A Study of Mechano-Catalysts for Overall Water Splitting

Michikazu Hara, Mutsuko Komoda, Hironori Hasei, Masaaki Yashima, Sigeru Ikeda, Tsuyoshi Takata, Junko N. Kondo, and Kazunari Domen*,‡

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan, and CREST, JST (Japan Science and Technology)

Received: September 24, 1999; In Final Form: November 17, 1999

Mechano-catalytic overall water splitting on Cu_2O, NiO, and Co_3O_4 was investigated in order to reveal the reaction mechanism. The experimental results indicated that metallic elements of these oxides were generated during the reaction. Also, elemental metals Cu, Ni, and Co were oxidized into Cu_2O, NiO, and Co_3O_4, respectively, when water was reduced into H_2 by the metal powders under the same reaction condition. The metallic particles covered with the metal oxides evolved both O_2 and H_2. These results suggest that a redox reaction between the metal and metal oxide may be responsible for H_2 and O_2 formation of the mechano-catalytic overall water splitting.

1. Introduction

Recently, the authors have reported that an overall water splitting has been accomplished by suspending metal oxides such as Cu_2O, NiO, Co_3O_4, and Fe_3O_4 in distilled water with magnetic stirring in a glass reaction vessel at room temperature, without injection of any other photonic or electric energies.[1−4] During our research work for developing photocatalytic systems to accomplish overall water splitting based on metal oxides under visible light irradiation, it was accidentally found that some Cu-(I)-containing oxides evolved H_2 and O_2 simultaneously from distilled water.[2,5] So, it was first regarded that the reaction was driven by the energy of visible light photons.[5] When further studies were conducted on the system, however, some unusual aspects judging from the conventional reaction mechanism of semiconductor-based photocatalytic reactions were found. For example, H_2 and O_2 evolution continued for a long period even after the irradiation was stopped. We at first tried to interpret such a phenomenon as photoexcited electrons and holes reacting with the components of the oxide, i.e., the excited states were localized to form chemical species such as Cu(0) and O^- species. Then, such energetic chemical species gradually reacted with water to form H_2 and O_2. If this mechanism were correct, it might be possible to obtain some amount of H_2 and O_2 after the irradiation was stopped. However, the amount should be much smaller than that of the catalyst employed, because no significant change of the catalyst before and after the reaction was observed by XRD and XPS. To our surprise, however, in carefully controlled reactions H_2 and O_2 evolution continued in dark and the total molar amount of evolved gases far exceeded that of the catalyst. However, when magnetic stirring of the catalyst was stopped, no evolution of H_2 and O_2 occurred. Thus, we realized that the H_2 and O_2 evolution is *not* due to photocatalytic reaction but to some other mechanism that had been missed.[1] From various phenomenological aspects, it has been confirmed that mechanical energy given to the oxide particles between a rotating stirring rod and a reaction vessel is responsible for the reaction. We, therefore, regarded the reaction converting mechanical energy into chemical energy as "mechano-catalytic" overall water splitting.[1−4] In the field of mechanochemistry or tribochemistry,[6−8] some stoichiometric reactions of $\Delta G > 0$ are known to proceed by irreversible processes derived from mechanical energy such as grinding or frictional wear of materials, but a catalytic reaction has not yet been reported. Various phenomena such as electrostatic charge formation, emission of exo-electron, etc. accompanied by the change of solid materials have been proposed as being responsible for such stoichiometric reactions in mechanochemistry.[6−8] These phenomena may be included in but still cannot fully explain the mechano-catalytic overall water splitting.

The phenomenological aspects of mechano-catalytic overall water splitting have been reported in detail in our previous papers, especially in ref 3. Some characteristic features to be noted of mechano-catalytic overall water splitting are as follows:

(1) The reaction proceeds by the mechanical energy provided by rubbing the oxide powder at the interface between a rotating stirring rod and the bottom of a reaction vessel. Any vigorous stirring without rubbing the bottom of the reaction vessel cannot cause the reaction, suggesting that the collision between the oxide particles or with the stirring rod is ineffective. The rate of H_2 and O_2 evolution monotonically increases with the rate of rotation of a stirring rod.

(2) The reaction is highly dependent on the type of oxide material. Effective materials are NiO, Co_3O_4, Cu_2O, Fe_3O_4, RuO_2, and IrO_2 among binary oxides. Interestingly, CuO and Fe_2O_3 are inert. Some ternary oxides containing Cu(I), Ni(II), or Co(II) such as $CuAlO_2$ and $CuFeO_2$ also show the activity. Typical photocatalysts such as TiO_2 and ZnO are completely inactive.

(3) The reaction is also dependent on the material of the bottom of the reaction vessel. Quartz and Pyrex glasses gave the best results among the materials examined so far. Alumina and CaF_2 also showed low but definite activity. Some organic materials such as PTFE and acrylate were also examined, and a small amount of H_2 but no O_2 was obtained.

(4) The conversion efficiency from mechanical to chemical energy is a few percent. Mechanical energy is that consumed at the interface between the rotating stirring rod and the bottom of the reaction vessel, *which was estimated by the torque and*

---

‡ CREST.

