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Recovery of rare metal compounds from nickel–metal hydride battery waste and their application to CH_4 dry reforming catalyst

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ABSTRACT

The recovery of valuable components such as nickel from nickel–metal hydride (Ni–MH) battery waste by chemical processes and their applications to CH_4 dry reforming catalysts were investigated. Three types of compound, identified by XRD analysis as NiO, CeO_2 and $LaCoO_3$ phases, were successfully separated from the waste by a series of chemical processes at room temperature using aqueous solutions of HCl, NaOH and NH_3, and Ni component of ≈70% in Ni–MH battery waste was recovered. The separated NiO, CeO_2 and $LaCoO_3$ showed catalytic activities for CH_4 dry reforming. In particular, the separated NiO easily reduced to Ni^0 at an initial stage, and exhibited excellent catalytic activity in terms of CH_4 conversion and stability. Furthermore, it was found that the resulting Ni from separated NiO exhibited an anomalous catalysis from the comparison with that from regent NiO.

1. Introduction

For a resource-poor nation such as Japan, it is desirable to establish a society that is oriented towards recycling of resources. However, many technicians and researchers have turned to the creation of high-functional materials rather than the development of resource-recovery technology. Rechargeable, high-powered nickel–metal hydride (Ni–MH) batteries are widely used as power sources for cell phones, digital cameras, hybrid cars and so on. On the other hand, a large quantity of Ni–MH battery waste discharged from Ni–MH battery production factories and spent Ni–MH batteries has been disposed of as waste even though they contain valuable transition and rare-earth elements. An amount of both the wastes is hundreds of tons per year in Japan. The establishment of a method of recovering these elements from the waste in an environmentally thoughtful way is therefore desirable. The recovery of these elements from spent Ni–MH batteries has previously examined by extraction with organic solvent, magnetic separation and electrochemical deposition [1–4]. We are studying recovery process of rare metals from Ni–MH battery waste and spent Ni–MH batteries and utilization of recovered metals for environmental conservation.

Over the last few decades, CH_4 dry reforming (Eq. (1)) has been studied with a view to producing synthesis gas with a lower H_2/CO ratio than that produced by steam reforming (Eq. (2)), in addition to producing hydrogen as a clean energy carrier.

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO, \quad \frac{H_2}{CO} = 1 \tag{1}$$

$$CH_4 + H_2O \rightarrow 3H_2 + CO, \quad \frac{H_2}{CO} = 3 \tag{2}$$

The synthesis of liquid fuels such as methanol and dimethyl ether requires synthesis gas with a lower H_2/CO ratio. Furthermore, the advantages of CH_4 dry reforming include the effective use of greenhouse gases as carbon sources, and the use of natural gas, containing CH_4, as a main component. Natural gas is a cleaner energy source than oil and coal since it contains less NO_x and no SO_x.

It has been reported that catalysts supported by noble metals (Pt, Rh, Ru, Pd and Ir) show good catalytic performance in CH_4 dry reforming [5–14]. From the viewpoint of the economics of large scale processes, however, it is better to use cheaper metals. Thus, supported Ni-based oxides [14,15] and lanthanoid perovskite type oxides [16–19] are promising as alternative catalysts for this reaction. Referring to previous reports, we selected the CH_4 dry reforming reaction as an application of valuable components such as nickel recovered from Ni–MH battery waste. Furthermore, because Ni-based compounds are reduced to nickel–metal during the CH_4 dry reforming, it is expected that the resulting nickel–metal can be reused as a raw material of Ni–MH batteries. In our previous paper, it was found that the CH_4 conversion over Ni-based compounds recovered from Ni–MH battery waste, which was estimated by a following equation, was superior to that over regent NiO and exhibited an unusual behavior, when the fed gas ratio of

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$CH_4/CO_2 = 1:1$ was employed at a flow rate of 50 ml/min [20].

$$CH_4\ \text{conversion}\ (\%) = \frac{\text{amount of consumed}\ CH_4}{\text{amount of fed}\ CH_4} \times 100$$

A large amount of carbon, which is undesirable for reusing nickel–metal, however, was deposited by side reaction. In the present report, we describe the recovery of rare metal compounds such as NiO, CeO_2 and $LaCoO_3$ from Ni–MH battery waste by chemical processes with acidic and basic solutions and their applications to CH_4 dry reforming catalysts by using the fed gas with low concentrations of CH_4 and CO_2 for diminishing the carbon deposition.

