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# Production of pure hydrogen from methane mediated by the redox of Ni- and Cr-added iron oxides

Sakae Takenaka\*, Noriko Hanaizumi, Van Tho Dinh Son, Kiyoshi Otsuka\*

Department of Applied Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo, 152-8552, Japan

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## Abstract

Methods for the formation of pure hydrogen from methane were proposed based on the reduction of Fe<sub>3</sub>O<sub>4</sub> with methane into iron metal followed by the oxidation of iron metal with water vapor into Fe<sub>3</sub>O<sub>4</sub>. Iron oxides without additives were deactivated quickly for the redox reaction due to the sintering. Addition of Cr cations to iron oxides prevented the sintering of iron species during the redox, but the reduction with methane of iron oxides containing Cr cations needed high temperatures (1023 K). Addition of Ni to iron oxides enhanced the reduction with methane and the subsequent oxidation with water vapor at low temperatures, but Ni species promoted the sintering of iron species during the redox. In contrast, the iron oxides containing both Ni and Cr species (denoted as Ni–Cr–FeO<sub>x</sub>) could produce pure hydrogen repeatedly with high reproducibility through the redox at temperatures <923 K. XANES and EXAFS studies showed that Ni species in Ni–Cr–FeO<sub>x</sub> were present as Ni–Fe alloys after the reduction with methane, whereas they were present as Ni metal crystallites after the oxidation with water vapor. Cr species in Ni–Cr–FeO<sub>x</sub> were always stabilized as octahedral Cr<sup>3+</sup>O<sub>6</sub> on the B sites in the ferrites Cr<sub>x</sub>Fe<sub>3 – x</sub>O<sub>4</sub> during the redox reactions.

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# 1. Introduction

Hydrogen is regarded as a candidate for a clean energy source to be substituted for fossil fuels in order to solve many environmental problems.  $H_2-O_2$  fuel cells such as polymer electrolyte fuel cells (PEFC) are a promising system for utilizing hydrogen with high efficiency. PEFC can convert directly the chemical energy of hydrogen into electricity through chemical reactions between hydrogen and oxygen. PEFC does not emit any pollutant gases such as NO<sub>x</sub> or SO<sub>x</sub>, because it operates at low temperatures. Widespread use of PEFCs requires a safe and environmentally benign technology for the storage and supply of pure hydrogen. We have proposed a new technology for the storage

\* Corresponding authors. Fax: +81 3 5734 2879.

E-mail address: stakenak@o.cc.titech.ac.jp (S. Takenaka).

and supply of pure hydrogen based on the redox reactions of iron oxides as shown in Eqs. (1) and (2) [1]:

 $Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O,$  (1)

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2. \tag{2}$$

Magnetite,  $Fe_3O_4$  is reduced with hydrogen into iron metal. Hydrogen is recovered through the oxidation of iron metal with water vapor into  $Fe_3O_4$ . Using this method, 1 mol of iron metal can store and supply 1.33 mol of hydrogen theoretically. The amount of hydrogen stored and supplied through the redox of iron oxides corresponds to 4.8 wt% of iron metal. Our method is very safe because hydrogen is stored chemically as iron metals. In addition, iron metals or iron oxides are easily available and inexpensive material. However, the method requires the supply of inexpensive hydrogen for the reduction of magnetite into iron metal. Hydrogen is produced through the steam reforming of methane, the main component of natural gas, followed by the water-

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gas-shift reaction of CO. Steam reforming of methane is usually performed at temperatures > 1000 K and the highly exothermic reaction requires a large energy input. Recently, we demonstrated the formation of hydrogen from methane based on the reduction of magnetite with methane instead of hydrogen (Eq. (3)) and the subsequent oxidation of iron metal with water vapor (Eq. (4)) [2]

 $Fe_3O_4 + CH_4 \rightarrow 3Fe + CO_2 + 2H_2O, \qquad (3)$ 

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2. \tag{4}$$

The principle of our method is analogous to the old steam iron process for the production of hydrogen-rich gas at high temperatures > 1073 K and high pressures > 70 bar, using a gas mixture of CO, CO<sub>2</sub>, and hydrogen from coal and biomass for the reduction of iron ores [3,4]. In addition, the sequential production of synthesis gas and hydrogen was proposed by the reduction of  $Fe_3O_4$  with methane (4CH<sub>4</sub> +  $Fe_3O_4 \rightarrow 3Fe + 8H_2 + 4CO$ ) and the subsequent oxidation of iron metal with water vapor [5–7]. The processes must be performed at temperatures > 1000 K, since the formation of synthesis gas from Fe<sub>3</sub>O<sub>4</sub> and methane is favorable at temperatures > 1000 K according to the thermodynamic equilibrium. However, the production of hydrogen based on the reduction of iron oxides with methane, followed by the oxidation of iron metal with water vapor, should be performed at temperatures as low as possible from an economical viewpoint. In addition, generally speaking, the sintering of iron species occurs more easily during the redox reactions at higher temperatures. The iron oxides are deactivated for the redox reactions by the sintering. However, the reduction of pure iron oxides with methane required temperatures > 1023 K and the pure iron oxides were deactivated quickly for the redox of Eqs. (3) and (4) due to the sintering [2]. We have found that the addition of Cr cations to the iron oxides mitigated the sintering of iron metal and/or iron oxides during the redox, although the reduction with methane of the iron oxides with Cr cations required temperatures > 1023 K [2]. Addition of Cu species to the iron oxide sample enhanced the redox reactions (Eqs. (3) and (4)) at low temperatures, but the sample containing only Cu species was deactivated quickly for the redox due to sintering. In contrast, the iron oxides containing both Cu and Cr species could produce pure hydrogen repeatedly with high reproducibility through the redox at low temperatures.

In the present study, we report the preferable effects of the addition of Ni and Cr species into iron oxides on the redox reactions. The iron oxides containing both Ni and Cr species could produce pure hydrogen repeatedly with high reproducibility through the reduction with methane and the subsequent oxidation with water vapor at lower temperatures, compared to the iron oxides with both Cu and Cr species. In addition, the role of Ni and Cr species added to the iron oxide samples on the redox reactions was examined on the basis of the local structures of these additives.

