Hydrogen Storage Characteristics using Redox of M/Fe₂O₃ (M=Rh, Ce and Zr) mixed oxides

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ABSTRACT:

M/Fe₂O₃ (M=Rh, Ce and Zr) mixed oxides were prepared using urea method to improve the hydrogen storage technology using the redox reaction of magnetite (Fe₃O₄). And their redox behaviors during the repeated cycles were studied using temperature programmed reaction (TPR) technique. The results of repeated redox tests showed that Rh added to iron oxide have an effect on lowering the re-oxidation temperature by water-splitting as well as reduction temperature corresponding to Fe₂O₃ → Fe₃O₄. Meanwhile, Ce and Zr additives played an important role in prevention of deactivation by repeated cycles. Finally, (Rh, Ce, Zr)/Fe₂O₃ sample added with Rh, Ce and Zr showed the lowest re-oxidation temperature by water-splitting and maintained high H₂ recovery in spite of the repeated redox cycles. Consequently, it is expected that (Rh, Ce, Zr)/Fe₂O₃ sample can be a feasible medium for chemical hydrogen storage using redox cycle of iron oxide.

KEYWORDS : Hydrogen storage, Modified iron oxide, Temperature programmed reduction (TPR)

1. Introduction

Many technologies for safe and effective storage of hydrogen have been reported and developed. A remarkable approach was recently proposed by Otsuka and coworkers [1]. The technology is based on a very simple redox reaction of magnetite as following procedure:

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\text{Step 1 : Chemical hydrogen storage (reduction of magnetite)} \\
\text{Fe}_3\text{O}_4 + 4\text{H}_2 \rightarrow 3\text{Fe} + 4\text{H}_2\text{O} \quad (1)
\]

\[
\text{Step 2 : Hydrogen recovery (water-splitting)} \\
3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2 \quad (2)
\]

This technology would have many advantages in terms of safety and storage capacity. However, in order to put this technology to practical use, water-splitting temperature by reduced iron metals for H₂ recovery have to be lowered (<573 K). Moreover, deactivation of iron oxide, which is caused by repeated cycles, have to be prevented. Otsuka et al. have examined effects of various metal additives in the reduced iron oxide on the production of hydrogen from at a temperature range of 373–873 K. They have reported that Al, Mo and Ce were favorable ones for preserving the Fe/Fe₃O₄ sample from decaying its reactivity by repeated cycles and that the addition of Rh or Ir enhanced the rate of H₂O decomposition remarkably at <573 K. They have also suggested that Rh metal would catalyze the dissociation of H₂O at low temperature [1-3]. However, more
detailed studies for the role of additives and redox behavior of modified iron oxide during the repeated cycles are still required and can be a significant work. Therefore, M/Fe₂O₃ (M=Rh, Ce and Zr), iron oxides which were modified with rhodium, cerium, zirconium or their combination were prepared by co-precipitation using urea method at different synthetic condition and characterized by TPR, XRD and SEM analysis. And their redox behaviors during repeated cycles were investigated using temperature programmed reaction (TPR) technique. The role of additives was discussed in detail.

2. Experimental

The iron oxides which were mixed with Rh, Ce, Zr or their combination as additives were prepared by co-precipitation using urea method as previous work [1]. Fe(NO₃)₃·9H₂O was used as the starting material for iron oxide and RhCl₃·xH₂O, (NH₄)₂Ce(NO₃)₆ and Zr(OCH₂CH₂CH₃)₄ for metal additives of Rh, Ce and Zr, respectively. The amounts of added metal additives were adjusted to be 3 mol% of total metal additives (M/(Fe+M) = 0.03). The co-precipitates was dried at 383 K for 24 h and then calcined in air at 573 K for 5 h. The resultant powders were obtained after thermal treatment at 773 K for 10 h. The sample without any additives was denoted as (n)/Fe₂O₃ and the samples with additives were denoted as (M)/Fe₂O₃ where M can be Rh, Ce, Zr or their combinations. The X-ray diffraction patterns of the samples were obtained by powder diffractometer (Rigaku, D/MAX III), using Cu Kα₁ radiation.