2. Experimental

2.1. Sample preparation

Waste discharged as a dross from a process for producing negative electrode materials of Ni–MH batteries in Mitsui Mining and Smelting Co. Ltd., Japan was employed in the experiment. The waste cannot be directly renewed, because it contains small amounts of oxides and contamination. It was, therefore, separated into different materials for recycling as follows: the wastes were treated with various concentrations of HCl, HNO_3 and H_2SO_4 solutions to dissolve the elements contained therein (solution 1); the dissolved metal ions in solution 1 were precipitated by adding NaOH solution (precipitate 1); and precipitate 1 was treated with certain acids and bases to separate different compounds.

2.2. Characterization

The samples were characterized by powder X-ray diffraction (XRD; Rigaku RINT2100/PC) with monochromated CuKα radiation. Chemical components of the waste were analyzed using an X-ray fluorescence technique (XRF; Rigaku RIX3000). Energy dispersive spectroscope (EDS; JEOL EX-54175JMU) and inductively coupled plasma atomic emission spectrometer (ICP-AES; Seiko Instruments SPS7700) were used for chemical analysis of the samples. Morphologies of the samples were observed by a scanning electron microscope (SEM; JEOL JSM-6380). The specific surface areas of the samples were evaluated from the measured isothermal adsorption of N_2 at 77 K based on the BET method (BEL-Japan BELSORP 18 PLUS). Thermo-gravimetric analysis (TG; Rigaku TG 8120) was carried out to estimate amounts of carbon deposition over the samples.

2.3. CH_4 dry reforming

CH_4 dry reforming was performed in a fixed-bed reactor consisting of a quartz–glass tube with an internal diameter of 12 mm ϕ under atmospheric pressure. Each powder sample of 1 g was held in place by glass wool. The reaction was carried out at 780 °C and the flow rate was controlled at $CH_4/CO_2/Ar = 1.5/1.5/47\ ml\ min^{-1}$. The vent gas was cooled with an ice-cooler to remove H_2O produced by side reactions. The gaseous products were analyzed by an on-line gas chromatograph (Shimadzu GC-8A) equipped with a thermal conductivity detector.

3. Results and discussion

3.1. Preliminary experiments on separation from waste

XRF analysis showed that the waste included Ni as a main element, plus several other elements such as La, Ce, Co, Mn and Nd, as listed in Table 1. To begin the separation process, preliminary experiments were carried out to determine optimum conditions at room temperature. First, a 10.0 g sample of the waste was treated with HCl, HNO_3 and H_2SO_4 solutions (200 ml each) for 24 h (solution 1). It was found that the waste was dissolved at acid concentrations greater than 2 M ($mol\ dm^{-3}$), while large amounts of insoluble waste remained when the acid concentration was lower than this value. Therefore, 2 M acid solution was used in the separation process. The effects of different stirring times were examined: ICP analysis showed that the metal ion concentrations in solution 1 increased with stirring time up to 24 h, and were $[Ni^{2+}] \approx 0.29$, $[La^{3+}] \approx 0.10$, $[Ce^{4+}] \approx 0.06$, $[Co^{2+}] \approx 0.06$, $[Mn^{2+}] \approx 0.03$ and $[Nd^{3+}] \approx 0.02$ M, respectively. Next, the pH of solution 1 was adjusted to 12 by addition of 2 M NaOH solution in order to cause precipitation of dissolved metal ions in the form of hydroxides (precipitate 1; $M^{n+} + nOH^- \rightarrow M(OH)_n$, M = Ni, La, Ce, Co, Mn and Nd), considering the solubility products, i.e., $K_{sp} = 1.8 \times 10^{-16}$ for $Ni(OH)_2$, 5.2×10^{-20} for $La(OH)_3$, 1.0×10^{-23} for $Ce(OH)_4$, 1.3×10^{-15} for $Co(OH)_2$, 9.4×10^{-14} for $Mn(OH)_2$ and 5.0×10^{-24} for $Nd(OH)_3$, respectively [21]. The amount of precipitate 1 obtained increased with pH up to 12, which implies that most of the metal ions present were precipitated at pH 12, because the metal ion concentrations estimated from K_{sp}s are $[Ni^{2+}] \approx 1.8 \times 10^{-12}$, $[La^{3+}] \approx 5.2 \times 10^{-14}$, $[Ce^{4+}] \approx 1.0 \times 10^{-15}$, $[Co^{2+}] \approx 1.3 \times 10^{-11}$, $[Mn^{2+}] \approx 9.4 \times 10^{-10}$ and $[Nd^{3+}] \approx 5.0 \times 10^{-18}$ M, respectively. Finally, precipitate 1 was calcined at 1000 °C for 1 h in order to allow identification of the resulting materials by XRD. It was found that the use of HCl or HNO_3 for waste dissolution caused no difference in the resulting materials, but sulfur compounds were produced when H_2SO_4 was used for waste dissolution.

