

## Methane to Hydrogen by Means of Redox of Modified Iron Oxides

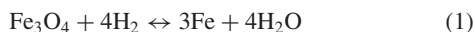
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(Received July 30, 2003; CL-030699)

CH<sub>4</sub> can be converted to pure H<sub>2</sub> by means of repeated reduction of modified iron oxides (Cu–Cr–FeO<sub>x</sub>) with CH<sub>4</sub> and subsequent oxidation of the reduced oxides with H<sub>2</sub>O.

H<sub>2</sub> is expected to become an important energy carrier for sustainable energy consumption with a reduced impact on the environment. A hydrogen-based energy system is regarded as a viable and advantageous option for delivering high quality energy services. In particular, H<sub>2</sub> should be used as a fuel for H<sub>2</sub>–O<sub>2</sub> fuel cells due to high conversion efficiency of chemical energy of H<sub>2</sub> into electricity without emission of any pollutant gases. However, one of the major obstacles to utilize H<sub>2</sub> as an energy carrier is the lack of safe, efficient and low cost storage systems suitable for various stationary and mobile applications.

With regard to this problem, we have proposed a simple, safe, and environmentally benign technology for the storage and supply of H<sub>2</sub> to fuel cells.<sup>1</sup> Our technology is based on a redox reaction of magnetite in Eq (1).



The principle of technology is analogous to the old steam iron process.<sup>2</sup> Fe<sub>3</sub>O<sub>4</sub> is reduced with H<sub>2</sub> into Fe metal. The recovery and the supply of H<sub>2</sub> can be done by the reverse reaction, i.e. the reoxidation of Fe metal with H<sub>2</sub>O. By means of this method, one mol of Fe can store and regenerate 1.33 mol of H<sub>2</sub>, which corresponds to 4.8 wt % of Fe metal. However, it should be noted that this method would stand on the condition that we can get cheap and pure H<sub>2</sub> in order to reduce Fe<sub>3</sub>O<sub>4</sub> into Fe metal.

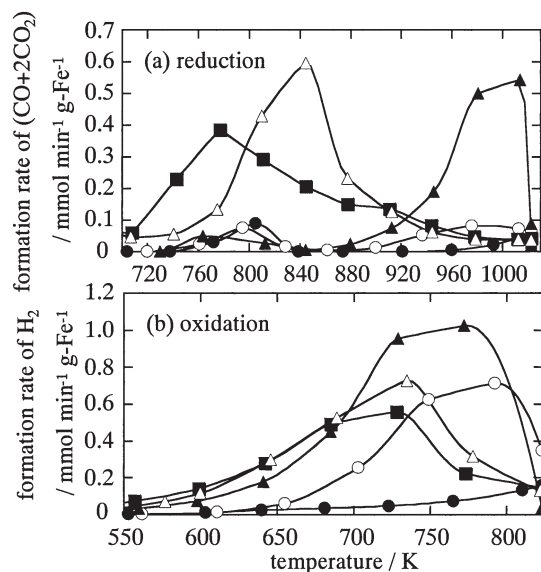
At present, H<sub>2</sub> is produced through steam reforming of CH<sub>4</sub>, the main component of natural gas, followed by water gas shift reaction of CO. The steam reforming of CH<sub>4</sub> requires temperatures higher than 1000 K as well as a large amount of energy input because it is a high endothermic reaction. Moreover, the H<sub>2</sub> from the process contains ca. 25 vol % of CO<sub>2</sub> and intolerable impurity of CO (1–2 vol %), thus a further purification is usually indispensable for the supply of H<sub>2</sub> to fuel cells. Therefore, if Fe<sub>3</sub>O<sub>4</sub> can be reduced directly with CH<sub>4</sub> instead of H<sub>2</sub>, our technology could be more attractive from the standpoint of the storage and supply of pure H<sub>2</sub> from natural gas as the primary energy source. In the present study, we demonstrate the possibility of a new technology for the storage and supply of H<sub>2</sub> based on CH<sub>4</sub>, i.e. Fe<sub>3</sub>O<sub>4</sub> is reduced with CH<sub>4</sub> into Fe metal and subsequently Fe metal is oxidized with H<sub>2</sub>O to form H<sub>2</sub>.