The TPR measurements were carried out using an apparatus described elsewhere. The water formed during reduction was removed by a cooling trap which was equipped in a gas line prior to the thermal conductivity detector. The temperature of reactor was linearly raised by electrical furnace. The hydrogen-argon mixture (5% H₂) was used for reduction of the samples at a flow rate of 40 ml min⁻¹. The water for re-oxidation was supplied by steam generator using argon as a carrier gas and the total flow (argon + steam) was maintained at a rate of 40 ml min⁻¹. The experimental procedure is explained as follows: The samples of 0.05g was mounted at the bed of tubular quart reactor and reduced by hydrogen with increasing temperature to 823 K at a heating rate of 7.5 K min⁻¹ (step 1). After cooling to room temperature, the re-oxidation of the samples by water was executed with increasing temperature to 873 K at a heating rate of 4 K min⁻¹. After reached to 873 K, the temperature was kept until no hydrogen formation by water decomposition was observed (step 2), and the steps 1 and 2 were repeated by three times.

3. Results and discussion

3.1. Effects of synthetic condition

Fig. 1 shows X-ray diffraction patterns of the (n)/Fe₂O₃ sample with increasing the urea concentration used as a precipitation agent. As shown in Fig. 1, it was confirmed that the prepared iron oxides were hematite (Fe₂O₃), with increasing the urea concentration, no changes in crystalline phase were observed. The H₂-TPR patterns at step 1 are presented in Fig. 2. As shown in Fig. 2, It was observed that the TPR pattern of (n)/Fe₂O₃ sample are composed of two reduction steps in which one peak in the range of ca. 523-723 K are
due to $H_2$ reduction of $Fe_2O_3 \rightarrow Fe_3O_4$ course and the continuous another peak in the next temperature range due to $H_2$ reduction of $Fe_3O_4 \rightarrow Fe$.

With increasing the urea concentration, max temperature for of $Fe_2O_3 \rightarrow Fe_3O_4$ reduction somewhat decreased, however, no big differences was found. Therefore, urea concentration used as a precipitant have little effect on the $H_2$-reduction of the resultant $Fe_2O_3$ powder.

Fig. 3 shows the SEM images of the (n)/$Fe_2O_3$ samples with increasing the urea concentration. As presented in Fig. 3, particle sizes of the prepared $Fe_2O_3$ powders are in the range of ca. 50-150nm and showed no apparent differences irrespective of increasing urea concentration. From the above results, it is concluded that urea concentration used as a precipitant do not affect the reduction behavior and particle size of the resultant $Fe_2O_3$ powders.

Fig. 4 presents the TPR profiles of the iron oxides mixed with various additives during three repeated cycles. As exhibited in Fig. 1(a), the TPR pattern of (n)/$Fe_2O_3$ sample showed two reduction steps, consisting of one peak in the range of ca. 573 to 673 K due to $H_2$ reduction of $Fe_2O_3 \rightarrow Fe_3O_4$ course and another peak in the next temperature range to 823 K due to $H_2$ reduction of $Fe_3O_4 \rightarrow Fe$ course. For TPR profiles of second and third cycle, it was observed that the reduction peak due to $Fe_2O_3 \rightarrow Fe_3O_4$ course disappeared and the peak due to $Fe_3O_4 \rightarrow Fe$ course still remained. This result indicates that the reduction of $Fe_2O_3$ proceed...
according to \( \text{Fe}_2\text{O}_3 \to \text{Fe}_3\text{O}_4 \to \text{Fe} \) courses only in the first cycle and thereafter the re-oxidation of the reduced Fe metal with water occurs according to \( \text{Fe} \to \text{Fe}_2\text{O}_3 \) course without regeneration of \( \text{Fe}_2\text{O}_3 \), in good agreement with data of previous work [2]. As displayed in Fig. 4(b) and (d), The \( \text{H}_2\)-TPR patterns of \((\text{Rh})/\text{Fe}_2\text{O}_3\) and \((\text{Zr})/\text{Fe}_2\text{O}_3\) samples were similar to that of \((n)/\text{Fe}_2\text{O}_3\) sample except for the difference in reduction temperature. Reduction temperature of \((\text{Rh})/\text{Fe}_2\text{O}_3\) sample corresponding to \( \text{Fe}_2\text{O}_3 \to \text{Fe}_3\text{O}_4 \) was lowered by ca. 130 K in comparison with that of \((n)/\text{Fe}_2\text{O}_3\) sample. This result is in good agreement with previous work that Rh facilitates reduction, presumably through \( \text{H}_2 \) dissociation and spillover to the oxide [5]. However, \((\text{Ce})/\text{Fe}_2\text{O}_3\) and \((\text{Zr})/\text{Fe}_2\text{O}_3\) samples make little difference in reduction temperature corresponding to \( \text{Fe}_2\text{O}_3 \to \text{Fe}_3\text{O}_4 \). This result indicates that Ce and Zr additives have no effect on lowering of reduction temperature corresponding to \( \text{Fe}_2\text{O}_3 \to \text{Fe}_3\text{O}_4 \) in contrast with Rh additive.