Table 1
Chemical components of Ni–MH battery waste.

Elements	Content (molar ratio)
Ni	48.1
La	16.7
Ce	10.3
Co	9.9
Mn	5.2
Nd	3.6
Others	6.2

Based on the results described above, the waste was dissolved in 2 M HCl solution, and the dissolved metal ions were then precipitated at pH 12 by addition of 2 M NaOH solution at room temperature. The XRD pattern of precipitate 1 calcined at 1000 °C showed a mixture of three types of crystalline phase, identified as NiO, CeO_2 and $LaCoO_3$, as shown in Fig. 1.

3.2. Individual separation of NiO, CeO_2 and $LaCoO_3$

Next, separation of NiO, CeO_2 and $LaCoO_3$ from the precipitate formed at pH 12 (precipitate 1) was examined. First, aqueous solutions of NH_3 (1–15 M, 200 ml) were added to precipitate 1 to extract Ni component via formation of an Ni–ammonium complex ($Ni(OH)_2 + 6NH_3 \rightarrow [Ni(NH_3)_6]^{2+} + 2OH^-$). After 12 h stirring, filter cakes were calcined at 1000 °C for 1 h. The XRD patterns of calcined filter cakes are shown in Fig. 2. It was found that the use of higher concentrations of aqueous NH_3 resulted in weaker XRD peaks due to NiO – which suggests that there was less nickel remaining in the precipitate – with the peaks disappearing after use of 7.5 and 15 M aqueous NH_3, as shown in Figs. 2d and e, respectively. In addition, quantitative analysis of Ni^{2+} ions in the NH_3 solutions by ICP revealed that the concentration of Ni^{2+} ions increased with increasing concentrations of aqueous NH_3 up to 7.5 M. The difference between the concentrations of Ni^{2+} ions after use of 7.5 and 15 M aqueous NH_3 was hardly observed. These results suggest that the Ni component may be extracted from precipitate 1 using 7.5 M aqueous NH_3. After filtration, the purple filtrate (solution 2) was heated to around 60 °C to cause decomposition of the

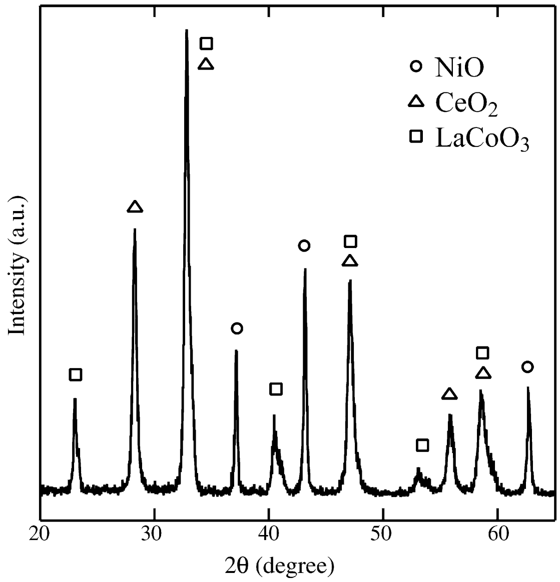

Fig. 1. XRD pattern of precipitate 1 calcined at 1000 °C for 1 h.

