p_{3/2}$) becomes smaller, as shown by the difference in the shaded parts of (a) and (b) in Fig. 5. This situation is reversed on the Ols to Fe3p (kinetic energy: ca. 1430 eV). In fact, the peak area ratio of metal-iron to oxide-iron was larger in the observation of the Fe3p electrons than in the $Fe2p_{3/2}$. For the surface oxide obtained after exposure to 200 Torr O_2 for 30 min, the observed peak area ratios of the Ols to the $Fe2p_{3/2}$ and to the Fe3p are about 1.0 and 1.9, respectively. This indicates that the Fe to O ratio is between about 1 : 1.2 and 1 : 1.5. On considering the differences in the kinetic energies (Ols-$Fe2p_{3/2}$: 180 eV, Fe3p-Ols: 480 eV), the Fe to O ratio is expected to be near 1 : 1.3. For the surface oxide $Fe_{1.0}O_{1.3}$, the negative charge of the oxygen is evaluated as about 1.1 using the positive charge of 1.5 for iron atom. The total area of the $Fe2p_{3/2}$ peaks decreased during the oxidation reaction. This might be due to the dilution of iron atoms with oxygen atoms (ionic radii: O^{2-}, 1.40 Å; Fe^{3+}, 0.64 Å) and the different mean escape depth between iron metal and oxide. For the surface oxide after exposure to 0.01 Torr O_2 for 1 min, the Fe to O ratio is approximately 1 : 0.7 and their estimated charges are $+1.1$

and -1.6 on Fe and O atoms, respectively. However, the binding energy difference was not observed for the oxygen atoms with the negative charges -1.1 and -1.6. This may be due to an inaccurate estimation of Fe to O peak area ratio in case b (Fig. 2).

The binding energy of Ols of the surface oxide is smaller than that of SiO_2 and Al_2O_3 by 3.7 and 1.7 eV, respectively, and larger than that of Fe_2O_3 by 0.3 eV. Although it is concluded from the chemical shift of $Fe2p_{3/2}$ that the surface oxide shows a larger covalent bonding than in other oxygen-coordinating compounds in the above discussion, of the metal oxides the surface oxide of iron exhibits larger ionicity than SiO_2 or Al_2O_3 as shown from the binding energy of Ols electrons. The linearity of the chemical shift-charge relation of the Ols peak is not so good as for the Nls or the Cls, but the negative charge of 0.5 corresponds roughly to the 3.5 eV shift.[7] The Ols binding energy of SO_4^{2-} is about 2.5 eV larger than that of Fe_2O_3 and the negative charge of oxygen in SO_4^{2-} was evaluated to be 0.83 from the positive charge of sulfur.[2] The 2.5 eV shift leads to the negative charge of about 1.18 for the oxygen in Fe_2O_3. The value is near that obtained from the positive charge of iron atom, 1.0, although the above relation could not be applied to the energy difference between the surface oxide and Fe_2O_3. In spite of larger negative charge the Ols binding energy of the surface oxide is larger by 0.4 eV than that of Fe_2O_3. We could not explain this although the Cls binding energy can not be taken as the same value for the two oxides as energy reference.

When the surface oxide was treated with H_2O, the low energy Ols was depressed followed by the enhancement of the high energy one (Fig. 4). The Ols main peak is also the high energy one when the fresh iron was exposed to H_2O (Fig. 3). The high energy Ols (532.6 eV) is located between the Ols binding energies of $Cd(OH)_2$ (532.7 eV) and KOH or $Ni(OH)_2$ (531.9 eV). This suggests that the hydroxyl group was formed on the reaction of the fresh iron or the surface oxide with H_2O. In the former, the reaction may be caused by a mixture of H_2O and O_2 remaining due to incomplete removal. When one oxide-oxygen was displaced by $2OH^-$, the total area of low and high energy Ols peaks should increase by the same amount with the decreased area of the low energy peak after reaction compared with the total area before reaction. In the spectrum the increase in the total area is actually indicated but the increased amount is somewhat smaller than expected. This is probably due to the depression of the Ols peaks caused by the increase of a contaminant hydrocarbon on the surface.

Fadley and Shirley[8] measured the photoelectron peaks of Fe foil heated in 10^{-2} Torr H_2 atmosphere and observed two oxygen peaks. The low energy Ols disappeared first at 360°C and was suggested to be assigned to more weakly adsorbed oxygen-containing

7) K. Siegbahn, et al., "ESCA Applied to Free Molecules," North-Holland Pub. Co., Amsterdam (1969).