## 2. Experimental

Iron oxide (Fe<sub>2</sub>O<sub>3</sub>) without any additives was prepared from Fe(OH)<sub>3</sub> that was precipitated from an aqueous solution of Fe(NO<sub>3</sub>)<sub>3</sub>  $\cdot$  9H<sub>2</sub>O during the hydrolysis of urea at 363 K. Iron oxides containing foreign metals were prepared from Fe(OH)<sub>3</sub> and the corresponding metal hydroxides that were precipitated from mixed aqueous solutions of  $Fe(NO_3)_3 \cdot 9H_2O$  and added metal cations during the hydrolysis of urea at 363 K. These precipitates were filtered and dried at 373 K for 10 h. The dried samples were calcined at 773 K for 10 h under air. The amount of foreign metal (M) added to the iron oxides was adjusted to 5 mol% to all the metal atoms, M/(M + Fe) = 0.05. When two types of metals (M1 and M2) were added to iron oxides, the amount of each metal was adjusted to 5 mol%  $(M_1/(M_1 + M_2 + Fe) = M_2/(M_1 + M_2 + Fe) = 0.05)$ . The iron oxide sample with M or the iron oxide sample with both  $M_1$  and  $M_2$  was denoted as M-FeO<sub>x</sub> or  $M_1$ -M<sub>2</sub>-FeO<sub>x</sub>, respectively. Al(NO<sub>3</sub>)<sub>3</sub>  $\cdot$  9H<sub>2</sub>O, (NH<sub>4</sub>)<sub>2</sub>TiO(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>  $\cdot$  2H<sub>2</sub>O,  $NH_4VO_3$ ,  $Cr(NO_3)_3 \cdot 9H_2O$ ,  $Co(NO_3)_2 \cdot 6H_2O$ ,  $Ni(NO_3)_2 \cdot$  $6H_2O$ ,  $Cu(NO_3)_2 \cdot 3H_2O$ ,  $ZrO(NO_3)_2 \cdot 6H_2O$ ,  $RhCl_3$ ,  $PdCl_2$ , IrCl<sub>3</sub>, and H<sub>2</sub>PtCl<sub>6</sub> were used as metal sources. Iron species in all the fresh iron oxide samples were present as Fe<sub>2</sub>O<sub>3</sub> mainly, regardless of the type of additives. Fe<sub>2</sub>O<sub>3</sub> in the fresh iron oxide samples was reduced with methane into iron metal in the first reduction and subsequently the metal was oxidized with water vapor into  $Fe_3O_4$  in the first oxidation. The oxidation of iron metal with water vapor into  $Fe_2O_3$  is thermodynamically impossible. The second and subsequent redox reactions were performed between Fe<sub>3</sub>O<sub>4</sub> and iron metal.

The reduction with methane and the subsequent oxidation with water vapor of the iron oxide samples were performed with a conventional gas-flow system with a fixed catalyst bed. The iron oxide samples (0.20 g as Fe metal) were packed in a quartz tube reactor (inner diameter = 1.8 cm and length = 60 cm). For the reduction, methane (30 ml min<sup>-1</sup>) and 101 kPa) was passed over the iron oxides at 473 K and the temperatures increased to 1023 K at 3 K min<sup>-1</sup>. The reduction of the iron oxides was continued at a constant temperature 1023 K until CO or CO2 was not observed in the effluent gases from the catalyst bed. After Ar was introduced in order to purge out methane remaining in the reactor, water vapor diluted with Ar  $(P(H_2O) = 18 \text{ kPa and})$ total flow rate = 70 ml min<sup>-1</sup>) was passed over the reduced iron oxides at 473 K. The temperatures increased to 823 K at 4 K min<sup>-1</sup>. The oxidation of the reduced samples with water vapor was continued at a constant temperature 823 K until the formation of hydrogen could not be observed in the effluent gases from a catalyst bed. During the reaction, a part of the effluent gases was sampled out and analyzed by a gas chromatograph. The detection limit of CO and  $CO_2$  in the effluent gases was ca. 50 ppm in the present study. Unless otherwise noted, the reduction with methane and the subsequent oxidation with water vapor were repeated under the same conditions. In order to estimate the amount of carbons deposited on the iron oxide samples during the redox reactions, carbons were oxidized with gaseous oxygen at 823 K after the redox reactions. The oxidation of carbons with  $O_2$  produced  $CO_2$  in addition to a trace of CO. The amount of carbons deposited on the samples was evaluated based on the amount of  $CO_2$  formed during the oxidation with  $O_2$ .

SEM images of the iron oxide samples were measured using a Hitachi FE-SEM S-800 (field emission gun scanning electron microscope).

X-ray absorption spectra (XANES and EXAFS) of the iron oxide samples were measured on the beam line BL-12C at the Photon Factory in the Institute of Materials Structure Science for High Energy Accelerator Research Organization at Tsukuba in Japan (Proposal Number 2002G108). Cr and Ni K-edge XANES and EXAFS of the iron oxide samples were measured with a fluorescence mode with a Si(111) two-crystal monochromator at room temperature. In order to prepare the iron oxide samples for the measurements of XANES and EXAFS, the reduction with methane at 923 K and the subsequent oxidation with water vapor at 773 K were performed. After the redox reaction, the iron oxide samples were cooled to room temperature under an Ar stream. Then, the sample was packed in a polyethylene bag under Ar atmosphere. The analysis of EXAFS data was performed by using an EXAFS analysis program, REX (Rigaku Co.). For EXAFS analysis, the oscillation was extracted from the EXAFS data by a spline-smoothing method. The oscillation was normalized by the edge height around 70-100 eV above the threshold. The Fourier transformation of  $k^3$ -weighted EXAFS oscillation was performed over a k-range of 3.5–14.5 Å<sup>-1</sup>. Inversely Fourier-transformed data for each Fourier peak were analyzed by a curve-fitting method, using theoretically phase-shift and amplitude functions derived by the FEFF8 program [8]. Error bars of the analysis were estimated by R factor ( $R_f$ ) defined as the following equation:

$$R_{\rm f} = \sum \left( k^3 \chi(k)^{\rm obs} - k^3 \chi(k)^{\rm calc} \right)^2 / \sum \left( k^3 \chi(k)^{\rm obs} \right)^2.$$

## 3. Results and discussion

#### 3.1. Modification of iron oxides with different metal species

Fig. 1 shows the changes in the formation rates of CO,  $CO_2$ , and hydrogen as a function of temperatures during the reduction of different iron oxides with methane. Cr cations were added in all the iron oxides shown in Fig. 1 in order to suppress the sintering of iron species during the redox reactions. We have reported that Cr cations prevented the sintering of iron species during the redox reactions of Eqs. (1) and (2) [9–11]. Iron oxides containing only Cr cations showed poor reactivity for the reduction with methane at temperatures < 1023 K, as will be demonstrated in Fig. 5. Therefore,



Fig. 1. Change in the formation rates of CO, CO<sub>2</sub>, and hydrogen as a function of temperatures during the reduction of different iron oxide samples with methane.  $\blacktriangle$ , Co–Cr–FeO<sub>x</sub>;  $\blacklozenge$ , Ni–Cr–FeO<sub>x</sub>;  $\bigcirc$ , Cu–Cr–FeO<sub>x</sub>;  $\bigtriangleup$ , Rh–Cr–FeO<sub>x</sub>;  $\blacktriangledown$ , Rh–Cr–FeO<sub>x</sub>;  $\blacktriangledown$ , Pd–Cr–FeO<sub>x</sub>;  $\bigtriangledown$ , Ir–Cr–FeO<sub>x</sub>;  $\blacktriangledown$ , Pd–Cr–FeO<sub>x</sub>.