Mechano-Catalysts for Overall Water Splitting

J. Phys. Chem. B, Vol. 104, No. 4, 2000 **781**

the rate of revolution in water with and without rubbing the bottom of the vessel. The chemical energy estimated by the rate of water decomposition was then divided by the mechanical energy (see ref 3 for details). A typical value for NiO in a Pyrex reaction vessel is 4.3%.

(5) The reaction rate depends on the ambient pressure. The reaction is typically carried out under reduced pressure where only water vapor remains in a closed gas circulation system. With increasing pressure of H_2 and O_2 in the system, the reaction rate decreases. Typically, when $30-100$ Torr (1 Torr = 133.3 Pa) of H_2 and O_2 mixture is accumulated, the system is evacuated to continue the reaction.

(6) Distilled water seems to be the best media for the reaction. Whenever any electrolytes are added, the rate of H_2 and O_2 evolution is retarded. When the reaction was carried out in a mixture of methanol and water, both H_2 and O_2 evolutions were observed, although the amount of O_2 was slightly less than stoichiometric. In water vapor atmosphere without liquid water, no reaction takes place.

(7) From the isotope experiment using a $H_2^{18}O/H_2^{16}O$ mixture, the isotope composition of evolved O_2 coincided with that of water within the experimental error.

(8) No photoirradiation effect is observed for all mechano-catalysts except Cu_2O.[1,2,4,5] However, even for Cu_2O it is not attributed to the photon energy conversion but to some effect that maintains the higher activity of the mechano-catalytic reaction by some unknown mechanism.[4]

In this work, we focused our attention on the chemical states of the catalysts during the mechano-catalytic overall water splitting on Cu_2O, NiO, and Co_3O_4 to find a clue that may lead to better understanding of the reaction mechanism of this new but somewhat curious reaction.

2. Experimental Section

Cu_2O, Nafion-deposited Cu_2O (Nafion/Cu_2O), NiO, and Co_3O_4 were used as mechano-catalysts in this study. NiO (particle size 1 μm, surface area 1.5 $m^2\ g^{-1}$) and Co_3O_4 (particle size 1 μm, surface area 1.0 $m^2\ g^{-1}$) were obtained from Kanto Chemical Co. and used as received. Cu_2O powder prepared from reduction of Fehling's solution was used.[1,4] Fehling's solution was prepared by boiling a mixture of 1.0 M aqueous $CuSO_4$ solution (50 cm^3), 1.3 M aqueous potassium sodium tartrate ($KNaC_4H_4O_6$) solution (50 cm^3), and 18.8 M aqueous NaOH solution (50 cm^3). Cu_2O was precipitated by adding 0.5 M aqueous D-glucose solution (25 cm^3) to boiling Fehling's solution with vigorous stirring under Ar flow. Cu_2O as a red precipitate was washed with distilled water (200 cm^3) $5-7$ times, followed by decantation and drying in vacuo. The particle size and surface area of Cu_2O were estimated to be $4-6$ μm and 2.5 $m^2\ g^{-1}$ by scanning electron microscope (SEM) and BET measurements, respectively. Next, $0.5-8.0$ wt % of Nafion was deposited onto the Cu_2O by evaporating solvent from a mixture of 1 g of Cu_2O, Nafion and 15 cm^3 of 2-propanol in a rotary evaporator at room temperature.[4] Nafion (5 wt % solution in a mixture of lower aliphatic alcohols and water) was obtained from Aldrich Chemical Co., Inc. No impurities were observed for Cu_2O, NiO, and Co_3O_4 by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements.

The reaction was carried out in a flat-bottomed reaction vessel made of Pyrex glass,[3] which was attached to a closed gas circulation system (about 800 cm^3) equipped with an evacuation line and a gas chromatograph. Each catalyst (0.1 g) was suspended in 120 cm^3 of distilled water by a PTFE-sealed
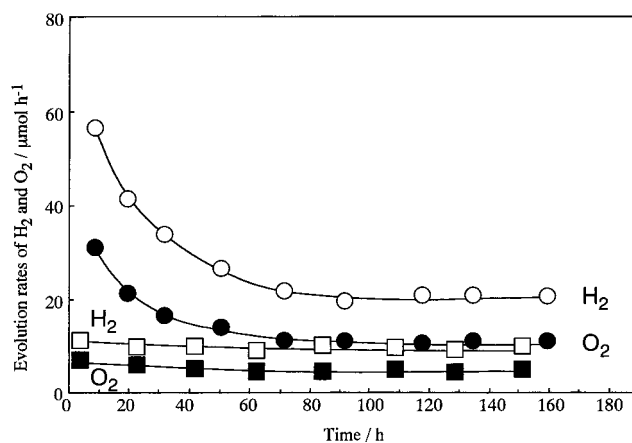

Figure 1. Time courses of the evolution rates of H_2 and O_2 on Cu_2O and Nafion (5 wt %)/Cu_2O. Open and filled squares are H_2 and O_2, respectively, on Cu_2O. Open and filled circles are H_2 and O_2, respectively, on Nafion/Cu_2O. The reaction system was evacuated at $20-30$ h intervals, and the evolution rates were measured after 5 h from the evacuation.

columnar stirring rod with a flat plane, which was rotated on the flat bottom of the reaction vessel. The stirring rod had a diameter of 8 mm and a length of 40 mm. The stirring rod was magnetically rotated (F205, Tokyo Garasu Kikai) at the revolution rate of 1200 rpm. Before reactions, the gas phase was completely evacuated to remove dissolved O_2 and N_2 in the distilled water, and only water vapor remained. The reaction was performed at room temperature in the dark, where the reaction vessel was completely shielded by aluminum foil. The evolved gas was accumulated and was analyzed by gas chromatography.

