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Methanation of carbon dioxide on Ni/(Zr–Sm)O_x catalysts†

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Ni/ZrO_2 and Ni/$(Zr_{0.9}Sm_{0.1})_{0.95}$ catalysts were prepared by wet impregnation, and their catalytic activities for methanation of carbon dioxide were compared with the highly active catalysts prepared from amorphous nickel–zirconium–samarium alloys. The Ni$(Zr_{0.9}Sm_{0.1})O_{1.95}$ catalyst showed higher activity for methanation of carbon dioxide than the samarium-free Ni/ZrO_2 catalyst with the same nickel content. The higher activity of the samarium-containing catalyst is associated with the formation of the (Zr–Sm)O_x oxide with a tetragonal ZrO_2 structure, similar to the Ni/(Zr–Sm)O_x catalysts prepared from the amorphous nickel–zirconium–samarium alloys. An increase in the nickel content from 30 to 60 mol% in cationic percentage results in a decrease in the activity, mainly because of a decrease in the surface area of the catalysts, although the activity of the catalysts prepared from amorphous nickel–zirconium–samarium alloys increases with the nickel content. Further, it was found that the activities of the Ni/(Zr–Sm)O_x catalysts prepared from the amorphous nickel–zirconium–samarium alloys are higher than those prepared by wet impregnation. Uniform dispersion of nickel in the catalysts prepared from amorphous single-phase alloys should be one of the reasons for the extremely high activity of the catalysts. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: carbon dioxide; methanation; nickel–zironium–samarium alloys

INTRODUCTION

In order to avoid global warming, induced by enormous amounts of carbon dioxide emissions, and to supply abundant renewable energy, we are proposing global CO_2 recycling,[1,2] which consists of electricity generation in deserts, hydrogen and CH_4 production at coasts close to the deserts and CO_2 recovery in energy-consuming districts. In deserts, electricity is generated by solar cells. At coasts close to the deserts, the electricity is used for hydrogen production by electrolysis of seawater, hydrogen is used for methane formation by the reaction with carbon dioxide, and methane is sent to energy-consuming districts. In energy-consuming districts, methane is used as a fuel, and the carbon dioxide formed is recovered and sent back to the coasts close to deserts. Production of methane by catalytic hydrogenation of carbon dioxide is selected in this system owing to its extremely higher reaction rate and higher selectivity on the well-designed catalysts in comparison with the production of other valuable organic substances. Moreover, we do not need to develop a new methane combustion system, since liquid natural gas (LNG), in which methane is a major component, has already been used as a fuel. The key materials needed to realize this global carbon dioxide recycling are electrodes for hydrogen and oxygen evolution in seawater electrolysis and a catalyst for methanation of carbon dioxide.

To deal with the enormous amounts of carbon dioxide emitted, precious metals are not allowed to be used for the electrodes in seawater electrolysis and the catalyst. Recently, we have tailored amorphous nickel–molybdenum cathodes, which are even more active than platinum for hydrogen evolution,[3] and manganese–molybdenum oxide anodes,[4,5] which produce oxygen predominantly without forming toxic chlorine in seawater electrolysis. Additionally, extremely active and selective catalysts for methanation of carbon dioxide have been obtained from amorphous nickel–zirconium

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alloys.[6–8] Using these novel materials, a prototype CO_2 recycling plant was successfully built on the roof of the Institute for Materials Research, Tohoku University, and substantiated our idea for global CO_2 recycling. Furthermore, it has been estimated that the energies and costs required to form liquefied methane in the large-scale global CO_2 recycling are comparable to those for production of LNG from natural gas wells.[9]

Concerning catalysts for methanation of carbon dioxide, the high activity of the Ni/ZrO_2 catalysts prepared from amorphous nickel–zirconium alloys is strongly correlated with the formation of tetragonal ZrO_2 phase.[8] Turnover frequency for methanation of carbon dioxide increases with an increase in the relative amount of tetragonal ZrO_2. When the tetragonal ZrO_2, which is essentially a metastable phase, is further stabilized by the addition of rare-earth elements, such as yttrium, cerium and samarium, to the amorphous nickel–zirconium alloy precursors of catalysts, the activity is enhanced.[10,11]

These amorphous alloy precursors of catalysts have been prepared by a single roller melt-spinning method, which is not well suited to the production of a large amount of catalyst precursors. If the formation of tetragonal ZrO_2 is the only essential factor in obtaining a remarkably high activity for methanation of carbon dioxide, similar catalysts with high activity would be expected to be obtained by a wet impregnation. In the present study, Ni/ZrO_2 and $Ni/(Zr–Sm)O_x$ catalysts have been prepared by a wet impregnation method, and their catalytic activities for methanation of carbon dioxide have been compared with the catalysts prepared from amorphous nickel–zirconium–samarium alloys.