Ni–ammonium complex and precipitation of the Ni component as $Ni(OH)_2$ ($[Ni(NH_3)_6]^{2+} + 2OH^- \rightarrow Ni(OH)_2 + 6NH_3$). The resulting $Ni(OH)_2$ was calcined at 1000 °C for 1 h to cause dehydration to NiO. The XRD pattern of the NiO obtained is shown in Fig. 3a. As a result, NiO of ≈3.1 g was prepared from Ni–MH battery waste of 10.0 g.

After removal of Ni, precipitate 1 was further treated to remove other components. The filter cake calcined at 1000 °C for 1 h after treatment with 7.5 M aqueous NH_3 (XRD pattern shown in Fig. 2d) was treated with 2 M HCl solution (100 ml) at room temperature in order to separate $LaCoO_3$ (solution 3), because CeO_2 was not dissolved in the HCl solution. The XRD pattern of the filter cake obtained after this treatment was identified as that of CeO_2, as shown in Fig. 3b. NaOH solution (2 M) was added to solution 3, adjusting pH to 12, in order to co-precipitate La and Co components (precipitate 2), and precipitate 2 was then calcined at 1000 °C for 1 h. The XRD pattern of calcined precipitate 2 was identified as that of $LaCoO_3$, as shown in Fig. 3c.

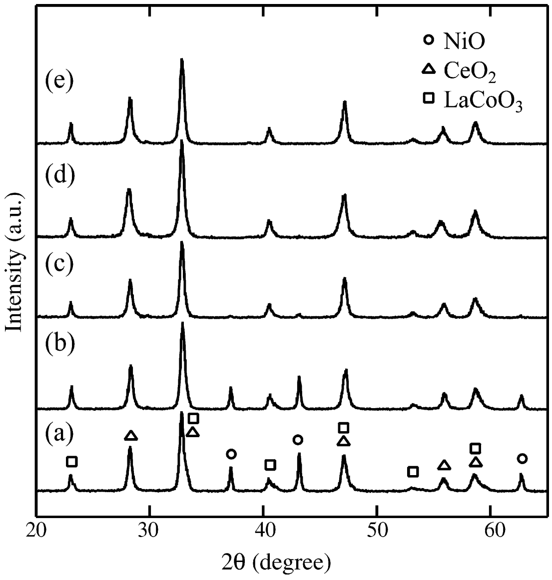

Fig. 2. XRD patterns of precipitate 1 calcined at 1000 °C for 1 h before and after treatments with 1–15 M aqueous NH_3 of 200 ml: (a) 0 M, (b) 1 M, (c) 5 M, (d) 7.5 M and (e) 15 M.

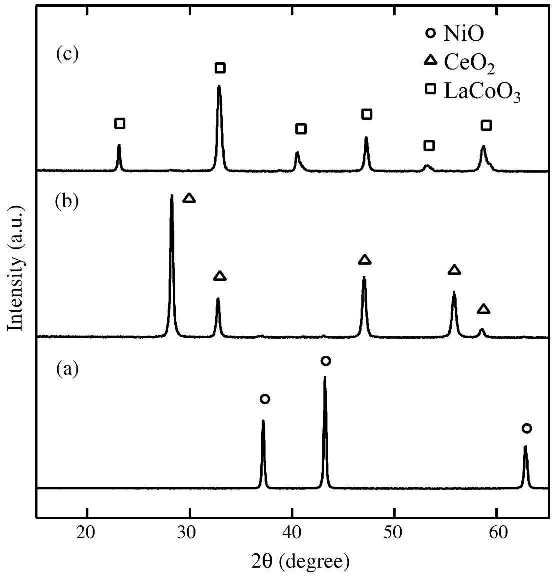

Fig. 3. XRD patterns of (a) NiO, (b) CeO_2 and (c) $LaCoO_3$ separated from Ni–MH battery waste.