For XPS and XRD measurements of catalysts after the reaction, the distilled water in the reaction vessel was evaporated in vacuo (1×10^{-2} Torr) at room temperature without exposure to the atmosphere. Each catalyst was recovered in a test tube made of Pyrex glass under Ar flow, and the test tube was sealed under vacuum. Catalysts were transferred from the test tubes to XPS apparatus using an Ar grove box to prevent oxidation by oxygen and water in air.

Mechano-catalytic overall water splitting in $KI-I_2$ solution was also examined. The reaction was performed in a cylindrical test tube made of Pyrex glass (a diameter of 30 mm and a length of 70 mm), being attached to the closed gas circulation system. The test tube, containing 40 cm^3 of $KI-I_2$ solution (KI 18 mM, and I_2 0.36 mM), 0.1 g of catalyst, and a PTFE-sealed columnar stirring rod with a flat bottom (5 mm in diameter, 12 mm length), was carefully evacuated by $4-5$ cycles of freezing by liquid N_2 and evacuation in order to remove dissolved O_2 and N_2 in the $KI-I_2$ solution without the sublimation of I_2 from the solution. The mechano-catalytic reaction was performed in a similar manner as above. After the reaction, the suspension was centrifuged, and the amount of I_2 in the supernatant solution was measured by UV-vis spectroscopy.

3. Results

3.1 Reduction of Cu_2O into Elemental Metal Cu during Mechano-Catalytic Overall Water Splitting. Figure 1 shows time courses of the rates of H_2 and O_2 evolution on Cu_2O and 5 wt % Nafion-deposited Cu_2O (Nafion/Cu_2O). Among various amounts of Nafion-deposited Cu_2O, 5 wt % Nafion/Cu_2O exhibited the highest activity.[4] Thus, 5 wt % Nafion/Cu_2O was used in this study. The reaction system was evacuated at

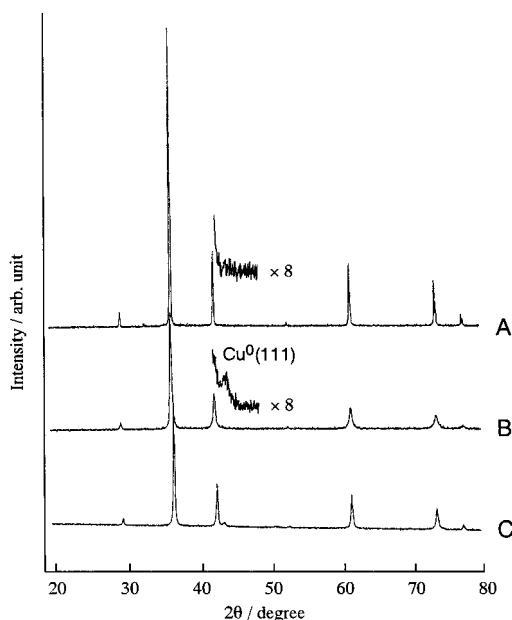**782** *J. Phys. Chem. B, Vol. 104, No. 4, 2000*

Hara et al.

Figure 2. XRD patterns of Cu_2O before and after the reaction for 160 h. A: Cu_2O before reaction. B: Cu_2O after reaction. C: Nafion/Cu_2O after reaction.

TABLE 1: Particle Size and BET Surface Rrea of Mechano-Catalysts before and after Reaction

	before reaction		after reaction	
	particle size (μm)	surface area ($m^2 g^{-1}$)	particle size (μm)	surface area ($m^2 g^{-1}$)
NiO	1	1.5	0.8−1	2.4
Co_3O_4	1	1.0	0.8−1	2.0
Cu_2O	4−6	2.5	<2	13.0
Nafion/Cu_2O	4−6	2.0	<2	12.5

Because mechano-catalytic overall water splitting proceeds by rubbing the catalysts,[1−4] one may suspect that the grinding of catalyst particles is responsible for the reaction. The particle sizes and surface areas of Cu_2O, Nafion/Cu_2O, NiO, and Co_3O_4 before and after the reaction for 24 h are summarized in Table 1. The particle sizes and surface areas were estimated by secondary electron microscope (SEM) and BET measurements, respectively. *The surface area of Cu_2O appeared larger than expected from the particle size because of the spiny shape of each particle.*[4] Each particle was ground to smaller particles during the reaction for 24 h, but the particles were not further ground during the subsequent reaction for 100 h. These results imply that the grinding of the metal−oxide particles is completed at the very early stage of the reaction and is not directly related to the reaction, because the rate of H_2 and O_2 evolution on the metal oxides is independent of the rate of grinding of the particles.

