Effect of a Small Amount of Zirconia Additive on the Activity and Stability of Iron Oxide during Repeated Redox Cycles

Kohei Urasaki, Yasushi Sekine, Naoshi Tanimoto, Eri Tamura, Eiichi Kikuchi, and Masahiko Matsukata
Department of Applied Chemistry, School of Science and Engineering, Waseda University,
3-4-1, Okubo, Shinjuku, Tokyo, 169-8555

(Received October 13, 2004; CL-041212)

Addition of an exceedingly small amount of zirconia onto iron oxide enhanced the activity for hydrogen production by the oxidation of partially reduced iron oxide. Sintering of iron oxide was also suppressed.

Steam–iron process[1–3] is a hydrogen production method operating two reactors. In the first reactor, iron oxide is reduced to metallic iron by reducing gas. The metallic iron is transported to the second reactor and reacts with steam to produce iron oxide and hydrogen. Pure hydrogen can be generated in this process through separation of carbon monoxide and carbon dioxide. Metallic iron can be transported safely as compared with transportation of hydrogen gas. These merits are attractive for proton-exchange membrane fuel cells.

The problems in this process have been a low reactivity of iron oxide and sintering during repeated redox cycles. One of the approaches to solve these problems is the addition of foreign elements to iron oxide.[4,5]

Igarashi et al. have reported that basic surface hydroxy group on zirconia can activate steam under the conditions of steam reforming of *n*-butane.[6,7] Otsuka et al. have reported that iron oxide coprecipitated with 3 mol % of zirconium showed enhanced rates of reduction and oxidation.[4,5] In this study, we added a small amount of zirconia onto the surface of iron oxide by an impregnation method and examined the effect of such modification of iron oxide surface on its redox behavior.

Iron oxide (hematite, Fe_2O_3) powder supplied from Kanto Chemical Co., Inc. was used as a sample. A small amount of zirconia was added to iron oxide by an impregnation method using an aqueous solution of zirconium nitrate. The unmodified and modified samples were dried overnight at the temperature of 393 K, followed by calcination at 873 K for 6 h.

All experiments were carried out in a continuous flow type reactor with a fixed bed of catalyst at 723 K and atmospheric pressure. In each experiment, pretreatment of the sample was carried out at 723 K with a mixture of steam ($25\,cm^3\,min^{-1}$) and helium ($75\,cm^3\,min^{-1}$) for 0.5 h. After the sample was reduced in a stream of the mixture of hydrogen ($15\,cm^3\,min^{-1}$) and helium ($45\,cm^3\,min^{-1}$), the partially reduced sample was reoxidized by the mixture of steam ($25\,cm^3\,min^{-1}$) and helium ($175\,cm^3\,min^{-1}$). This redox cycle was repeated for five times in the range of the reduction degree of 30–50 mol %. The reduction degree of iron oxide was defined as $\Delta W/W_L \times 100$, where ΔW and W_L are the weight change of a sample and the total amount of oxygen in the fresh sample, respectively.

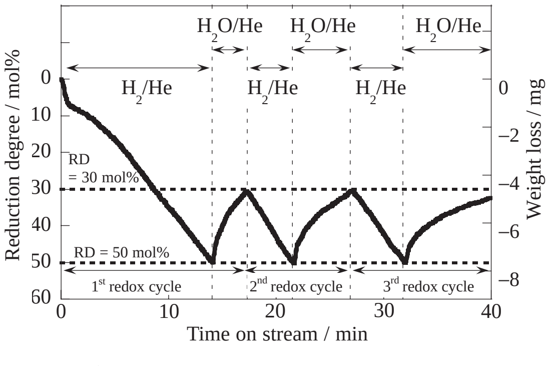

Figure 1. Redox cycles of iron oxide.