Table 2
Chemical components of separated NiO, CeO_2 and $LaCoO_3$.

Elements	Content (molar ratio)		
	NiO	CeO_2	$LaCoO_3$
Ni	97.4	–	12.4
La	0.6	–	56.3
Ce	–	62.6	–
Co	2.0	0.7	16.6
Mn	–	30.7	14.6
Nd	–	6.1	–

The procedure for separation of individual compounds from the Ni–MH battery waste is summarized in Fig. 4. The chemical components of the three separated samples by ICP along with EDS analyses are listed in Table 2. Consequently, Ni component of ≈70% in Ni–MH

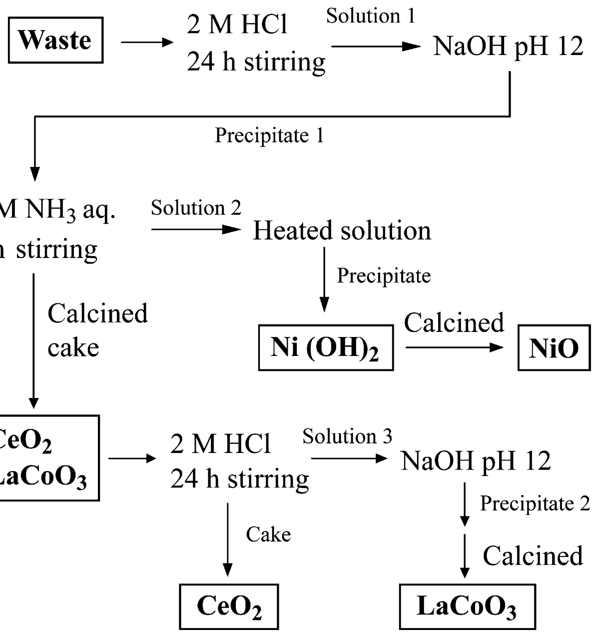

Fig. 4. Procedure for individual separation of NiO, CeO_2 and $LaCoO_3$ from Ni–MH battery waste.

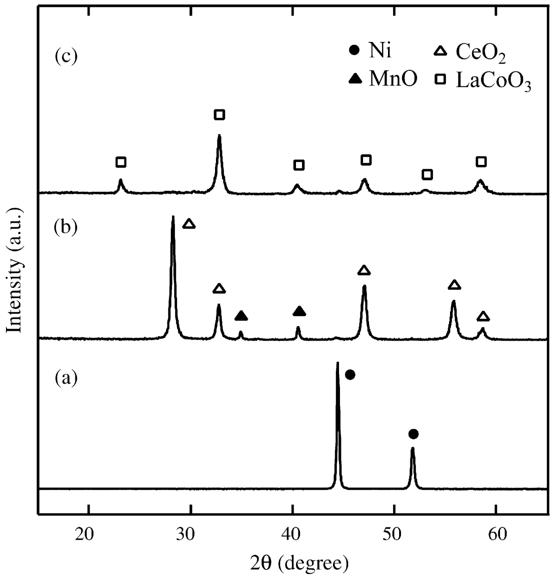

Fig. 5. XRD patterns of (a) NiO, (b) CeO_2 and (c) $LaCoO_3$ after CH_4 dry reforming.