3.2 Reduction of NiO and Co_3O_4 during Mechano-Catalytic Overall Water Splitting. Whereas Cu_2O was reduced into metallic Cu during the reaction as confirmed by XRD, no metallic Ni or Co was observed on NiO or Co_3O_4 after the reaction for 50 h. These results, however, do not immediately mean that NiO and Co_3O_4 are not reduced into the metals during reaction; metallic species might not be observed on these metal oxides after the reaction as a result of instantaneous reoxidation of the metallic species by the reaction with water. To examine whether NiO and Co_3O_4 are reduced into the metals during the reaction, the mechano-catalytic overall water splitting reactions on NiO and Co_3O_4 were performed in $KI−I_2$ solution. $KI−I_2$ solution is often utilized for the detection of metals in metal oxides.[9,10] I_2 in $KI−I_2$ solution oxidizes transition metals such as Ni and Co, denoted as M, as shown by the formula $M + I_2 \rightarrow MI_2$. The amount of metal is estimated from the amount of consumed I_2 or I_3^-.

Figure 3 shows time courses of H_2 and O_2 evolution on NiO and Co_3O_4 in $KI−I_2$ solution (pH = 6.7). At the early stages of both reactions (1 h), O_2 but no H_2 evolution was observed. The H_2 evolution with O_2 began in the subsequent reactions. UV−vis spectra of the $KI−I_2$ solution before and after the reaction (4 h) are shown in Figure 4. The absorption peaks due to I_3^- at 290 and 350 nm after reaction decreased in intensity by 40−60% compared to those before reaction, indicating the decrease of I_2 in the solution. The amounts of decreased I_2 in the reactions on NiO and Co_3O_4 were estimated to be about 5.8 and 8.6 μmol, respectively (I_2 concentration before reaction was 0.36 mM (14 μmol in the reaction test tube)). When each metal oxide was kept in $KI−I_2$ solution for 4 h without stirring, there was no noticeable difference in the UV−vis spectra of the $KI−I_2$ solution before and after the experiments. One of the possible explanations for the decrease of I_2 is the formation of hydroiodic acid, which might be formed when evolved H_2 reacts with I_2 in the solution. Assuming that the consumed I_2 was reacted to form HI, each solution after the reaction was expected to become acidic, at about pH = 4. However, the pH of each $KI−I_2$ solution
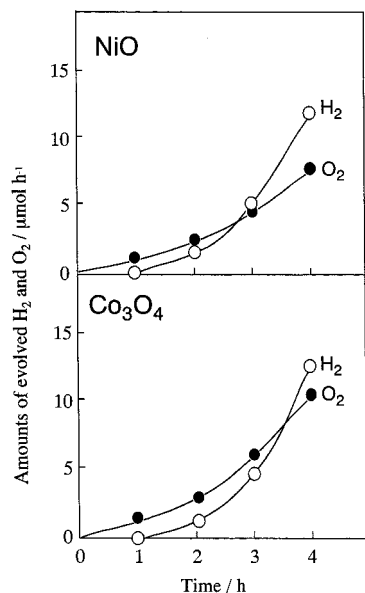
20−40 h intervals because the rates of H_2 and O_2 evolution gradually decreased with the accumulation of the evolved gas. A similar effect of gaseous pressure was observed for other three active oxides, i.e., NiO, Co_3O_4, and Fe_3O_4, as mentioned above.[1,3] The evolution rates were measured at 5 h after each evacuation. Stoichiometric H_2 and O_2 evolution proceeded without any decrease in activity for 150 h on Cu_2O. The rates of H_2 and O_2 evolution on Nafion/Cu_2O were much higher than those on the bare Cu_2O, especially at the early stage of the reaction (0−24 h), but they gradually decreased with reaction time. The rates of H_2 and O_2 evolution on Nafion/Cu_2O were almost constant after 90 h and were about 2 times higher than those on bare Cu_2O. Total amounts of evolved H_2 after 150 h were 1.3 and 3.5 mmol on the bare Cu_2O and Nafion/Cu_2O, respectively, and much exceeded the amount of the employed Cu_2O (0.1 g, 0.7 mmol).