Iron oxide alone and with foreign metal additives (M) were prepared by co-precipitation from aqueous solutions containing cations of Fe and M.<sup>3</sup> The amounts of added metal were adjusted to be 5 mol % of total metal cations. Hereafter, iron oxide samples without and with a foreign metal (M) were denoted as FeO<sub>x</sub> and M–FeO<sub>x</sub>, respectively. Reduction of the iron oxide samples with CH<sub>4</sub> (101.3 kPa) and the subsequent oxidation of the reduced samples with H<sub>2</sub>O were carried out by using a conventional

gas-flow system. For the reduction, CH<sub>4</sub> was introduced into a tubular reactor packed with the iron oxide samples (0.2 g) at 473 K and the temperature at the reactor was raised to 1023 K by a rate of 3 K min<sup>–1</sup>. The temperature was kept at 1023 K until the formation of CO and CO<sub>2</sub> could not be observed. After CH<sub>4</sub> was purged out with Ar, H<sub>2</sub>O vapor (18.5 kPa) was contacted with the reduced iron oxide samples at 473 K and the temperature was increased linearly with time to 823 K by a rate of 4 K min<sup>–1</sup>. The oxidation with H<sub>2</sub>O was continued until the H<sub>2</sub> formation could not be observed. The reduction and the subsequent oxidation of the iron oxide samples were carried out repeatedly under the same conditions. During the reactions, a part of effluent was sampled out and analyzed by G. C. Detection limit of CO and CO<sub>2</sub> was ca. 0.1 vol %.

In the case of repeated redox reactions of Eq (1), we have reported that modification of iron oxides with Al, V, Cr, Ga, and Mo species prevented sintering of iron species, while iron oxide particles without those additives were deactivated dramatically during the redox due to the sintering.<sup>3</sup> The modification of iron oxides with Rh or Ir improved the activity of both the reduction and oxidation.<sup>3</sup> However, because of a high price of these precious metals, we should look for cheaper alternatives. In this work, we have looked for a favorable combination of non-precious metal additives to iron oxide for the repeated reduction with CH<sub>4</sub> and reoxidation of the reduced iron oxide with H<sub>2</sub>O. The best modified iron oxide was Cu–Cr–FeO<sub>x</sub>. We demonstrate the redox performance of this sample in comparison with other samples based on Cr–FeO<sub>x</sub>.