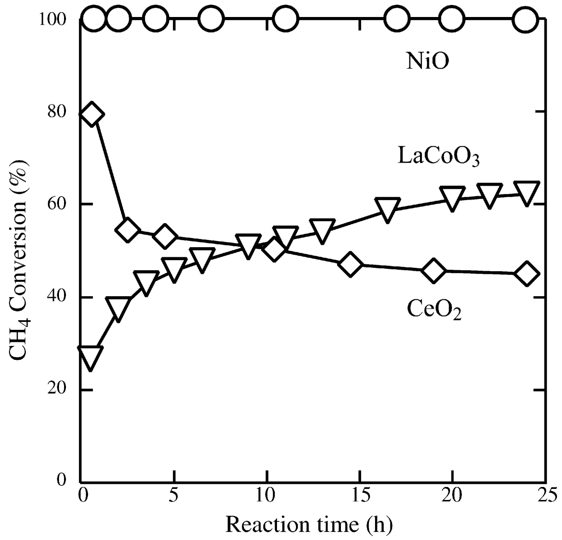

Fig. 6. CH_4 conversions over separated NiO, CeO_2 and $LaCoO_3$ as a function of reaction time.

battery waste was found to be recovered as NiO with purity of about 97 mol%. CeO_2 and $LaCoO_3$ were thought to form solid solutions such as $(Ce_{0.63}Mn_{0.31}Nd_{0.06})O_2$ and $La(Co_{0.38}Mn_{0.34}Ni_{0.28})O_3$, respectively.

3.3. Characterization of the separated samples after CH_4 dry reforming

Fig. 5 shows the XRD patterns of the separated samples after 24 h of CH_4 dry reforming at 780 °C. NiO was reduced to Ni^0, and no other XRD peaks were detected. Because the XRD pattern of NiO after 30 min reaction indicated the presence of only the Ni^0 phase, and because CH_4 conversion over NiO was enhanced after 30 min, it is thought that the reduction of NiO was probably completed within this time. No structural change was observed in $LaCoO_3$; that is, Mn and Ni components contained in $LaCoO_3$ were still present in the Co sites (the B site of the perovskite structure) after CH_4 dry reforming. In contrast, the Mn component contained in CeO_2 was separated out and converted to MnO after the reaction.

3.4. Catalytic performances

The temperature ranges based on the free energy changes estimated for corresponding reactions, as listed in Table 3, were taken into consideration in choosing the reaction temperature for CH_4 dry reforming (Eq. (1)). The reaction can proceed spontaneously when the temperature is higher than 640 °C. Considering temperature ranges in which spontaneous reactions occur for the reactions depicted in Eqs. (2)–(5) (Eqs. (3)–(5) are shown in Table 3), it was found that temperature range from 700 to 835 °C was appropriate for CH_4 dry reforming. The reaction temperature for the present study was therefore fixed at 780 °C, which is consistent with temperatures reported in many other studies [8,9,11,12,18].

Table 3
Appropriate temperature ranges estimated from free energy changes of corresponding reactions.

Reaction		Enthalpy change [22]	Temperature range (°C)
$CH_4 + CO_2 \rightarrow 2H_2 + 2CO$	(1)	$\Delta H_{298} = 247\ kJ\ mol^{-1}$	≥640
$CH_4 + H_2O \rightarrow 3H_2 + CO$	(2)	$\Delta H_{298} = 206\ kJ\ mol^{-1}$	≥613
$CH_4 \rightarrow 2H_2 + C$	(3)	$\Delta H_{298} = 74\ kJ\ mol^{-1}$	≥531
$CO_2 + C \rightarrow 2CO$	(4)	$\Delta H_{298} = 172\ kJ\ mol^{-1}$	≥700
$CO_2 + H_2 \rightarrow CO + H_2O$	(5)	$\Delta H_{298} = 41\ kJ\ mol^{-1}$	≥835