Figure 2 shows the XRD patterns of Cu_2O and Nafion/Cu_2O before and after the reaction for 150 h. The XRD pattern of Nafion/Cu_2O before the reaction was the same as that of the bare Cu_2O (Figure 2A). A small but clear peak due to metallic Cu (Cu(111)) appeared in the XRD pattern for Cu_2O after the reaction (Figure 2B), which was absent before the reaction (Figure 2A). The peak became observable in a XRD pattern of Cu_2O even after the reaction for 10 h, and the shape and intensity remained unchanged after 20 h. The XRD pattern of Nafion/Cu_2O after reaction (Figure 2C) exhibited a larger diffraction of metallic Cu than in Figure 2B. The behavior of the diffraction peak due to metallic Cu in Nafion/Cu_2O was similar to that in bare Cu_2O. When Cu_2O and Nafion/Cu_2O were allowed to stand in distilled water for 500 h without stirring, H_2 and O_2 were not evolved at all, and no diffraction peak of metallic Cu appeared in the XRD patterns for both samples. These results indicate that there is a reducing process of Cu_2O into metallic Cu during the mechano-catalytic reaction on Cu_2O and Nafion/Cu_2O. Taking into account the results that the amount of metallic Cu formed on Nafion/Cu_2O was larger than that on the bare Cu_2O and that Nafion/Cu_2O had a higher activity for water splitting, the reduction process of Cu_2O into metallic Cu may be involved in the catalytic reaction cycle.

Mechano-Catalysts for Overall Water Splitting

J. Phys. Chem. B, Vol. 104, No. 4, 2000 **783**

Figure 3. Time courses of H_2 and O_2 evolution on NiO and Co_3O_4 in $KI-I_2$ solution. Open and filled squares are H_2 and O_2, respectively.
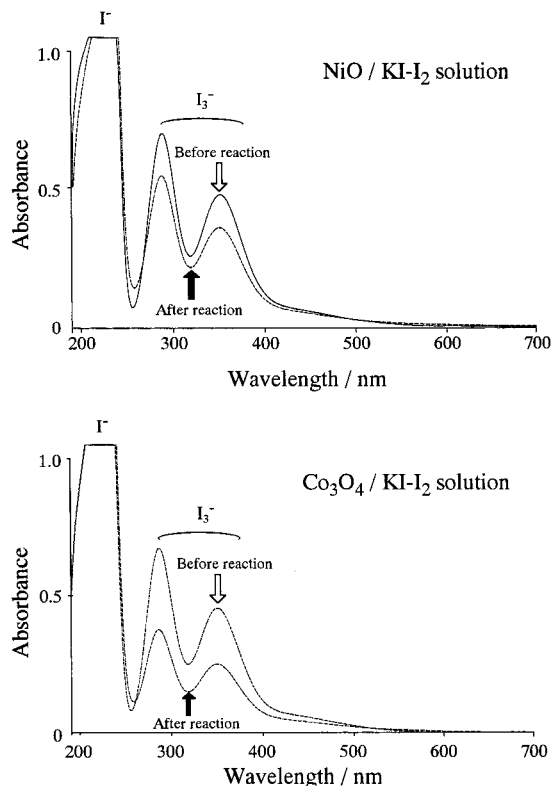

Figure 4. UV−vis spectra of $KI-I_2$ solution with NiO and Co_3O_4 before and after reaction.

remained unchanged throughout the reaction (pH = 6.7−6.9). This indicates that hydroiodic acid was not produced in $KI-I_2$ solution. On the other hand, atomic absorption spectrometry showed that Ni and Co ions were dissolved in the solution after the reaction in $KI-I_2$ solution. The solution and NiO or Co_3O_4 were separated from the suspension after the reaction by centrifugation and subsequent filtration, and dissolved Ni and Co ions in the solutions were analyzed by the absorption lines of Ni and Co (Ni 232.00 nm, Co 240.73 nm). The amounts of dissolved Ni and Co ions after the reaction were estimated to be 3.6 μmol (9.4×10^{-5} M) and 6.0 μmol (1.5×10^{-4} M), respectively. When the reaction was performed in distilled water
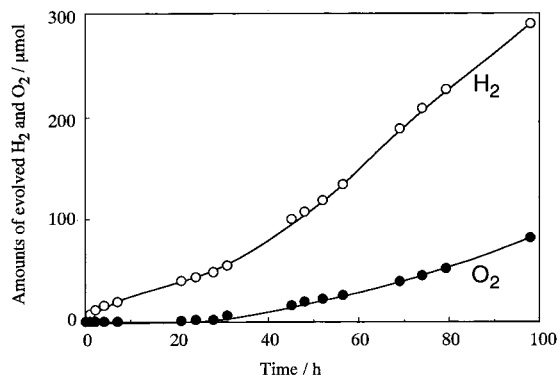

Figure 5. Time courses of H_2 and O_2 evolution on elemental metal Cu powder. Open and filled squares are H_2 and O_2, respectively.

without $KI-I_2$ in a similar manner as above, dissolved Ni or Co ions were not detected after the reaction. The reasonable interpretation of the decrease of I_2 without the decrease of pH and with the dissolution of Ni and Co ions is the reduction of I_2 by metallic Ni and Co. When I_2 reacts with metallic Ni or Co, NiI_2 or CoI_2 is formed, and the pH of the solution dissolving NiI_2 or CoI_2 will be kept almost unchanged. These results, therefore, indicate the formation of metallic Ni and Co on NiO and Co_3O_4, respectively, during the mechano-catalytic overall water splitting on these oxides.