Co, Ni, Cu, Rh, Pd, Ir, or Pt was added to Cr-FeO<sub>x</sub> to enhance the redox reaction at low temperatures. During the reduction with methane, the formation of CO, CO<sub>2</sub>, H<sub>2</sub>O, and hydrogen was observed by G.C. However, quantitative analysis for the formation of H<sub>2</sub>O was not satisfactory in the present study. Therefore, the formation rate of CO and CO<sub>2</sub> during the reduction with methane was used as an index of the reactivity of each iron oxide for the reduction with methane. As shown in Fig. 1, the formation of CO<sub>2</sub> was observed in the reduction of many iron oxide samples at temperatures < 700 K, where CO was not formed. The formation of  $CO_2$  at temperatures < 700 K could be ascribed to the reduction of Fe<sub>2</sub>O<sub>3</sub> into Fe<sub>3</sub>O<sub>4</sub>, which was confirmed by XRD patterns of these samples. The formation rate of CO<sub>2</sub> increased again in the temperature range > 700 K, where CO was also formed. The formation of CO and CO2 at temperatures > 700 K resulted from the reduction of Fe<sub>3</sub>O<sub>4</sub> into iron metal. The peaks of the formation rates of CO and CO<sub>2</sub> due to the reduction of Fe<sub>3</sub>O<sub>4</sub> into iron metal were positioned at higher temperatures in the following order, Rh–Cr–FeO<sub>x</sub> < Ir–Cr–FeO<sub>x</sub> < Pt–Cr–FeO<sub>x</sub> < Ni–Cr–FeO<sub>x</sub> < Pd–Cr–  $FeO_x < Cu-Cr-FeO_x \approx Co-Cr-FeO_x$ . When the formation



Fig. 2. Change in the formation rates of hydrogen, CO, and CO<sub>2</sub> as a function of temperatures during the oxidation of different iron oxide samples with water vapor.  $\blacktriangle$ , Co–Cr–FeO<sub>x</sub>;  $\blacklozenge$ , Ni–Cr–FeO<sub>x</sub>;  $\bigcirc$ , Cu–Cr–FeO<sub>x</sub>;  $\bigtriangleup$ , Rh–Cr–FeO<sub>x</sub>;  $\blacktriangledown$ , Pd–Cr–FeO<sub>x</sub>;  $\bigtriangledown$ , Pt–Cr–FeO<sub>x</sub>.

rates of CO and CO2 crossed over the maxima, the formation of hydrogen was enhanced. It is generally accepted that iron metal catalyzed the methane decomposition into hydrogen and carbons (CH<sub>4</sub>  $\rightarrow$  C + 2H<sub>2</sub>) [12,13]. The formation of hydrogen during the reduction of the iron oxide samples with methane would result from the methane decomposition catalyzed by iron metal in the samples. Note that the methane decomposition deposited carbons on the iron oxides. For example, the amount of carbons deposited on Cu–Cr–FeO<sub>x</sub> during the reduction with methane was estimated to ca. 5 mol per mole of iron atom in Cu–Cr–FeO<sub>x</sub> (C/Fe = 5), which corresponded to 0.72 g per 1 g of Cu–Cr–  $FeO_x$  (42 wt% in the Cu–Cr–FeO<sub>x</sub> after the redox reaction). The deposition of carbons on the iron oxides would result in the stoppage of gases in the reactor. Therefore, the amount of carbons deposited on the iron oxides should be decreased as low as possible.

After the reduction of the iron oxides with methane shown in Fig. 1, the oxidation with water vapor was performed. Formation rates of hydrogen, CO, and CO<sub>2</sub> during the oxidation of the iron oxide samples with water vapor were plotted against temperatures in Fig. 2. Because the formation rates of any products were very slow in the temperature range < 500 K, the results in the temperature range from 500 to 823 K are shown in Fig. 2. The formation rate of hydrogen during the oxidation with water vapor increased

Table 1	
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Total amounts of hydrogen, CO, and  $CO_2$  formed in the oxidation of the reduced iron oxide samples with water vapor

Sample	H <sub>2</sub> /Fe	CO/Fe	CO <sub>2</sub> /Fe	H <sub>2</sub> */Fe
Co–Cr–FeO <sub>x</sub>	1.7	0.02	0.04	1.4
Ni–Cr–FeO <sub>x</sub>	1.7	0.05	0.18	1.3
$Cu-Cr-FeO_x$	1.8	0.01	0.08	1.6
Rh–Cr–FeO <sub>x</sub>	1.3	< 0.01	0.01	1.3
$Pd-Cr-FeO_x$	1.5	0.01	0.03	1.4
$Ir-Cr-FeO_x$	1.4	< 0.01	0.02	1.4
$Pt-Cr-FeO_X$	1.4	< 0.01	< 0.01	1.4

with temperature. The kinetic curves of the formation rate of hydrogen for Ni–Cr–FeO<sub>x</sub>, Cu–Cr–FeO<sub>x</sub>, Rh–Cr–FeO<sub>x</sub>, and Ir–Cr–FeO<sub>x</sub> were similar; i.e., the formation rate of hydrogen reached the maximum at around 720-760 K. Pt- $Cr-FeO_x$  showed higher activity for the hydrogen formation at lower temperatures compared to the other samples. During the oxidation with water vapor, CO and CO<sub>2</sub> were also produced in addition to hydrogen. CO and CO2 would be formed by the gasification with water vapor of carbons which had been deposited on the iron oxides during the reduction with methane. Formation of CO or CO<sub>2</sub> was not desirable from a viewpoint of the formation of pure hydrogen from methane. The amounts of hydrogen, CO, and CO<sub>2</sub> formed during the oxidation with water vapor were roughly estimated by integrating the formation rates of these products with time. The amounts of these products are summarized in Table 1. The amounts of these products were divided by moles of iron atoms in the samples, which are denoted as H<sub>2</sub>/Fe, CO/Fe, and CO<sub>2</sub>/Fe. The amounts of hydrogen formed by the oxidation of Co-Cr-FeO<sub>x</sub>, Ni-Cr-FeO<sub>x</sub>, Cu- $Cr-FeO_x$ , and  $Pd-Cr-FeO_x$  with water vapor were higher than the theoretical value  $H_2/Fe = 1.33$ , whereas  $H_2/Fe$ values for the other samples were similar to the theoretical one. The excess amounts of hydrogen would be formed by the gasification with water vapor of carbons deposited on the samples during the reduction with methane. The amount of hydrogen formed by only the redox of iron oxides (denoted as  $H_2*/Fe$ ) was estimated by the subtraction of the amount of hydrogen formed through the gasification of carbons with water vapor from the total amount of hydrogen formed during the oxidation of the iron oxides with water vapor, assuming that CO and CO<sub>2</sub> were formed according to the following reactions;  $C + H_2O \rightarrow CO + H_2$  and  $C + H_2O \rightarrow CO_2 + 2H_2$ .  $H_2*/Fe$  values for all the iron oxides were similar to the theoretical value, suggesting that the redex between iron metal and Fe<sub>3</sub>O<sub>4</sub> was utilized completely for all the samples.  $Pt-Cr-FeO_x$ ,  $Rh-Cr-FeO_x$ , and Ir–Cr–FeO<sub>x</sub> are suitable mediators for the hydrogen formation from methane because these samples could be reduced with methane at low temperatures and the amounts of CO and CO<sub>2</sub> formed during the oxidation with water vapor were very small. However, Pt, Rh, and Ir are very expensive metal, compared to Cu and Ni. Ni–Cr–FeO<sub>x</sub> is a candidate of the promising mediators for the formation of hydrogen, because