In order to investigate the cooperative effect, we have prepared the iron oxides mixed with two component additives based on Rh additives, and the \( \text{H}_2\)-TPR profiles are exhibited in Fig. 4(e) and (f). As shown in Fig. 4(e), it is obviously observed that reduction temperature corresponding to \( \text{Fe}_2\text{O}_3 \to \text{Fe}_3\text{O}_4 \) decreased by co-

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Fig. 4. \( \text{H}_2\)-TPR profiles of the samples during three repeated cycles. Sampling weight: 50 mg, heating rate: 7.5 K/min and reducing gas: 5% \( \text{H}_2/\text{Ar} \).

Fig. 5. \( \text{H}_2 \) evolution of the samples during three repeated cycles. Sampling weight: 50 mg, heating rate: 4 K/min and oxidizing gas: \( \text{H}_2\text{O}/\text{Ar} \).
addition of Rh additive. Therefore, it is revealed that Rh additive can promote the reduction corresponding to \( \text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \), in spite of co-addition of another additive. On the other hand, reduction temperature of all samples corresponding to \( \text{Fe}_3\text{O}_4 \rightarrow \text{Fe} \) course were similar to that of \( (n)/\text{Fe}_2\text{O}_3 \) sample. This suggests that reduction reaction corresponding to \( \text{Fe}_3\text{O}_4 \rightarrow \text{Fe} \) course proceed very slowly.

Fig. 5 shows the \( \text{H}_2 \) evolution by re-oxidation of samples with water after \( \text{H}_2 \) reduction during three repeated cycles. As exhibited in Fig. 5(a), \( \text{H}_2 \)-evolution peak of \( (n)/\text{Fe}_2\text{O}_3 \) sample, which was due to reoxidation by water-splitting according to \( \text{Fe} \rightarrow \text{Fe}_3\text{O}_4 \) course, was found in the temperature range of ca. 650 to 850 K. With increasing the number of repeated cycles, the maximum peaks shifted to higher temperature and the slopes of the peaks decreased, presumably indicating that the reaction rate decreased. These results can be explained to be due to the deactivation of iron oxide by the sintering. For \( (\text{Rh})/\text{Fe}_2\text{O}_3 \) sample, it was observed that the water-splitting temperature were considerably lowered in comparison with that of \( (n)/\text{Fe}_2\text{O}_3 \) sample as might be expected. These results suggest that Ru additive promotes the re-oxidation of Fe metal to \( \text{Fe}_3\text{O}_4 \) through \( \text{H}_2\text{O} \) dissociation into \( \text{H} \) and \( \text{OH} \) in good agreement with previous work [2]. With increasing the redox cycles as shown in Fig. 5, the re-oxidation temperature of \( (\text{Rh})/\text{Fe}_2\text{O}_3 \) sample by water-splitting increased, while the intensities of the peaks remarkably decreased. Consequently, it is indicated that Ru additives play an important role in promoting the \( \text{H}_2 \) reduction and re-oxidation by water-splitting but have little effect on the prevention of deactivation due to sintering of iron oxide. Meanwhile, \( (\text{Ce})/\text{Fe}_2\text{O}_3 \) and \( (\text{Zr})/\text{Fe}_2\text{O}_3 \) samples presented the \( \text{H}_2 \) evolution peaks of two steps unlike that of \( (n)/\text{Fe}_2\text{O}_3 \) sample and no decrease in the re-oxidation temperature, but no decrease of amount of \( \text{H}_2 \) evolution in contrast with \( (\text{Rh})/\text{Fe}_2\text{O}_3 \) sample. These results indicate that Ce and Zr additives play an important role in the prevention of deactivation by sintering of iron oxide during the repeated redox cycles. As shown in Fig. 5(e) and (f), iron oxides mixed with two component additives clearly exhibited the decrease in the re-oxidation temperature and no big changes in amount of \( \text{H}_2 \) evolution during the repeated cycles. These results seems to be due to cooperative effect by co-addition of Rh and another species, such as Ce and Zr which have an effect on prevention of deactivation of iron oxide. Consequently, it suggests that the iron oxides could simultaneously gain two effects not only on promoting the reduction and re-oxidation but also on preventing from deactivation by co-addition of Rh and another species with thermal stability such