3.3 Reduction and Overall Splitting of Water by Metallic Powders. The results mentioned above are indicative of the formation of metallic states in the metal oxide during the mechano-catalytic reaction. This, however, does not necessarily mean that metals themselves directly participate in the reaction because the metals might be formed as byproducts. To investigate the role of metals in the reaction, the reaction of water with metallic Cu powder was examined first. CuO powder (0.11 g, 1.4 mmol) was reduced at 423 K for 24 h by H_2 in the reaction vessel. It was confirmed by the amount of consumed H_2 during reduction, XPS, and XRD that CuO was completely reduced to metallic Cu. The particle size and the surface area of the metallic Cu were estimated to be 6 μm and 1.0 m^2 g^{-1} by SEM and BET measurements. After H_2 reduction, the reaction vessel was evacuated at 423 K for 1 h and then cooled to room temperature. Next, 120 cm^3 of distilled water, from which dissolved air (N_2 and O_2) was removed by evacuation, was poured into the reaction vessel through the reaction system. This experimental procedure allowed us to conduct the reaction free from air. The metallic Cu powder and distilled water were magnetically stirred as mentioned in the preceding section. Figure 5 shows time courses of H_2 and O_2 evolution on metallic Cu. Only H_2 was evolved at the early stage of the reaction, and O_2 evolution was accompanied after reaction for 30 h. The ratio of H_2 to O_2 (H_2/O_2) evolution rate approached 2:1 with reaction time.

The XP spectra and XRD patterns of the Cu powder before and after the reaction are shown in Figure 6. A Cu 2p XP spectrum of CuO is also shown in Figure 6C as a reference. Cu^0 and Cu^+ are distinguishable from Cu^{2+} by the satellite structure of Cu 2p spectrum as shown in the figure, and Cu $L_3M_{4,5}M_{4,5}$ Auger spectrum clearly distinguishes Cu^0 and Cu^+.[11] The XP spectra and XRD patterns showed that the surface of metallic Cu is oxidized into Cu_2O during the reaction, and most of the surface and subsurface of metallic Cu was oxidized into Cu_2O after the reaction. These results confirm that metallic Cu on the surface was oxidized into Cu_2O by reducing water into H_2 at the early stage of the reaction when only H_2 was evolved.
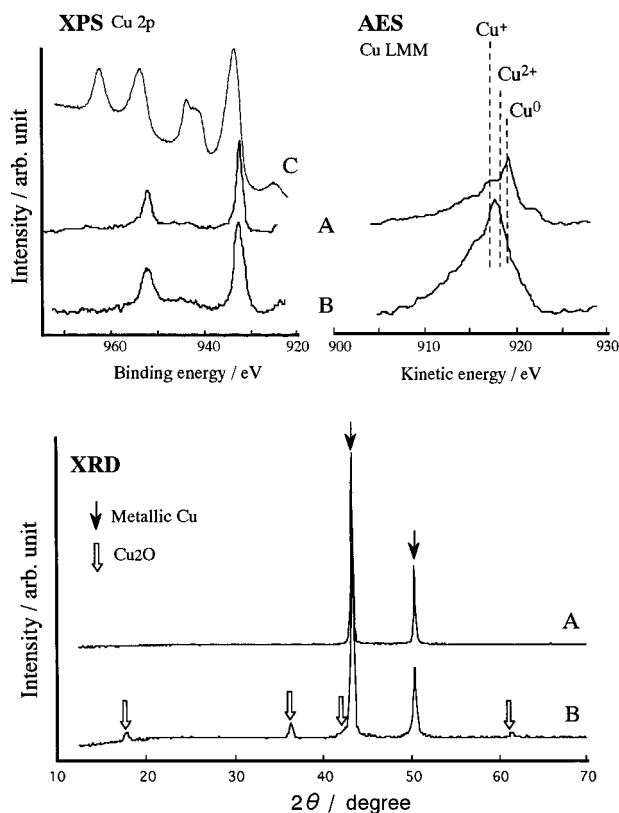
Figure 6. XP spectra and XRD patterns of metallic Cu before (A) and after (B) the reaction. Included (C) is a reference XP spectrum of CuO. The binding and kinetic energies were referenced to the Au 4f7/2 level at 83.8 eV.
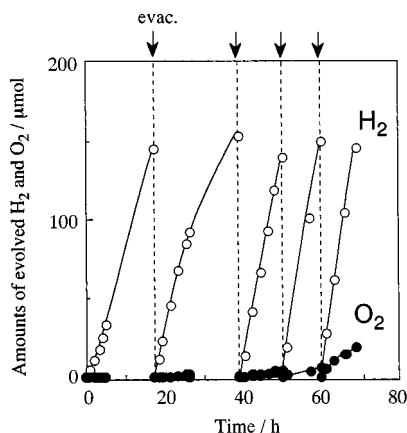

Figure 7. Time courses of H_2 and O_2 evolution on elemental metal Ni powder. Open and filled squares are H_2 and O_2, respectively.

When the surface of Cu particle was covered with a certain amount of Cu_2O, O_2 started evolving with H_2.