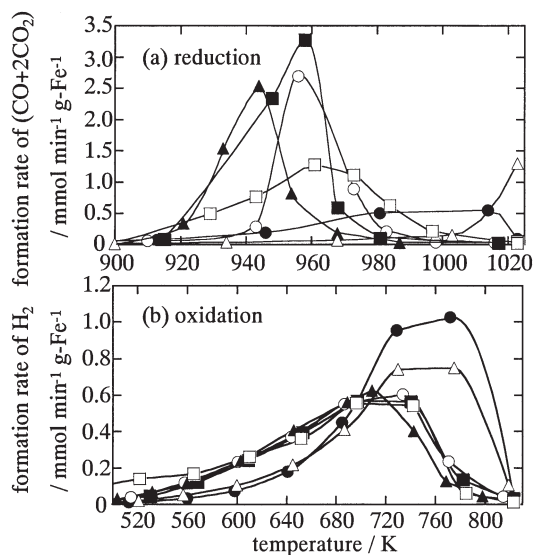
Figure 1 shows the results for the reduction with CH<sub>4</sub> and oxidation with H<sub>2</sub>O for different iron oxide samples. As shown in Figure 1a, the formation of CO and CO<sub>2</sub> could be observed due to the reduction of iron oxide samples with CH<sub>4</sub>. The formation of hydrogen was relatively slow compared to CO and CO<sub>2</sub>, in particular, CO and CO<sub>2</sub> were formed without H<sub>2</sub> at early period of the reduction. Therefore, the hydrogen in the reacted methane was mostly used for the reduction of the iron oxide samples. However, the quantitative analysis of H<sub>2</sub>O by G. C. in this work was not satisfactory. Therefore, the formation rate of CO<sub>x</sub> (= CO + 2 × CO<sub>2</sub>) was used as a reduction index of the iron oxide samples in this work. The rates were plotted against temperature in Figure 1a. Reduction of FeO<sub>x</sub> or Cr–FeO<sub>x</sub> proceeded slowly in the temperature range 700–1023 K. On the other hand, addition of Rh, Ir, or Cu into Cr–FeO<sub>x</sub> dramatically improved the reduction with CH<sub>4</sub>. For the reduction of Rh–Cr–FeO<sub>x</sub>, Ir–Cr–FeO<sub>x</sub> and Cu–Cr–FeO<sub>x</sub>, the maximum formation rates of CO<sub>x</sub> were observed at around 770, 840, and 980 K, respectively. These results suggest that modification with Rh, Ir, or Cu enhanced the reduction of iron oxides with CH<sub>4</sub>. For these samples, the formation of H<sub>2</sub> was accelerated after CO and CO<sub>2</sub> were formed. These results suggested that H<sub>2</sub> was formed through the CH<sub>4</sub> decomposition catalyzed by reduced iron oxides.<sup>4</sup> In fact, deposition of carbons could be observed on the iron oxide samples after the reduction with CH<sub>4</sub>.



**Figure 1.** Changes of the formation rates of CO<sub>x</sub> in the reduction with CH<sub>4</sub> and the formation rates of H<sub>2</sub> in the oxidation with H<sub>2</sub>O for different iron oxide samples as a function of temperatures. ●, FeO<sub>x</sub>; ○, Cr-FeO<sub>x</sub>; ▲, Cu-Cr-FeO<sub>x</sub>, △, Ir-Cr-FeO<sub>x</sub>; ■, Rh-Cr-FeO<sub>x</sub>.

Figure 1b shows the results for the oxidation with H<sub>2</sub>O of iron oxide samples reduced with CH<sub>4</sub>. The formation rate of H<sub>2</sub> for Cr-FeO<sub>x</sub> increased with a rise of temperatures from 550 to 770 K, although the reactivity of FeO<sub>x</sub> was very low even at 823 K. Furthermore, Cu-Cr-FeO<sub>x</sub>, Rh-Cr-FeO<sub>x</sub>, and Ir-Cr-FeO<sub>x</sub> formed H<sub>2</sub> at lower temperatures than Cr-FeO<sub>x</sub>. The kinetic curves of H<sub>2</sub> formation were similar each other among the three samples (Cr-FeO<sub>x</sub> with Cu, Rh, or Ir). During the oxidation with H<sub>2</sub>O, a little formation of CO and CO<sub>2</sub> was also observed, although the results were not shown in Figure 1. These products would be formed by gasification of carbons deposited from CH<sub>4</sub> with H<sub>2</sub>O. The total amounts of H<sub>2</sub>, CO, and CO<sub>2</sub> formed during the oxidation with H<sub>2</sub>O were roughly estimated by integrating the formation rates of these products through the whole temperature range (temperature was raised linearly with time). The amounts of H<sub>2</sub>, CO, and CO<sub>2</sub> per 1 mol of Fe were 1.8, 0.01, and 0.11 mol for Cu-Cr-FeO<sub>x</sub>, 1.4, 0.0, and 0.04 mol for Ir-Cr-FeO<sub>x</sub> and 1.3, 0.0, and 0.01 mol for Rh-Cr-FeO<sub>x</sub>, respectively. The amount of H<sub>2</sub> formed for Cu-Cr-FeO<sub>x</sub> was the highest among the three samples, probably because the H<sub>2</sub> produced by the gasification of deposited carbons with H<sub>2</sub>O must be counted.