Fig. 3. Change in the formation rates of CO, CO<sub>2</sub>, and hydrogen as a function of temperatures during the reduction with methane of Ni–FeO<sub>x</sub> containing different cations.  $\bigcirc$ , Ni–Al–FeO<sub>x</sub>;  $\square$ , Ni–Ti–FeO<sub>x</sub>;  $\blacktriangle$ , Ni–V–FeO<sub>x</sub>;  $\blacksquare$ , Ni–V–FeO<sub>x</sub>.

Ni–Cr–FeO<sub>x</sub> can be reduced with methane at lower temperatures than Pd–Cr–FeO<sub>x</sub>, Cu–Cr–FeO<sub>x</sub>, and Co–Cr–FeO<sub>x</sub>. In addition, the reactivity of Ni–Cr–FeO<sub>x</sub> for the hydrogen formation through the oxidation with water vapor was almost the same as those of Rh–Cr–FeO<sub>x</sub> and Ir–Cr–FeO<sub>x</sub>.

We have examined the effects of different additives to the iron oxides on the redox of Eqs. (1) and (2) [9-11]. Al-FeO<sub>x</sub>, Ti-FeO<sub>x</sub>, V-FeO<sub>x</sub>, and Zr-FeO<sub>x</sub> in addition to  $Cr-FeO_x$  also could store and supply hydrogen repeatedly through the redox of Eqs. (1) and (2). The specific surface areas of these iron oxide samples remained high after the redox reactions, whereas the specific surface area of iron oxide without additives decreased seriously during the redox [9–11]. These results implied that the addition of Al, Ti, Cr, V, or Zr to the iron oxides prevented the sintering of iron species during the redox. Therefore, Al, Ti, V, or Zr species were added to Ni–FeO<sub>x</sub>. The results of the reduction with methane and the subsequent oxidation with water vapor for Ni–Al–FeO<sub>x</sub>, Ni–Ti–FeO<sub>x</sub>, Ni–Cr–FeO<sub>x</sub>, Ni–V–FeO<sub>x</sub>, and Ni–Zr–FeO<sub>x</sub> were shown in Figs. 3 and 4, respectively. A peak for the CO<sub>2</sub> formation due to the reduction of Fe<sub>2</sub>O<sub>3</sub>



Fig. 4. Change in the formation rates of hydrogen, CO, and CO<sub>2</sub> as a function of temperatures during the oxidation with water vapor of Ni–FeO<sub>x</sub> containing different cations.  $\bigcirc$ , Ni–Al–FeO<sub>x</sub>;  $\square$ , Ni–Ti–FeO<sub>x</sub>;  $\blacktriangle$ , Ni–V–FeO<sub>x</sub>;  $\blacksquare$ , Ni–V–FeO<sub>x</sub>.

into Fe<sub>3</sub>O<sub>4</sub> was observed for all the samples at around 760 K, although these peaks were very small. When the temperature increased to 840 K, CO and CO<sub>2</sub> were formed through the reduction of Fe<sub>3</sub>O<sub>4</sub> into iron metal. The formation rates of CO and CO<sub>2</sub> reached the maxima at around 940 K for all the samples except for Ni–Ti–FeO<sub>x</sub>. The maximum formation rate of CO for the reduction of Ni–Cr–FeO<sub>x</sub> was appreciably higher than those for the other samples. These results suggested that Ni–Cr–FeO<sub>x</sub> was reduced with methane more quickly, compared to the other iron oxides shown in Fig. 3.

Fig. 4 shows the changes in the formation rates of hydrogen, CO, and CO<sub>2</sub> as a function of temperatures during the oxidation with water vapor of Ni–FeO<sub>x</sub> containing different cations. The kinetic curves of the formation rate of hydrogen for Ni–Al–FeO<sub>x</sub>, Ni–Cr–FeO<sub>x</sub>, and Ni–Zr–FeO<sub>x</sub> were similar. The formation rate of hydrogen for the three samples increased with temperature and it reached the maximum at around 750 K. In contrast to these samples, Ni–Ti–FeO<sub>x</sub> and Ni–V–FeO<sub>x</sub> showed poor activities for the formation of hydrogen. It should be noted that the formation rates of CO and CO<sub>2</sub> during the oxidation of Ni–Cr–FeO<sub>x</sub> with water vapor were higher compared to those for the other samples. However, the formation of CO and CO<sub>2</sub> during the oxidation of Ni–Cr–FeO<sub>x</sub> with water vapor was negligible in the second and subsequent redox cycle, as will be described below.

From the results described above, Ni–Al–FeO<sub>x</sub>, Ni–Cr– FeO<sub>x</sub>, and Ni–Zr–FeO<sub>x</sub> were effective mediators for the formation of hydrogen through the reduction with methane and



Fig. 5. Change in the formation rates of CO, CO<sub>2</sub>, and hydrogen as a function of time on stream during the reduction with methane of FeO<sub>x</sub> ( $\bullet$ ), Cr–FeO<sub>x</sub> ( $\odot$ ), Ni–FeO<sub>x</sub> ( $\blacktriangle$ ), and Ni–Cr–FeO<sub>x</sub> ( $\triangle$ ).

the subsequent oxidation with water vapor. In particular, Ni– Cr–FeO<sub>x</sub> showed a higher reactivity for the reduction with methane compared to Ni–Al–FeO<sub>x</sub> and Ni–Zr–FeO<sub>x</sub>.