Figure 7 shows time courses of H_2 and O_2 evolution on the metallic Ni powder obtained by the reduction of 0.1 g of NiO (1.3 mmol) by H_2 at 673 K. The reaction was carried out in a similar manner as mentioned above. Only H_2 was evolved at the early stage of the reaction, similarly to the case of metallic Cu, and O_2 evolution was observed after reaction for 40 h. The XP spectrum and XRD pattern for the metallic Ni after reaction showed that the surface was covered with NiO. The decomposition of water by Co powders proceeded as well, and the surface after the reaction was also covered with Co_3O_4 (and/or CoO).

From these results, it is concluded that metallic Cu, Ni, and Co are oxidized into Cu_2O, NiO, and Co_3O_4, respectively, by reducing water into H_2 under the reaction condition of mechano-
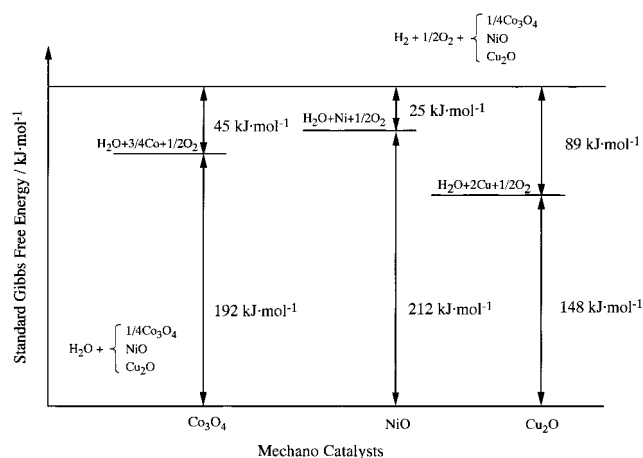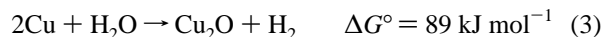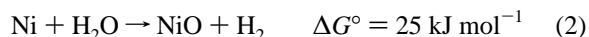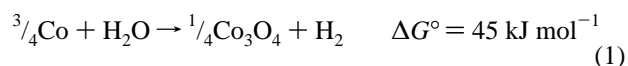

Figure 8. Standard Gibbs free energy changes of the redox model for mechano-catalytic overall water splitting.
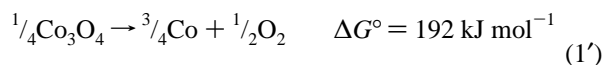
catalytic overall water splitting. When these metallic powders are covered with the metal oxides, simultaneous O_2 and H_2 evolution occurs.

4. Discussion

In this work, it was found that there existed a reduction process of Cu_2O into metallic Cu during mechano-catalytic overall water splitting. The experiments in KI−I_2 solution indicated that NiO and Co_3O_4 were also reduced into metallic Ni and Co, respectively. In the reaction of water with metallic powders, metals were oxidized into the metal oxides by reducing water into H_2. Taking these results into consideration, the metals formed in the metal oxides during mechano-catalysis are expected to participate in the catalytic reaction cycle for overall water splitting. Therefore, we tentatively propose a redox model for the reaction mechanism of mechano-catalytic overall water splitting. On the basis of this assumption, thermodynamic aspects of the overall water splitting reaction are examined. Standard Gibbs free energy changes, $\Delta G°$, at 298 K for water reduction by elemental metals are as follows:

$$^3/_4Co + H_2O \rightarrow {}^1/_4Co_3O_4 + H_2 \qquad \Delta G° = 45 \text{ kJ mol}^{-1} \tag{1}$$

$$Ni + H_2O \rightarrow NiO + H_2 \qquad \Delta G° = 25 \text{ kJ mol}^{-1} \tag{2}$$

$$2Cu + H_2O \rightarrow Cu_2O + H_2 \qquad \Delta G° = 89 \text{ kJ mol}^{-1} \tag{3}$$

Standard free energy changes at 298 K for metal oxide reduction accompanied by O_2 formation are as follows:

$$^1/_4Co_3O_4 \rightarrow {}^3/_4Co + {}^1/_2O_2 \qquad \Delta G° = 192 \text{ kJ mol}^{-1} \tag{1′}$$

$$NiO \rightarrow Ni + {}^1/_2O_2 \qquad \Delta G° = 212 \text{ kJ mol}^{-1} \tag{2′}$$

$$Cu_2O \rightarrow 2Cu + {}^1/_2O_2 \qquad \Delta G° = 148 \text{ kJ mol}^{-1} \tag{3′}$$

As the standard free energy change for overall water splitting at 298 K is 237 kJ mol^{-1}, the redox mechanism divides the increment of the free energy into two steps, as shown by the above equations and also in Figure 8. Of course, the energies for both steps are provided by mechanical energy consumed at the interface. Although both steps are so-called uphill reactions, water reduction steps, reactions 1−3, are relatively facile. The existence of these steps was experimentally confirmed in this

study. In contrast, the reduction steps of metal oxides, reactions $1'-3'$, are accompanied by large increase of free energies. The formation of metallic species during mechano-catalysis in distilled water was substantiated in the present work. Judging from eqs $1'-3'$, these reactions should proceed without water and even in vacuo. However, we were not able to observe any O_2 evolution in vacuo or even in water vapor using attached metal-oxide powders on the bottom of a stirring rod (for details, see ref 3). This fact may suggest more complicated process for O_2 formation than the simple reactions $1'-3'$.