During experiments, the weight change of a sample was measured by a tapered element oscillating microbalance (TEOM, Rupprecht & Patashnick Co., Inc.) which is a high performance mass analyzer determining the mass by measuring the frequency of vibration.[8]

Figure 1 shows the changes in the weight of unmodified sample and the reduction degree during repeated redox cycles. The weight change of the sample was monitored to control the reduction degree between 30–50 mol % during repeated redox cycles. The XRD patterns shown in Figure 2 indicated that the partially reduced samples with the reduction degrees of 30 and 50 mol % showed the reflection peaks corresponding to magnetite (Fe_3O_4) and metallic iron, respectively, while hematite observed in the fresh sample disappeared. Rapid reduction of hematite to give magnetite took place in the first reduction step until

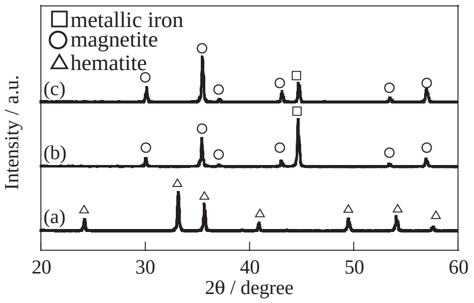

Figure 2. XRD patterns of iron oxide (a) before reaction, (b) after the first reduction and (c) after the first oxidation.

Table 1. Initial oxidation rate and surface area of iron oxide

Cycle number	Initial oxidation rate /μmol s^{-1}	SA[a] /m^2 g-cat^{-1}	r_{ox}[b] /μmol s^{-1} m^{-2}
1st	1.64	5.93	5.53
2nd	1.33	5.62	4.73
3rd	1.2	5.09	4.72
4th	0.89	3.96	4.49
5th	0.79	3.28	4.82

[a] Specific surface area calculated by BET method.
[b] Initial oxidation rate per specific surface area.

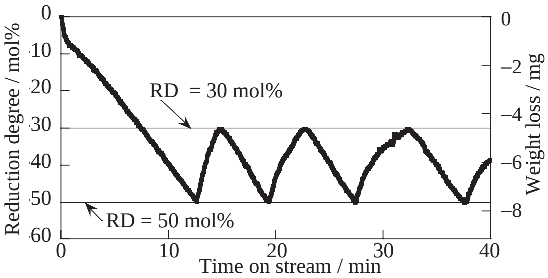

Figure 3. Redox cycles of zirconia-modified iron oxide.

the reduction degree reached 10.3 mol % in agreement with 11.1 mol %, the calculated weight change during the reduction from hematite to give magnetite. After the rapid reduction in the early stage of reaction, the redox of partially reduced iron oxide between magnetite and metallic iron ($Fe_3O_4 + 4H_2 \leftrightarrow 3Fe + 4H_2O$) mostly took place. We, thus, consider the oxidation of metallic iron with steam to give hydrogen and the reduction of magnetite with hydrogen in the following discussion.

With the progress of the redox cycles, the oxidation rate of the partially reduced sample decreased, while the reduction rate was not largely changed. One of the crucial reasons for deactivation could be the sintering of particles in the samples. Specific surface areas of the used samples were determined by nitrogen adsorption. Table 1 lists the initial oxidation rate, the rate of oxidation at the onset of the oxidation step, and the specific surface areas of samples at the reduction degree of 50 mol % in each redox cycle. The initial oxidation rate was determined by the slopes of the change of the reduction degree. Both the specific surface areas of the used samples and the initial oxidation rate significantly decreased with the repetition of redox cycles. On the other hand, the initial oxidation rate per the specific surface area (r_{ox}) was hardly changed. Therefore, we concluded that the sintering of the sample caused the decrease in the oxidation rate, while the influence of the sintering on the reduction rate is still open question.