# 3.2. Redox performance of Ni-Cr-FeO<sub>x</sub>

The reduction with methane and the subsequent oxidation with water vapor for FeO<sub>x</sub>, Ni-FeO<sub>x</sub>, Cr-FeO<sub>x</sub>, and Ni-Cr- $FeO_x$  were performed in order to clarify the role of each additive on the redox reaction. The results for the reduction with methane and the subsequent oxidation with water vapor are shown in Figs. 5 and 6, respectively. In the reduction of  $FeO_x$  with methane, the peaks of the formation of CO and CO<sub>2</sub> due to the reduction of Fe<sub>3</sub>O<sub>4</sub> into iron metal were observed at around 270 min, where the reaction temperature had reached 1023 K. The addition of Cr cations into  $FeO_x$  improved the reactivity slightly for the reduction with methane, but Cr-FeO<sub>x</sub> was reduced after the reaction temperature had reached 1023 K. In contrast, the addition of Ni species to  $FeO_x$  enhanced the reduction with methane at low temperatures. The peaks of the formation rates of CO and  $CO_2$  during the reduction of Ni–FeO<sub>x</sub> were observed at around 160 min, although the peaks were very small. The addition of both Ni and Cr species to  $FeO_x$  was the most



Fig. 6. Change in the formation rates of hydrogen, CO, and CO<sub>2</sub> as a function of time on stream during the oxidation with water vapor of FeO<sub>x</sub> ( $\bullet$ ), Cr–FeO<sub>x</sub> ( $\bigcirc$ ), Ni–FeO<sub>x</sub> ( $\blacktriangle$ ), and Ni–Cr–FeO<sub>x</sub> ( $\triangle$ ).

effective for the reduction with methane. The peaks of the formation rates of CO and CO<sub>2</sub> in the reduction of Ni–Cr–FeO<sub>x</sub> were located at almost the same positions as those for Ni–FeO<sub>x</sub>. In addition, the maximum formation rates of CO and CO<sub>2</sub> in the reduction of Ni–Cr–FeO<sub>x</sub> were significantly higher than those for Ni–FeO<sub>x</sub> and Cr–FeO<sub>x</sub>. These results strongly implied that Ni species in the iron oxide samples act as active sites for methane during the reduction.

Fig. 6 shows the change in the formation rates of hydrogen, CO, and CO<sub>2</sub> with time on stream in the oxidation with water vapor of  $FeO_x$ ,  $Cr-FeO_x$ ,  $Ni-FeO_x$ , and  $Ni-Cr-FeO_x$ . The oxidation of  $FeO_x$  with water vapor produced hydrogen after 40 min, where the temperature reached 620 K.  $Cr-FeO_x$  also formed hydrogen after 40 min, indicating that the addition of Cr cations into the iron oxide samples did not enhance the hydrogen formation at low temperatures. However, the formation rate of hydrogen after 50 min for  $Cr-FeO_x$  was higher than that of  $FeO_x$ . The higher formation rate of hydrogen for  $Cr-FeO_x$  might result from the larger surface area [11]. Table 2 shows the specific surface areas of FeO<sub>x</sub>, Cr-FeO<sub>x</sub>, Ni-FeO<sub>x</sub>, and Ni-Cr-FeO<sub>x</sub> before and after the first redox cycle. The surface areas of  $FeO_x$  and  $Cr-FeO_x$  decreased after the first redox reaction. However, the surface area of Cr-FeO<sub>x</sub> after the first cycle was significantly larger than that of  $FeO_x$ . Therefore, the reactivity of  $Cr-FeO_x$  for the hydrogen formation would be higher than that of  $FeO_x$ . On the other hand, the formation rate of hy-

Table 2 Specific surface areas of  $FeO_x$ ,  $Cr-FeO_x$ ,  $Ni-FeO_x$ , and  $Ni-Cr-FeO_x$ 

Sample	Composition (as mole ratio)	Specific surface area (m <sup>2</sup> g <sup>-1</sup>	.)
		Before the redox	After the first cycle <sup>a</sup>
FeO <sub>x</sub>	Fe only	30	3
$Cr-FeO_x$	Cr:Fe = 5:95	46	12
$Ni-FeO_x$	Ni:Fe = 5:95	50	< 1
Ni–Cr–FeO <sub><math>x</math></sub>	Ni:Cr:Fe = 5:5:90	38	10

<sup>a</sup> Specific surface areas of the samples after the first cycle were measured after the removal of carbons deposited on the samples by the oxidation with air at 823 K.

drogen for Ni–FeO<sub>x</sub> was extremely low even at 823 K. We have reported that Ni–FeO<sub>x</sub> was deactivated more quickly for the redox of Eqs. (1) and (2) compared to  $FeO_r$  [9]. In the previous study, it was found that Ni in Ni–FeO<sub>x</sub> promoted the sintering of iron species during the redox [9]. In the present case, the surface area of Ni–FeO<sub>x</sub> (< 1 m<sup>2</sup> g<sup>-1</sup>) was smaller than that of  $\text{FeO}_x$  (3 m<sup>2</sup> g<sup>-1</sup>) after the first redox cycle, as shown in Table 2. Ni–FeO<sub>x</sub> would show low reactivity for the hydrogen formation through the oxidation with water vapor because iron metals in the Ni–FeO<sub>x</sub> had been aggregated seriously during the reduction with methane. In contrast, the addition of both Ni and Cr species to  $FeO_x$ enhanced the formation of hydrogen at low temperatures; i.e., hydrogen was formed at temperatures > 500 K for Ni- $Cr-FeO_x$ , whereas the formation of hydrogen for  $FeO_x$  and  $Cr-FeO_x$  required temperatures > 620 K. These results implied that Ni species added to the iron oxide sample act as active sites for the hydrogen formation. The formation rate of hydrogen for Ni–Cr–FeO<sub>x</sub> was significantly higher than that for Ni–FeO<sub>x</sub>. Table 2 shows that the surface area of Ni– Cr–FeO<sub>x</sub> (10 m<sup>2</sup> g<sup>-1</sup>) was significantly larger than that of Ni–FeO<sub>x</sub> (< 1 m<sup>2</sup> g<sup>-1</sup>) after the first redox cycle. These results indicated that Cr cations in Ni–Cr–FeO<sub>x</sub> prevented the sintering of iron species during the redox. Therefore, Ni- $Cr-FeO_x$  showed high reactivity for the hydrogen formation through the oxidation with water vapor.

Ni–Cr–FeO<sub>x</sub> should be utilized repeatedly for the hydrogen formation through the reduction with methane and the subsequent oxidation with water vapor. Therefore, four redox cycles for Ni–Cr–FeO<sub>x</sub> were repeated under the same conditions as those shown in Figs. 1-6. The results for the reduction with methane and the subsequent oxidation with water vapor are shown in Figs. 7 and 8, respectively. The formation rates of CO and CO<sub>2</sub> during the first reduction of Ni–Cr–FeO<sub>x</sub> with methane increased significantly at temperatures > 840 K and their formation was terminated at around 960 K. The formation rate of hydrogen through the methane decomposition was accelerated from ca. 900 K, where the formation rates of CO and CO<sub>2</sub> crossed over the maxima. The kinetic curves of the formation rates of CO and  $CO_2$  during the reduction of Ni–Cr–FeO<sub>x</sub> did not change appreciably in four cycles. These results indicated that Ni- $Cr-FeO_x$  could be reduced with methane repeatedly with high reproducibility. However, carbons were deposited on Ni–Cr–FeO<sub>x</sub> by methane decomposition during the reduc-



Fig. 7. Change in the formation rates of CO, CO<sub>2</sub>, and hydrogen as a function of temperatures during the reduction of Ni–Cr–FeO<sub>x</sub> with methane. •, the first reduction;  $\bigcirc$ , the second reduction;  $\blacktriangle$ , the third reduction;  $\triangle$ , the fourth reduction.

tion. The amount of carbons deposited on Ni–Cr–FeO<sub>x</sub> in the reduction with methane of each redox cycle was estimated to C/Fe = ca. 5–7, which corresponded to carbon deposition of 0.72–1.01 g per 1 g of Ni–Cr–FeO<sub>x</sub> in each redox cycle. After four redox cycles, the total amount of carbons deposited on Ni–Cr–FeO<sub>x</sub> reached C/Fe = ca. 26, which corresponded to 3.74 g per 1 g of Ni–Cr–FeO<sub>x</sub> (79 wt% in the sample after four redox cycles).