8) C. S. Fadley and D. A. Shirely, Phys. Rev. Lett., 21, 980 (1968).

gases. The high energy Ols, remaining even at 600°C, was assigned to the oxygen of the surface oxide. From the present study, the low energy one is more accurately assigned to the surface oxide-oxygen, and the disappearance of this peak after heating in the hydrogen stream can, therefore, be explained by the reduction of the oxide-oxygen with H_2 and consequent formation of hydroxyl group giving the high energy Ols peak. The hydroxyl group formation on iron surface will be also expected for the iron metal immersed in an aqueous solution. Experiments on the degree of depression of the low energy peak after reaction with H_2O suggested the hydroxyl group formation to be easier for the iron metal with fewer oxide layer. As an extreme case, Fe_2O_3 showed no such formation of hydroxyl group even after being exposed to H_2O for 2 hr although the high energy Ols peak may be due in part to the hydroxyl group formed already during the production of the Fe_2O_3. Such behavior was also observed for the acetylacetone adsorption on oxygen treated metal by UV absorption spectra.[1] Acetylacetone adsorption was accelerated after iron or manganese film was exposed to oxygen (1 Torr) for 1 min, but not detected on the metal oxide obtained by heating the metal film in the air at 200°C for 1.5 hr.

Hydrogen bonding is explained by the formation of molecular complex where partial electron transfer occurs from the proton-accepting species to the antibonding orbital of, for example, O–H bond of the proton donating species,[9] the O–H dissociation being an extreme case. The above hydroxyl group formation on the iron surface is also expected to occur followed by electron transfer from oxygen of the surface oxide to the antibonding orbital of H_2O. Thus, a higher reactivity to H_2O will be expected for the iron metal with a slight oxidation, where the oxygen atom has more localized orbital, donating electrons to H_2O, than for one in bulk oxide because of incomplete formation of the bulk oxide structure.

The $Fe2p_{3/2}$ chemical shift to low energy on reaction with H_2O suggests that the Fe–O bond became more covalent in the hydroxide.

Iron surface is easily oxidized to give approximately

20 Å of oxide under the conditions of 10^{-4} Torr oxygen and room temperature.[10] This oxide layer increased to about 25 Å at 760 Torr O_2. Under the present oxidation conditions of 100 Torr O_2, 30 min, and room temperature, the iron surface is expected to be oxidized approximately to the same depth. The peak area of low energy Ols for fresh iron has 1/9 area of the corresponding one obtained after oxidation with 100 Torr O_2 for 30 min. Assuming 25 Å thickness of the latter surface oxide, the oxide layer for fresh iron is estimated to be thinner than 3 Å. However, a relatively rapid formation of four oxide layers has been reported under the condition of 2×10^{-7} to 5×10^{-6} Torr and 24°C.[11] On the other hand, assuming the four oxide layers for the present fresh iron, a thickness larger than 100 Å is derived for the surface oxide after exposing to 100 Torr O_2. Further attempts are necessary for a quantitative discussion on the depth of the oxide layers. The escape depth of electrons for the above metal with the surface oxide is slightly larger than the thickness of the oxide layer obtained after reaction with 100 Torr O_2 for 30 min, since the genuine Fe peak still can be detected but with weak intensity. Estimated range of escape depth: 8 Å for 362 eV electrons in case of Ag[12] and ca. 100 Å for 860 eV electrons in that of iodostearic acid.[2] In the case of Au, an escape depth of 22 Å has been observed for 1200 eV electrons.[13] From these results and the dependence of the depth on the kinetic energy of electrons and on the atomic number of materials, the depth of the oxide for the fresh iron seems to be thinner than four oxide layers.

The above photoelectron data indicate the important role of oxygen in the dissolution reaction of metals into aqueous solution; in this case for iron, the formation of a transient oxide to bulk oxide with high reactivity to H_2O was revealed.

9) a) R. S. Mulliken and W. B. Person, "Molecular Complexes," Wiley-Interscience, New York, 1969. b) N. Mataga and T. Kubota, "Molecular Interactions and Electronic Spectra," Marcel Dekker, Inc., New York, 1970.

10) J. Kruger and H. T. Yolken, Corosion, 20, 29 (1964).
11) S. Chang and W. H. Wade, J. Phys. Chem., 74, 2484 (1970).
12) P. W. Palmberg and T. N. Rhodin, J. Appl. Phys., 39, 2425 (1968).
13) Y. Baer, P. Heden, J. Hedman, M. Klasson, and C. Nordling, Solid State Comm., 8, 1479 (1970).