An exceedingly small amount of zirconia (0.23 mol %) was added to the iron oxide. Figure 3 shows the changes in the weight and reduction degree of the zirconia-modified sample with repeated redox cycles. The oxidation rate of zirconia-modified sample was larger than that of unmodified sample. Table 2 lists the initial oxidation rate and the specific surface areas of modified samples at the reduction degree of 50 mol % in each redox cycle. The r_{ox} as well as the initial oxidation rate was significantly enhanced by adding zirconia as compared with unmodified sample, as shown in Table 1. On the other hand, the effect of zirconia addition on the reduction of iron oxide was not observed because the initial reduction rate per surface area (r_{red}) of zirconia-modified sample ($r_{red} = 1.78\ \mu\text{mol s}^{-1}\ \text{m}^{-2}$) hardly changed with unmodified sample ($r_{red} = 1.75\ \mu\text{mol s}^{-1}\ \text{m}^{-2}$). We, thus, consider that the main role of zirconia is to enhance the oxidation of metallic iron with steam. On the other hand, the sintering of sample was also decreased in comparison with the unmodified sample although the specific surface area of zirconia-modified sample decreased from 5.89 m^2 g-cat^{-1} (after the first reduction) to 3.76 m^2 g-cat^{-1} (after the fifth reduction). We supposed that enhanced oxidation of the surface of partially reduced sample inhibited the sintering of the sample. We have been studying the modeling of the sintering behavior of unmodified and zirconia-modified iron oxide during repeated redox cycles and will report these results in the near future.

Table 2. Initial oxidation rate and surface area of zirconia-modified iron oxide

Cycle number	Initial oxidation rate $/\mu\text{mol s}^{-1}$	SA $/\text{m}^2$ g-cat^{-1}	r_{ox} $/\mu\text{mol s}^{-1}\ \text{m}^{-2}$
1st	2.00	5.89	6.79
2nd	1.76	5.81	6.06
3rd	1.74	5.88	5.92
4th	1.34	4.67	5.74
5th	1.09	3.76	5.80

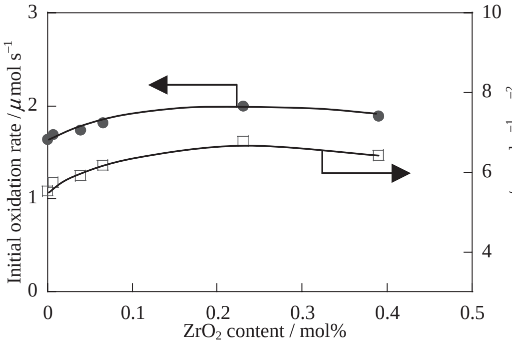

Figure 4. Effect of ZrO_2 content on the activity for the oxidation of partially reduced iron oxide.

The samples with different amounts of added zirconia were examined. Figure 4 shows the r_{ox} and the initial oxidation rate of the samples in the first oxidation cycle. It is noteworthy that the initial oxidation rate was increased by an exceedingly small amount of added zirconia, 0.23 mol %. The further addition of zirconia to iron oxide above 0.23 mol % hardly influenced the oxidation rate. It is very interesting that catalytic activity is enhanced by the addition of an extremely small amount of metal oxide. The detailed role of zirconia

In summary, an exceedingly small amount of zirconia added onto the surface of iron oxide accelerated the activity of the oxidation of partially reduced sample with steam in steam–iron reaction and the sintering of the sample could be suppressed by accelerating the oxidation rate. The main role of zirconia would enhance the activation of steam to produce hydrogen.

References

1 P. B. Tarman and R. Bilijetina, *Coal Process. Technol.*, **5**, 114 (1979).
2 V. Hacker, R. Fankhauser, G. Faleschini, H. Fuchs, K. Friedrih, M. Muhr, and K. Kordesch, *J. Power Sources*, **86**, 531 (2000).
3 S. Fukase and T. Suzuka, *Appl. Catal., A*, **100**, 1 (1993).
4 K. Otsuka, C. Yamada, T. Kaburagi, and S. Takenaka, *Int. J. Hydrogen Energy*, **28**, 335 (2003).
5 K. Otsuka, T. Kaburagi, C. Yamada, and S. Takenaka, *J. Power Sources*, **122**, 111 (2003).
6 A. Igarashi, T. Ohtaka, and S. Motoki, *Catal. Lett.*, **13**, 189 (1992).
7 A. Igarashi, T. Ohtaka, T. Honnma, and C. Fukuhara, *Stud. Surf. Sci. Catal.*, **75**, 2083 (1993).
8 "TEOM Series 1500 Pulse Mass Analyzer," Rupprecht & Patashnick Co., Inc. (1994).

Published on the web (Advance View) January 15, 2005; DOI 10.1246/cl.2005.230