The formation rate of hydrogen during the first oxidation of the reduced Ni–Cr–FeO<sub>x</sub> with water vapor increased at temperatures higher than 560 K and it reached the maxi-



Fig. 8. Change in the formation rates of hydrogen, CO, and CO<sub>2</sub> as a function of temperatures during the oxidation of Ni–Cr–FeO<sub>x</sub> with water vapor.  $\bullet$ , the first oxidation;  $\bigcirc$ , the second oxidation;  $\blacktriangle$ , the third oxidation;  $\triangle$ , the fourth oxidation.

Table 3

Total amounts of hydrogen, CO, and CO<sub>2</sub> formed in the oxidation of Ni–Cr– $FeO_x$  with water vapor

Repetition number	H <sub>2</sub> /Fe	CO/Fe	CO <sub>2</sub> /Fe	H <sub>2</sub> */Fe
1	1.7	0.05	0.18	1.3
2	1.5	0.02	0.08	1.3
3	1.4	0.02	0.09	1.2
4	1.3	< 0.01	0.02	1.3

mum at 720 K, as shown in Fig. 8. Reproducible kinetic curves of the formation rate of hydrogen were observed in the second and subsequent oxidation. In the oxidation of Ni–Cr–FeO<sub>x</sub> with water vapor, the formation rate of hydrogen became slow at around 770 K and it increased again at temperatures higher than 800 K, where the formation of CO and CO<sub>2</sub> was also enhanced. The formation of CO, CO<sub>2</sub>, and hydrogen was continuous after the temperature reached 823 K. These products would be formed by the gasification of deposited carbons with water vapor. The total amounts of hydrogen, CO, and CO<sub>2</sub> formed during the oxidation of Ni–Cr–FeO<sub>x</sub> with water vapor are summarized in Table 3. Total amounts of hydrogen formed in the first, the second, and the third oxidation were higher than the theoretical value ( $H_2/Fe = 1.33$ ). Excess amounts of hydrogen would be formed through the gasification of deposited carbons with water vapor. H<sub>2</sub>\*/Fe values in the four cycles



Before the reaction

After four redox cycles

Fig. 9. SEM images of Ni–Cr–FeO<sub>x</sub> before the reaction and after four redox cycles.

were similar to the theoretical value. These results strongly suggested that most of the iron species in Ni–Cr–FeO<sub>x</sub> were reduced with methane and subsequently oxidized with water vapor.

As described earlier, Ni–Cr–FeO<sub>x</sub> could produce hydrogen repeatedly through the reduction with methane and the subsequent oxidation with water vapor. However, carbons were deposited on Ni–Cr–FeO<sub>x</sub> by the methane decomposition during the redox reactions. Fig. 9 shows SEM images of Ni–Cr–FeO<sub>x</sub> before the redox and after the four redox cycles shown in Figs. 7 and 8. SEM image showed that the fresh Ni–Cr–FeO<sub>x</sub> was composed of small particles with relatively uniform diameters (20-30 nm). On the other hand, filamentous carbons were observed in the SEM image of the Ni–Cr–FeO<sub>x</sub> after the redox. It is well accepted that Ni metal and Fe metal catalyze the methane decomposition to form filamentous carbons [12-14]. Deposition of filamentous carbons on the Ni–Cr–FeO<sub>x</sub> must cause the stoppage of gases in the reactor. In addition, Ni–Cr–FeO<sub>x</sub> formed CO and CO<sub>2</sub> in addition to hydrogen through the oxidation of carbon with water vapor. It should be noted that the oxidation of Ni-Cr- $FeO_x$  with water vapor did not form CO or CO<sub>2</sub> at al in the temperature range < 760 K in the second oxidation (Fig. 8). Therefore, the redox reaction of Ni–Cr–FeO<sub>x</sub> was performed repeatedly under the following conditions. For the reduction, methane was passed over Ni–Cr–FeO<sub>x</sub> at 473 K. The temperature of the reactor increased to 873 K at 3 K min<sup>-1</sup>. For the oxidation, water vapor balanced with Ar was passed over the reduced Ni–Cr–FeO<sub>x</sub> at 473 K and the temperature increased to 673 K at 4 K min<sup>-1</sup>. The results for the reduction with methane and the oxidation with water vapor are shown in Figs. 10 and 11, respectively. Kinetic curves of the formation rates of CO and CO<sub>2</sub> from the second to the fourth reduction with methane are similar, as shown in Fig. 10. In addition, the formation rate of hydrogen through the methane decomposition became lower by decreasing the reduction temperature from 1023 K (Fig. 7) to 873 K. The amount of carbons deposited on Ni–Cr–FeO<sub>x</sub> in the first reduction was estimated to C/Fe = ca. 5, which corresponded to 0.72 g per 1 g of Ni–Cr–FeO<sub>x</sub>. After the second reduc-



Fig. 10. Change in the formation rates of CO, CO<sub>2</sub>, and hydrogen with time on stream during the reduction of Ni–Cr–FeO<sub>x</sub> with methane.  $\bullet$ , the first reduction;  $\bigcirc$ , the second reduction;  $\blacktriangle$ , the third reduction;  $\bigtriangleup$ , the fourth reduction.

tion, the amount of carbons deposited in each reduction was estimated to C/Fe = 2–3, which corresponded to carbon deposition of 0.29–0.43 g per 1 g of Ni–Cr–FeO<sub>x</sub> in each redox cycle. The total amount of carbons deposited on Ni– Cr–FeO<sub>x</sub> during the four redox reactions in Figs. 10 and 11 (C/Fe = ca. 11; 1.58 g per 1 g of Ni–Cr–FeO<sub>x</sub>; 61 wt% in Ni–Cr–FeO<sub>x</sub> after the four redox cycles) was smaller than that deposited during the four redox reactions in Figs. 7 and 8 (C/Fe = ca. 26; 3.74 g per 1 g of Ni–Cr–FeO<sub>x</sub>; 79 wt% in Ni–Cr–FeO<sub>x</sub> after the four redox cycles). These results indicated that deposition of carbons on Ni–Cr–FeO<sub>x</sub> during the reduction with methane could be suppressed to some extent by decreasing the reduction temperatures.