Fig. 6. \( \text{H}_2 \) evolution profiles by re-oxidation of \( (\text{Rh, Ce, Zr})/\text{Fe}_2\text{O}_3 \) sample during three repeated cycles. 
Sampling weight : 50 mg, heating rate : 4 K/min and oxidizing gas : \( \text{H}_2\text{O}/\text{Ar} \).
as Ce and Zr, respectively.

To investigate the effect of three component additives, we have prepared the (Rh, Ce, Zr)/Fe₂O₃ sample added with all of Rh, Ce and Zr species and also performed the redox test for it. For comparison, (Rh, Mo)/Fe₂O₃ sample, which have been reported to exhibit the excellent performance in previous work [2], was prepared and the redox tests were carried out under the same condition as that of this experiment. The results were exhibited in Fig. 6 as compared with (n)/Fe₂O₃ sample. (Rh, Ce, Zr)/Fe₂O₃ sample showed H₂ evolution peak at much lower temperature than that of (n)/Fe₂O₃ sample due to promoting effect on re-oxidation by Rh species. Moreover, no decrease in the intensity and area of the peak was found and no peak shifted to higher temperature with increasing the number of repeated cycles, in contrast with Fe-O/(n) and (Rh, Mo)/Fe₂O₃ samples. Therefore, it seems that these results were attributed to a synergistic effect by Rh, Ce and Zr additives.

Fig. 7 shows the SEM images of the (n)/Fe₂O₃ and (Zr)/Fe₂O₃ samples before and after the three repeated cycles. As exhibited in Fig. 7(a) and (b), it is clearly observed that the particle size of (n)/Fe₂O₃ considerably increased by sintering of iron oxide, while (Zr)/Fe₂O₃ sample makes no big changes in particles size in spite of repeated cycles as shown in Fig. (c) and (d). Therefore, It is evidenced that Zr additive can play an important role in prevention sintering of iron oxide during the repeated redox cycles.

Fig. 7. SEM images of (n)/Fe₂O₃ and (Zr)/Fe₂O₃ samples before and after three redox cycles. (a) (n)/Fe₂O₃ samples before three redox cycles, (b) (n)/Fe₂O₃ samples after three redox cycles, (c) (Zr)/Fe₂O₃ samples before three redox cycles and (d) (Zr)/Fe₂O₃ samples after three redox cycles.
4. Conclusion and Summary

In this study, M/Fe\textsubscript{2}O\textsubscript{3}(M=Rh, Ce and Zr), iron oxides which were mixed with rhodium, cerium, zirconium or their combination were prepared by co-precipitation using urea method at different synthetic condition and characterized by TPR, XRD and SEM analysis. And their redox behaviors during repeated cycles were investigated using temperature programmed reaction (TPR) technique. From the results, it was revealed that physical property and reduction behavior of iron oxide were little affected by urea concentration as a precipitant. Rh additive had an effect on lowering the re-oxidation temperature by water-splitting as well as reduction temperature corresponding to Fe\textsubscript{2}O\textsubscript{3}→Fe\textsubscript{3}O\textsubscript{4}. Meanwhile, Ce and Zr additives played an important role in prevention of deactivation by repeated cycles. (Rh, Ce, Zr)/Fe\textsubscript{2}O\textsubscript{3} sample added with Rh, Ce and Zr showed the lowest re-oxidation temperature by water-splitting and maintained high H\textsubscript{2} recovery in spite of the repeated redox cycles. Consequently, it is expected that (Rh, Ce, Zr)/Fe\textsubscript{2}O\textsubscript{3} sample can be a feasible medium for chemical hydrogen storage using redox cycle of iron oxide.

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