Fig. 6 shows CH_4 conversion as a function of reaction time using three separated samples as catalysts. NiO showed excellent performance and stability, with a CH_4 conversion of 100% continuing for 24 h and without a CH_4 conversion exhibiting a parabolic behavior as shown in the previous paper [20]. Furthermore, the comparison with regent NiO, shown in Fig. 7, revealed that CH_4 conversion over separated NiO was superior to that over regent NiO. Namely, the former lasted 100% over a period of 9 d, whereas the latter rapidly decreased after 2 d of reaction. Fig. 8 shows SEM micrographs of separated and regent NiO after CH_4 dry reforming. The resulting Ni from separated NiO was hardly sintered, whereas the resulting Ni from regent NiO was sintered, and grains abnormally grew. Sintering of catalyst particles has been elucidated to cause deactivation [23–25]. The components such as Co and La in the separated NiO, as listed in Table 2, might inhibit the sintering of Ni particles. In the case of $LaCoO_3$, CH_4 conversion gradually increased, reaching around 60% after 24 h of reaction. This behavior was considered to

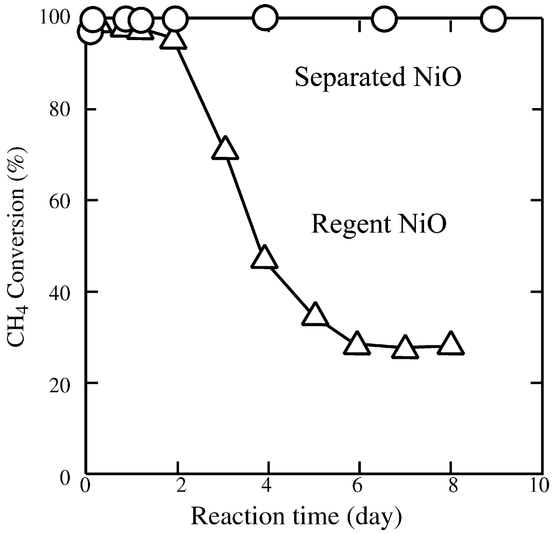

Fig. 7. CH_4 conversions over separated NiO and regent NiO as a function of reaction time.

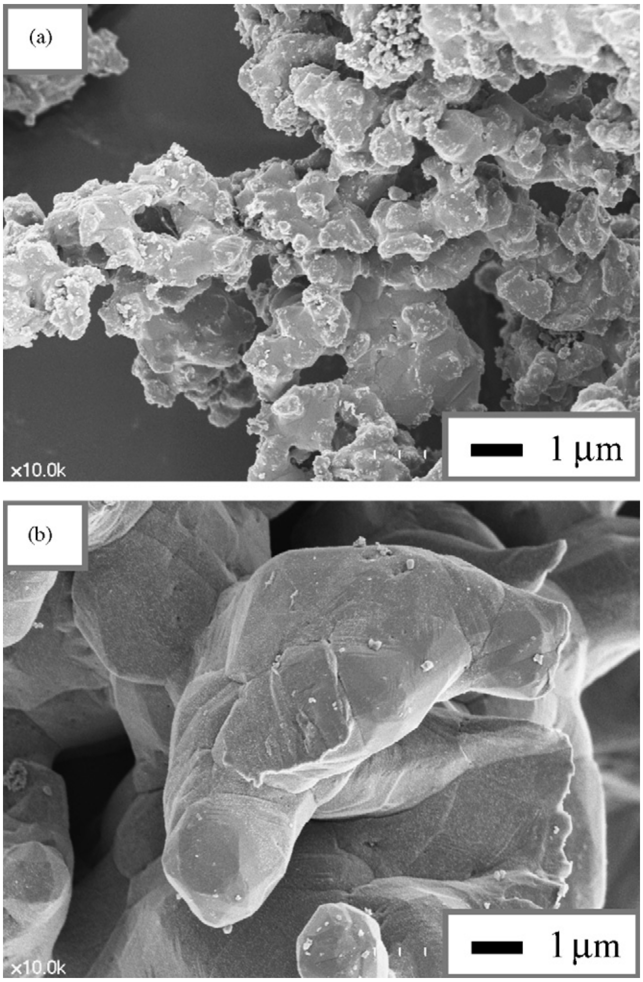

Fig. 8. SEM micrographs of (a) separated NiO and (b) regent NiO after CH_4 dry reforming.

be due to the gradual reduction of small amounts of Ni^{2+} ions in $LaCoO_3$ to Ni^0 active species, referring to the previous report [19]. In contrast, CH_4 conversion over CeO_2 decreased with increasing reaction time, although it showed a relatively high value at the very beginning.