Figure 2 shows the results of the repeated redox cycles for Cu-Cr-FeO<sub>x</sub> sample. From the first to the 7th cycle, the redox reactions were repeated under the same conditions as those shown in Figure 1. The results for the first, the third and the 7th cycle were shown in Figure 2. It is worth while noting that the peak for the formation rate of CO<sub>x</sub> was shifted to lower temperatures with the repeated cycles, that is, Cu-Cr-FeO<sub>x</sub> could be reduced more easily with the repeated cycles. In addition, the kinetic curves of H<sub>2</sub> formation did not change appreciably with the repeated cycles (2–7 cycles), except for the first one. Thus, the total amount of H<sub>2</sub> formed by the redox of Cu-Cr-FeO<sub>x</sub> at each cycle was kept almost constant (ca. H<sub>2</sub> 1.3 mol per Fe 1 mol). The high maximum formation rate of H<sub>2</sub> at the first oxidation may be due to the contribution of the gasification of deposited carbons with H<sub>2</sub>O. However, the formation of CO and CO<sub>2</sub> could not be observed at all from the third to the 7th oxidation.



**Figure 2.** Change of the formation rates of CO<sub>x</sub> in the reduction with CH<sub>4</sub> and the formation rates of H<sub>2</sub> in the oxidation with H<sub>2</sub>O for Cu-Cr-FeO<sub>x</sub> as a function of temperatures. ●, the 1<sub>st</sub> cycle; ○, the 3<sub>rd</sub> cycle; ▲, the 7<sub>th</sub> cycle; △, the 8<sub>th</sub> cycle; ■, the 10<sub>th</sub> cycle; □, the 11<sub>th</sub> cycle.

After the 7th oxidation, the deposited carbons on the sample were oxidized with O<sub>2</sub> at 823 K. The oxidation of deposited carbons produced CO<sub>2</sub> in addition to a trace of CO. The total formation amount of CO<sub>x</sub> was estimated to be 15.6 mol per 1 mol of Fe.

After the oxidation of deposited carbons described above, further three redox cycles of Cu-Cr-FeO<sub>x</sub> were repeated, which correspond to the 8th and the 10th cycle in Figure 2. The reduction rate of Cu-Cr-FeO<sub>x</sub> for the 8th cycle was very slow, but the reduction was improved for the 10th cycle. This observation was similar to that from the first to the third cycle, indicating that Cu-Cr-FeO<sub>x</sub> is a quite stable redox mediator for the storage and supply of H<sub>2</sub> from CH<sub>4</sub>.

After the 10th oxidation, the Cu-Cr-FeO<sub>x</sub> was heated from 473 to 1023 K under a stream of Ar instead of CH<sub>4</sub>. CO and CO<sub>2</sub> were formed as shown in Figure 2a (the 11th cycle), although the maximum formation rate of them was lower compared to those under the CH<sub>4</sub> stream (the third, 7th and 10th cycle). At the 11th oxidation, a similar kinetic curve of H<sub>2</sub> formation to those for the other cycles was observed. This result indicated that deposited carbons from CH<sub>4</sub> worked as a reductant for Cu-Cr-FeO<sub>x</sub>.

From the results described above, we concluded that H<sub>2</sub> without CO and CO<sub>2</sub> can be formed with high reproducibility through the repeated reduction of Cu-Cr-FeO<sub>x</sub> with CH<sub>4</sub> and the subsequent oxidation of the reduced one with H<sub>2</sub>O. Cu and Cr K-edge XAFS of Cu-Cr-FeO<sub>x</sub> showed that Cu and Cr species were always present as Cu metal and ferrite containing Cr<sup>3+</sup> (Cr<sub>x</sub>Fe<sub>3-x</sub>O<sub>4</sub>) during the redox. It is likely that Cr<sub>x</sub>Fe<sub>3-x</sub>O<sub>4</sub> prevented the sintering of iron species and Cu metal worked as the sites which can activate CH<sub>4</sub> for the reduction and H<sub>2</sub>O for the oxidation.

#### References

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