Another point to be considered is the result of the isotope experiment, as mentioned in the Introduction. If the redox mechanism operates, O_2 should come from oxygen atoms in the oxide catalyst. However, the isotope experiment showed that the isotope composition in evolved O_2 exactly coincided with that in water within our experimental accuracy. This seems to oppose the redox mechanism, because it indicates that the oxygen atoms in metal oxides are not incorporated in the cycle of mechano-catalytic overall water splitting. Possible explanations based on the redox mechanism are that the amount of incorporated oxygen is very small compared with our experimental accuracy or that isotope exchange between the oxygen atoms in metal oxide and in water is rapid during the mechano-catalytic reaction.

As a whole, the experimental results in this work indicate the possibility of the redox mechanism for mechano-catalytic overall water splitting, but there exist several facts to be answered before the model is accepted.

The proposed reaction scheme is only for "exit" of mechanical energy and does not explain the overall reaction including the conversion process of mechanical energy into the redox reaction. In the field of mechanochemistry or tribochemistry, many reactions are known to proceed by mechanical energy.[12,13] As mechano-catalytic overall water splitting also proceeds by mechanical energy, reaction mechanisms proposed in mechanochemistry may be applicable to the catalytic reaction. One of the possible explanations of this phenomenon is "electrostatic charge separation" or "triboelectricity" due to frictional motion between two different materials, i.e. a catalyst powder and glass of a reaction vessel. From this point of view, we carried out several experiments and discussed the mechanism, as reported in our previous paper.[3] However, as has been discussed, the overall reaction mechanism seems to be more complicated despite the apparent simplicity of the reaction.

It is an important and interesting subject to reveal the reaction mechanism of this novel water splitting reaction ,not only from a fundamental but also from an application point of view. It may provide how to estimate the maximum efficiency of this reaction and the way to improve the efficiency. Therefore, further study on the reaction mechanism is now undergoing in our laboratory.

5. Summary

The chemical states of mechano-catalysts Cu_2O, NiO, and Co_3O_4 for overall water splitting were investigated. There are three major findings:

(1) Cu_2O, NiO, and Co_3O_4 are reduced into metallic Cu, Ni, and Co, respectively, during mechano-catalytic overall water splitting.

(2) Metallic Cu, Ni, and Co were oxidized into Cu_2O, NiO, and Co_3O_4, respectively, by reducing water into H_2, and these metallic powders covered with the metal oxides exhibit the activity of simultaneous evolution of O_2 and H_2.

(3) A redox reaction mechanism between metal and metal oxide is proposed for H_2 and O_2 evolution in mechano-catalytic overall water splitting, although it is still speculative.

References and Notes

(1) Ikeda, S.; Takata, T.; Kondo, T.; Hitoki, G.; Hara, M.; Kondo, J. N.; Domen, K.; Hosono, H.; Kawazoe, H.; Tanaka, A. *J. Chem. Soc. Chem. Comun.* **1998**, 2185.
(2) Ikeda, S.: Tanaka, A.; Hosono, H.; Kawazoe, H.; Hara, M.; Kondo, J. N.; Domen, K. *Stud. Surf. Sci. Catal.* **1999**, *121*, 301.
(3) Ikeda, S.; Takata, S.; Komoda, M.; Tanaka, A.; Hosono, H.; Kawazoe, H.; H.; Hara, M.; Kondo, J. N.; Domen, K. *Phys. Chem. Chem. Phys.* **1999**, *1*, 4485.
(4) Hara, M.; Kondo, T.; Yashima, M.; Ikeda, S.; Takata, T.; Kondo, J. N.; Domen, K. *Appl. Catal. A*, in press.
(5) Hara, M.; Kondo, T.; Komoda, M.; Ikeda, S.; Shinohara, K.; Tanaka, A.; Kondo, J. N.; Domen, K. *Chem. Commun.* **1998**, 357.
(6) Thiessen, P. A.; Heinicke, G.; Scober, E. *Z. Anorg. Allg. Chem.* **1970**, *377*, 20.
(7) Thiessen, P. A.; Meyer, K.; Heinicke, G. *Grundlagen der Tribochemie*; Akademie-Verlag: Berlin, 1967.
(8) Heinicke, G; Sigrist, K. *Z. Anorg. Allg. Chem.* **1967**, *350*, 148.
(9) Uchijima, T.; Takahashi, M.; Yoneda, Y. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2767.
(10) Gravelle, P. G.; Shobaky, G. El.; Urbain, H. *Compt. Rend.* **1966**, *262*, 549.
(11) Larson, P. E. *J. Electron. Spectrosc. Relat. Phenom.* **1974**, *4*, 213.
(12) Shaw, M. C. *J. Appl. Mechanics* **1948**, *15*, 37.
(13) Mori, S.; Kawada, T.; Xu, W.-C. *Appl. Surf. Sci.* **1997**, *108*, 391.