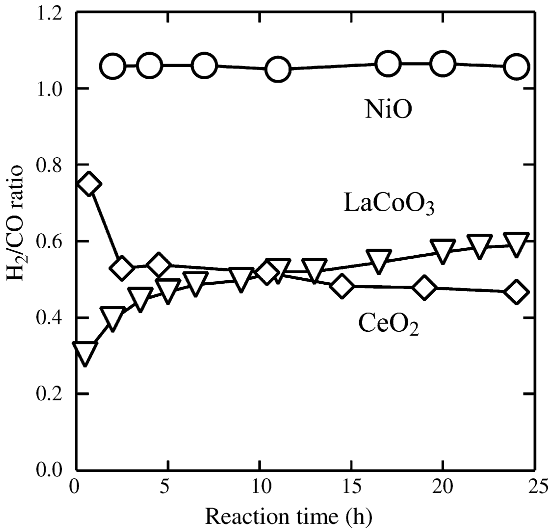

Fig. 9. H_2/CO ratios over separated NiO, CeO_2 and $LaCoO_3$ as a function of reaction time.

Fig. 9 shows H_2/CO ratios as a function of reaction time for CH_4 dry reforming using the three separated samples as catalysts. The H_2/CO ratio for separated NiO was slightly larger than 1.0, indicating that in CH_4 dry reforming, the rate of CO production reaction (Eq. (4)) was slower than that of H_2 production reaction (Eq. (3)), and consequently carbon deposition occurred. This was supported by TG analysis showing that a small amount of carbon, i.e., about 2 mass%, coexisted with the resulting Ni from separated NiO after 24 h of reaction, though no XRD peaks assigned to carbon (graphite) were detectable on the XRD patterns, as shown in Fig. 5a. Compared with the previous results [20], the present experimental conditions were found to reduce the amount of deposited carbon to less than one-100th. For the other samples, the H_2/CO ratios were smaller than 1.0, suggesting that the reverse water-gas shift reaction (Eq. (5)) occurred simultaneously with the main reaction (Eq. (1)). The specific surface areas of the three separated samples were measured to about 7, 62 and 9 $m^2\,g^{-1}$ for NiO, CeO_2 and $LaCoO_3$, respectively. However, no significant relationship between CH_4 conversions and specific surface areas was observable.

4. Conclusion

The recovery of valuable components from Ni–MH battery waste and their applications to CH_4 dry reforming catalysts have been investigated. The experimental results led to the following conclusions.

Three kinds of compound, identified by XRD analysis as NiO, CeO_2 and $LaCoO_3$ phases, were successfully recovered by the procedure prescribed in Fig. 4. Namely, the waste was treated with HCl solution, and then dissolved transition and rare-earth metal ions were precipitated by adding NaOH solution at room temperature. Ni component was extracted from the precipitate by treating with aqueous NH_3. After filtration, NiO was obtained by calcination of $Ni(OH)_2$ yielded by heating the filtrate. Thereby, the Ni component of ≈70% in Ni–MH battery waste was recovered as NiO with purity of ≈97 mol%. The calcined filter cake, which was a mixture of CeO_2 and $LaCoO_3$ phases, was treated with HCl solution to dissolve $LaCoO_3$ at room temperature. After filtration, $LaCoO_3$ was obtained by calcination of the co-precipitate yielded by adding NaOH solution to the filtrate. The separated NiO, CeO_2 and $LaCoO_3$ were considered to form solid solutions.

The separated NiO, CeO_2 and $LaCoO_3$ showed catalytic activity for CH_4 dry reforming. In particular, the separated NiO, easily reduced to Ni^0 at the initial stage, exhibited excellent performance and stability, with a CH_4 conversion of 100% continuing over a period of 9 d, and its catalytic activity was superior to that of regent NiO. Consequently, we found that nickel recovered from Ni–MH battery waste exhibited an anomalous catalysis.

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