The formation rate of hydrogen during the first oxidation of Ni–Cr–FeO<sub>x</sub> with water vapor increased with temperatures and it reached the maximum at around 673 K, as shown in Fig. 11. In the second and subsequent oxidation, the reproducible kinetic curves of the formation rate of hydrogen were observed. CO and CO<sub>2</sub> were also formed in the first oxidation of Ni–Cr–FeO<sub>x</sub> with water vapor. However, CO or CO<sub>2</sub> were not formed at all in the second and subsequent oxidation. The amount of hydrogen formed was



Fig. 11. Change in the formation rates of hydrogen, CO, and CO<sub>2</sub> with time on stream during the oxidation of Ni–Cr–FeO<sub>x</sub> with water vapor.  $\bullet$ , the first oxidation;  $\bigcirc$ , the second oxidation;  $\blacktriangle$ , the third oxidation;  $\triangle$ , the fourth oxidation.

maintained at  $H_2/Fe = 1.2$  during the four oxidations of Ni–Cr–FeO<sub>x</sub> with water vapor. These results indicated that Ni–Cr–FeO<sub>x</sub> can form pure hydrogen repeatedly with high reproducibility through the reduction with methane and the subsequent oxidation with water vapor. When the reduction of Ni–Cr–FeO<sub>x</sub> with methane was terminated compulsorily at 150 min (Fig. 10), the total amount of carbons deposited on Ni–Cr–FeO<sub>x</sub> during the four redox cycles was decreased to C/Fe = ca. 4, which corresponded to 0.58 g per 1 g of Ni–Cr–FeO<sub>x</sub> (37 wt% in Ni–Cr–FeO<sub>x</sub> after the four redox cycles). In addition, Ni–Cr–FeO<sub>x</sub> produced pure hydrogen of H<sub>2</sub>/Fe = 1.1 repeatedly with high reproducibility in the second and subsequent oxidations with water vapor.

### 3.3. Structures of Ni and Cr species in Ni–Cr–FeO<sub>x</sub>

As described previously, Ni–Cr–FeO<sub>x</sub> could form hydrogen repeatedly through the reduction with methane and the subsequent oxidation with water vapor. The structures of Cr and Ni species in Ni–Cr–FeO<sub>x</sub> were investigated in order to clarify the role of these additives on the redox. XRD patterns of Ni–Cr–FeO<sub>x</sub> after the redox reactions were measured. Diffraction peaks due to iron metal and Fe<sub>3</sub>O<sub>4</sub> appeared in the XRD patterns of Ni–Cr–FeO<sub>x</sub> after the redox reaction, but any diffraction lines assignable to compounds containing Cr or Ni species were not observed. This result implies that Cr and Ni species in the Ni–Cr–FeO<sub>x</sub> are highly dispersed. Therefore, XANES and EXAFS spectra for Ni–Cr–FeO<sub>x</sub> af-



Fig. 12. Ni *K*-edge XANES spectra of Ni–Cr–FeO<sub>*X*</sub> after the redox and of Ni foil. (a) Ni foil; (b) Ni–Cr–FeO<sub>*X*</sub> after the first reduction; (c) Ni–Cr–FeO<sub>*X*</sub> after the second reduction; (d) Ni–Cr–FeO<sub>*X*</sub> after the first oxidation; (e) Ni–Cr–FeO<sub>*X*</sub> after the second oxidation.

ter the redox reactions were measured in order to examine the local structures of Ni and Cr species. Fig. 12 shows Ni K-edge XANES spectra of Ni–Cr–FeO<sub>x</sub> after the reduction with methane (spectra (b) and (c)) and after the oxidation with water vapor (spectra (d) and (e)) as well as XANES spectrum of Ni foil (spectra (a)). Features of Ni K-edge XANES spectra of the Ni–Cr–FeO<sub>x</sub> after the oxidation with water vapor were similar in shape to that of Ni foil, indicating that Ni species in the Ni–Cr–FeO<sub>x</sub> after the oxidation were present as Ni metal crystallites. Threshold of XANES spectra for the Ni–Cr–FeO<sub>x</sub> after the reduction with methane was consistent with that for Ni foil. In general, the threshold of XANES spectra for metal species is sensitive to the oxidation states of the metal species [15]. Therefore, Ni species in the Ni–Cr–FeO<sub>x</sub> after the reduction were of the metallic state (zero-valent). However, Ni K-edge XANES for the Ni-Cr- $FeO_x$  after the reduction with methane was not similar to that for Ni foil of fcc structure, but to the spectrum for Fe metal of bcc structure [13]; i.e., a peak appeared at 8352 eV in the spectra of the Ni–Cr–FeO<sub>x</sub> after the reduction, whereas two peaks were observed at 8350 and 8358 eV in the spectra of Ni foil and the Ni–Cr–FeO<sub>x</sub> after the oxidation. It was reported that these peaks in XANES spectra were sensitive to the crystal structure of metals [16–18]. The XANES spectra of Ni–Cr–FeO<sub>x</sub> after the reduction were compatible with that of Fe–Ni alloys of bcc structure [16,17]. Therefore, Ni species in the Ni–Cr–FeO<sub>x</sub> after the reduction with methane



Fig. 13. Cr *K*-edge XANES spectra of Ni–Cr–FeO<sub>*x*</sub> after the redox and of references (Cr foil and Cr<sub>2</sub>O<sub>3</sub>). (a) Cr foil; (b) Cr<sub>2</sub>O<sub>3</sub>; (c) Ni–Cr–FeO<sub>*x*</sub> after the first reduction; (d) Ni–Cr–FeO<sub>*x*</sub> after the second reduction; (e) Ni–Cr–FeO<sub>*x*</sub> after the first oxidation; (f) Ni–Cr–FeO<sub>*x*</sub> after the second oxidation.

would be present as Ni–Fe alloys of bcc structure, whereas they were present as Ni metal crystallites of fcc structure after the oxidation with water vapor. The XANES spectrum of the Ni–Cr–FeO<sub>x</sub> after the first reduction was similar to that after the second reduction, and the spectrum of the sample after the first oxidation resembled that after the second oxidation. Therefore, the structures of Ni species in Ni–Cr– FeO<sub>x</sub> changed reversibly during the redox reactions.

