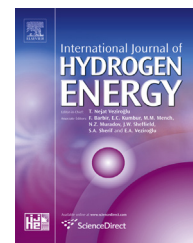


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# Biogas reforming over BaTi<sub>1-x</sub>Sn<sub>x</sub>O<sub>3</sub>-supported Ni-based catalysts recovered from spent Ni-metal-hydride batteries

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## ABSTRACT

BaTi<sub>1-x</sub>Sn<sub>x</sub>O<sub>3</sub>-supported Ni-based catalysts recovered from spent Ni-metal-hydride (Ni-MH) batteries [wNi/BaTi<sub>1-x</sub>Sn<sub>x</sub>O<sub>3</sub> (x = 0.0, 0.2, 0.4, 0.6, and 1.0)] were prepared. Their catalytic activities for model biogas reforming reactions were examined at 800 °C and compared with that of wNi/γ-Al<sub>2</sub>O<sub>3</sub>. According to the results, wNi/BaTi<sub>0.8</sub>Sn<sub>0.2</sub>O<sub>3</sub> exhibited high reforming performance and high sustainability among the catalysts tested. wNi/γ-Al<sub>2</sub>O<sub>3</sub> exhibited unsustainability due to carbon deposition, although its performance was excellent for a short time. BaTi<sub>0.8</sub>Sn<sub>0.2</sub>O<sub>3</sub> functioned as an inhibitor, depressing carbon deposition. This function was likely due to the mobile oxide ions and alkaline earth oxides in the catalyst supports.

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## Introduction

Biogas, which is generated by the CH<sub>4</sub> fermentation of anaerobic bacteria in garbage, stockbreeding waste, sewage sludge, and so on, is an environmentally friendly energy source. Most biogas, composed primarily of CH<sub>4</sub> and CO<sub>2</sub>, is not effectively utilized, although a small amount of biogas is used as a fuel for thermal-power generation. More applications of biogas are, therefore, desirable. Recently, shale gas, which is a natural gas consisting primarily of CH<sub>4</sub>, has attracted a great deal of attention, and the expectation for the

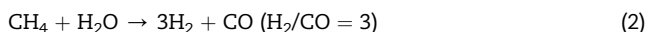
overall usage of CH<sub>4</sub> is increasing. CH<sub>4</sub> is important as a major raw material of gas chemistry as well as a clean fuel. In gas chemistry, CH<sub>4</sub> is converted into a synthesis gas (syngas) consisting of H<sub>2</sub> and CO for the syntheses of industrial liquid fuels such as methanol and dimethyl ether via either the dry reforming reaction (1) or the steam reforming reaction (2), using catalysts. Moreover, syngas is useful as a fuel in solid oxide fuel cells (SOFCs).



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Given these reforming reactions, biogas should also be convertible to syngas via a similar process. Consequently, biogas can be effectively used, because  $\text{CO}_2$  in biogas is convertible into available CO.

Although supported noble metal catalysts (Rh, Ru, Pd, etc.) reportedly show good catalytic performance for both reforming reactions (1) and (2) [1–5], industrially, the use of noble metal catalysts is not feasible due to their high costs. Thus, supported Ni-based metals [6–14] and Ni-based perovskites [15–17] are promising as alternative catalysts for these reactions. As Ni-based metals, however, cause carbon deposition due to the decomposition of  $\text{CH}_4$ , the supported Ni-based metals with high durability against carbon deposition have been intensively studied [6,18]. Above all, oxide-ion-conducting oxides and perovskite-type oxides are widely noted as supports for Ni-based metals, since the mobile oxide ions in the supports oxidize  $\text{CH}_x$  fragments adsorbed on Ni-based metals and/or reduce  $\text{CH}_4$  activation and dissociation [10–13]. Furthermore, alkali and alkaline earth metal oxides in the supports were reported to reduce carbon deposition [19].

Rechargeable, high-powered nickel-metal-hydride (Ni-MH) batteries are widely used as power sources for digital cameras, hybrid cars, and so on. However, large quantities of spent Ni-MH batteries are disposed of as waste even though they contain valuable transition and rare-earth elements. Given the desirability of establishing a resource-recycling-oriented society, it is significant to study the resource recovery of spent Ni-MH batteries. Therefore, we have developed a resource recovery process for Ni-based compounds from spent Ni-MH batteries and employed the resulting Ni-based compounds as catalysts for the  $\text{CH}_4$  dry reforming reaction [20–22]. Consequently, we found that the reforming performance over the Ni-based compounds was superior to that over the reagent NiO, provided that the Ni-based compounds and NiO were reduced to Ni-based and Ni metals, respectively, at the initial stage of the reforming reaction. Small amounts of impurities in the Ni-based compounds were considered in order to improve the reforming performance. A large amount of carbon, however, was deposited during the progression of the  $\text{CH}_4$  dry reforming reaction.