Fig. 13 shows Cr K-edge XANES spectra of Ni-Cr- $FeO_x$  after the reduction with methane (spectra (c) and (d)) and after the oxidation with water vapor (spectra (e) and (f)), as well as XANES spectra of reference samples, Cr foil (spectrum (a)), and Cr<sub>2</sub>O<sub>3</sub> (spectrum (b)). The position of threshold of XANES spectrum for Cr foil was different from that for Cr<sub>2</sub>O<sub>3</sub>. The threshold of XANES spectra for all the Ni–Cr–FeO<sub>x</sub> appeared at the same position irrespective of the different treatments (after the oxidation or after the reduction). The threshold of the spectra for the Ni–Cr–FeO<sub>x</sub> was consistent with that for  $Cr_2O_3$ , suggesting that Cr species in the Ni–Cr–FeO<sub>x</sub> were always stabilized as  $Cr^{3+}$ . XANES spectra of all the Ni–Cr–FeO<sub>x</sub> showed a small preedge peak at 5990 eV, which was characteristic of octahedral CrO<sub>6</sub> of trivalent Cr cations [19,20]. In general, when metal cations are introduced into magnetite, the cations are placed in tetrahedral A sites and in octahedral B sites with a unit cell written as  $(Fe_8^{3+})_A(Fe_8^{3+}Fe_8^{2+})_BO_{32}$ . It was proposed that Cr cations enter the B site as  $Cr^{3+}$  in the magnetite lattice [21]. Taking these results into consideration, Cr cations in Ni–Cr–FeO<sub>x</sub> were always stabilized as  $Cr^{3+}O_6$  on the B site in the ferrites  $Cr_xFe_{3-x}O_4$  during the redox reactions of Ni–Cr–FeO<sub>x</sub>. Therefore, a small part of iron species in Ni–Cr–FeO<sub>x</sub> was present as  $Cr_xFe_{3-x}O_4$ even after the reduction with methane; i.e., a small part of iron species was not reduced into iron metal.

Fig. 14 shows Cr *K*-edge  $k^3$ -weighted EXAFS for Ni– Cr–FeO<sub>x</sub> after the reduction with methane (spectra (a) and (b)) and after the oxidation with water vapor (spectra (c) and (d)). Fourier transforms of Cr *K*-edge  $k^3$ -weighted EX-AFS for Ni–Cr–FeO<sub>x</sub> (RSF; radial structure function) are shown in Fig. 15. The features of  $k^3$ -weighted EXAFS and Fourier transforms of EXAFS for all the Ni–Cr–FeO<sub>x</sub> were similar irrespective of the different treatments, i.e., after the reduction or after the oxidation. Therefore, the local structure around Cr cations in Ni–Cr–FeO<sub>x</sub> did not change appreciably during the repeated redox. A strong peak was observed at around 1.7 Å in the RSFs for all the Ni–Cr–FeO<sub>x</sub>. Inversely Fourier-transformed data for Fourier peak in a *R* range of 0.9 to 1.9 Å were analyzed by a curve-fitting method. The curve-fitting for Cr *K*-edge EXAFS was performed on *k* space in a *k* range of 4.5 to 14.0 Å<sup>-1</sup>. The structural parameters evaluated by the curve-fitting are listed in Table 4. For the Ni–Cr–FeO<sub>x</sub> after the first reduction, the coordination number and the interatomic distance of Cr–O bonds were estimated to 6.2 and 1.98 Å, respectively. The coordination number or the interatomic distance of Cr–O bonds did not change appreciably after the subsequent redox reactions of Ni–Cr–FeO<sub>x</sub>. These results strongly suggest



40 (d) 30 FT (c) 20 (b) 10 (a) 0 1 2 3 4 5 6 R / angstrom

Fig. 14. Cr *K*-edge  $k^3$ -weighted EXAFS of Ni–Cr–FeO<sub>x</sub> after the redox. (a) Ni–Cr–FeO<sub>x</sub> after the first reduction; (b) Ni–Cr–FeO<sub>x</sub> after the second reduction; (c) Ni–Cr–FeO<sub>x</sub> after the first oxidation; (d) Ni–Cr–FeO<sub>x</sub> after the second oxidation.

Fig. 15. Fourier transforms of Cr *K*-edge  $k^3$ -weighted EXAFS of Ni–Cr–FeO<sub>x</sub> after the redox. (a) Ni–Cr–FeO<sub>x</sub> after the first reduction; (b) Ni–Cr–FeO<sub>x</sub> after the second reduction; (c) Ni–Cr–FeO<sub>x</sub> after the first oxidation; (d) Ni–Cr–FeO<sub>x</sub> after the second oxidation.

Table 4

Structural p	parameters	of Cr s	pecies in	Ni-	$Cr-FeO_X$	estimated	by the	e curve-fitting	for Cr	K-edge E	EXAFS
							~			<u> </u>	

Condition	Shell	CN <sup>a</sup>	R <sup>b</sup> (Å)	DW <sup>c</sup> (Å)	$\Delta E^{\mathbf{d}}$ (eV)	$R_{\rm f}$ (%)
After the first reduction	Cr–O	$6.2 \pm 0.4$	1.98	0.045	-0.3	5.0
After the first oxidation	Cr–O	$6.2 \pm 0.3$	1.98	0.045	-0.5	5.1
After the second reduction	Cr–O	$5.7 \pm 0.5$	1.98	0.039	-0.3	4.5
After the second oxidation	Cr–O	$6.3 \pm 0.5$	1.99	0.044	0.4	6.2

<sup>a</sup> Coordination number of Cr–O bonds.

<sup>b</sup> Interatomic distance of Cr–O bonds.

<sup>c</sup> Debye–Waller factors.

<sup>d</sup> Threshold energy shift.



that Cr species in Ni–Cr–FeO<sub>x</sub> were always present as  $CrO_6$  during the redox reactions; i.e., they were stabilized on the B site in the ferrites  $Cr_xFe_3 - {}_xO_4$ .

As described previously, the addition of Ni species in iron oxides enhanced the reduction with methane and the oxidation with water vapor at low temperatures. Ni species in Ni- $Cr-FeO_x$  were present as Ni-Fe alloys after the reduction with methane and as Ni metal crystallites after the oxidation with water vapor. These Ni species in the Ni–Cr–FeO<sub>x</sub> would act as active sites for methane molecules in the reduction and for water molecules in the oxidation. On the other hand, the addition of Cr cations to the iron oxides prevented the sintering of iron metals and/or iron oxides during the redox reactions. XANES and EXAFS studies indicated that Cr cations in the Ni–Cr–FeO<sub>x</sub> were always stabilized on the B site in the ferrites  $Cr_x Fe_{3-x}O_4$ . The ferrites  $Cr_x Fe_{3-x}O_4$ may be always localized on the surface of Ni-Cr-FeO<sub>x</sub> during the redox reactions. Iron oxide samples would be aggregated due to the contacts between iron metal particles during the redox reactions at high temperatures. The ferrites  $Cr_xFe_{3-x}O_4$  present on the surface of Ni–Cr–FeO<sub>x</sub> would inhibit the contact between iron metal particles.

# 4. Conclusion

We approved the following conclusions on the basis of the results described previously:

- 1. Ni–Cr–FeO<sub>x</sub> can produce pure hydrogen repeatedly with high reproducibility through the reduction with methane and the subsequent oxidation with water vapor.
- 2. Ni species in Ni–Cr–FeO<sub>x</sub> were present as Ni–Fe alloys after the reduction with methane and as Ni metal crystallites after the oxidation with water vapor. Cr species

in Ni–Cr–FeO<sub>x</sub> were always stabilized as octahedral  $Cr^{3+}O_6$  on the B sites in the ferrites  $Cr_xFe_{3-x}O_4$ .

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