Based on the information mentioned above, we are developing catalysts for biogas reforming reactions with the aim of utilizing the resulting syngas as a fuel for SOFCs, using the Ni-based metals recovered from spent Ni-MH batteries. In the present study, catalyst supports, which were expected to have sustainable resistance to carbon deposition, were studied, and  $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$  ( $0 \leq x \leq 1$ ) was selected as a support for the Ni-based metals.  $\text{Sn}^{4+}$  was substituted for  $\text{Ti}^{4+}$  in  $\text{BaTiO}_3$  given that the substitution might result in an increase in the number of mobile oxide ions, because  $\text{Sn}^{4+}$  is more easily reduced than  $\text{Ti}^{4+}$  under a reductive atmosphere. Consequently, the resistance to carbon deposition was improved by  $\text{Sn}^{4+}$  substitution. Thus, we report the preparation of these catalysts and their reforming performance for model biogas.

## Experimental methods

### Preparation and characterization of catalysts

Ni-based compounds recovered from the anode materials of spent Ni-MH batteries, which were provided by Mitsui Mining and Smelting Co., Ltd., Japan, were employed as catalysts. The recovery process has been described elsewhere [22]. Namely, 10 g of anode material were dissolved with 200 mL of 2 M (mol/dm<sup>3</sup>) HCl solution, and after that, 900 mL of 5 M  $\text{NH}_3$  (aq.) was added to the solution to obtain Ni– $\text{NH}_3$  complexes and precipitate other metal ions out as their hydroxides. Furthermore, the mixed solution was stirred while bubbling air through it for 12 h to precipitate out manganese and cobalt ions as hydroxides and/or oxides; it was then filtered. The obtained purple filtrate was used as the Ni (*w*Ni) source. The chemical compositions of *w*Ni obtained by the processes mentioned below, i.e., drying, heating, and reducing, were analyzed with an X-ray fluorescence (XRF; Rigaku ZSX Primus II) technique.

Perovskite-type oxides,  $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$  ( $x = 0.0, 0.2, 0.4, 0.6$ , and 1.0), were utilized as catalyst supports. In the preparation of  $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ , fixed amounts of starting materials,  $\text{BaCO}_3$  (99.9%, Kanto Chemical),  $\text{TiO}_2$  (99.0%, Kanto Chemical), and  $\text{SnO}_2$  (98.0%, Wako Pure Chemical Industries), were mixed, ground in a ball-mill for 24 h using ethanol, and heated at 1200 °C for 12 h. The products were identified by powder X-ray diffraction (XRD), using a Rigaku RINT2100/PC diffractometer with monochromated  $\text{CuK}\alpha$  radiation.  $\gamma\text{-Al}_2\text{O}_3$  (99.99%, Taimei Chemicals), which is frequently used as a catalyst support, was employed for comparison with  $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ . The specific surface areas of the samples were evaluated with the measured isothermal adsorption of  $\text{N}_2$  at 77 K based on the Brunauer–Emmett–Teller (BET) method (BEL-Japan BELSORP 18 PLUS).

These supports were immersed in the purple solution mentioned above to produce a *w*Ni loading of 5 mass%. The impregnated compounds were dried at 110 °C for 12 h, calcined at 700 °C for 4 h to decompose the Ni– $\text{NH}_3$  complexes into oxides, and then treated for 2 h at 600 °C with 3%  $\text{H}_2$  flow. The resulting catalysts, *w*Ni/ $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$  and *w*Ni/ $\gamma\text{-Al}_2\text{O}_3$ , were identified by XRD and employed in the reforming tests for model biogas.

### Reforming tests

The reforming reaction was performed under atmospheric pressure in a flow-type fixed-bed reactor consisting of a quartz tube with an internal diameter of 12 mm. The thermocouple was inserted from the bottom of the quartz tube, and glass wool was set on top of it. Each powder sample of 0.3 g was held in place by glass wool. The reaction was carried out at 800 °C, and the flow rate of the fed gas was controlled at  $\text{CH}_4/\text{CO}_2/\text{Ar} = 15/10/75$  mL/min with 3 vol%  $\text{H}_2\text{O}$  as a model biogas to simulate the composition of real biogas. The space velocity was estimated to be about 15,000 1/h. The vent gas was cooled with an ice-cooler to remove  $\text{H}_2\text{O}$  that was fed and produced by side reactions. The gaseous products were analyzed by an on-line gas chromatograph

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