EXPERIMENTAL

ZrO_2 and $(Zr_{0.9}Sm_{0.1})O_{1.95}$ catalyst supports were prepared from a ZrO_2 sol aqueous solution of pH 4 (Nissan Chemicals, NSZ-30A) and a sol solution containing $Sm(NO_3)_3$ (Zr:Sm = 9:1), respectively. The solutions were dried at about 353 K and calcined at 773 K. 30 mol% Ni/ZrO_2 and 15, 30, 50 and 60 mol% $Ni/Zr_{0.9}Sm_{0.1}O_{1.95}$ catalysts were prepared by an ordinal wet impregnation method. The structures of the catalysts and catalyst supports were determined by X-ray diffraction using Cu Kα radiation. Nitrogen physisorption was carried out at 77 K using a Belsorp 28SA automatic gas adsorption apparatus to determine the BET surface areas and pore size distribution of catalysts and catalyst supports. The pore size distribution was determined by a D–H method.[12] Prior to the nitrogen physisorption measurements, the catalysts were reduced in flowing hydrogen at 573 K for 2 h and then evacuated at the same temperature for 3 h.

The catalytic reaction was performed at several temperatures in a fixed bed flow glass reactor. A gas mixture of CO_2 and hydrogen (1:4, volume ratio) was passed continuously on the catalyst at an atmospheric pressure with a reactant gas flow rate (F/W) of 5400 ml g^{-1}_{-cat} h^{-1}, unless otherwise mentioned. At each temperature, the almost steady-state conversion was obtained within 15 min. After the reaction the gas mixture was analyzed using a Chrompac McroGC CP2002 gas chromatograph equipped with a thermal conductivity detector.

RESULTS AND DISCUSSION

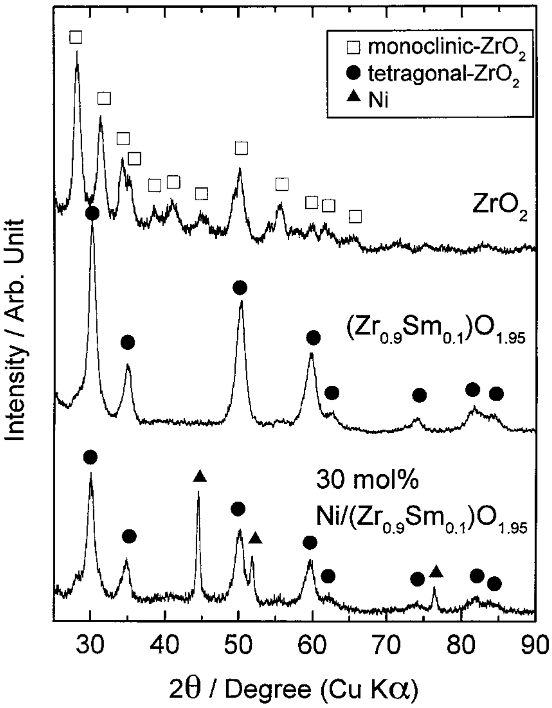

Figure 1 X-ray diffraction patterns of ZrO_2 and $(Zr_{0.9}Sm_{0.1})O_{1.95}$ prepared from ZrO_2 aqueous sol solution with and without $Sm(NO_3)_3$, together with 30 mol% Ni/$(Zr_{0.9}Sm_{0.1})O_{1.95}$ prepared by wet impregnation.

Figure 1 shows to X-ray diffraction patterns of

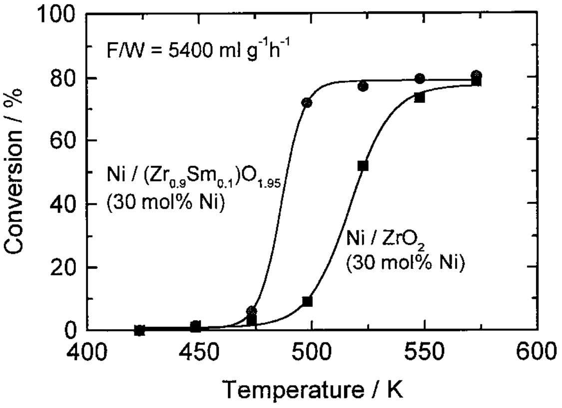

Figure 2 The conversion of carbon dioxide on the 30 mol% Ni/ZrO$_2$ and 30 mol% Ni/(Zr$_{0.9}$Sm$_{0.1}$)O$_{1.95}$ catalysts prepared by wet impregnation as a function of reaction temperature.

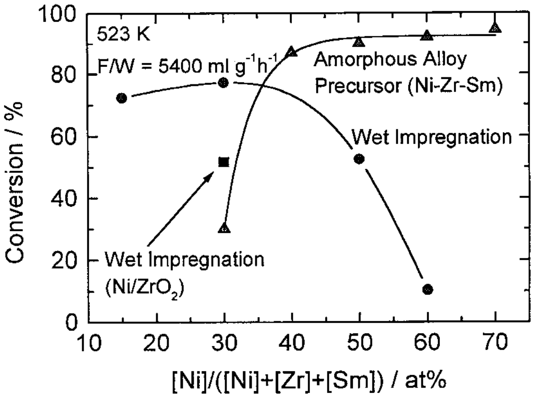

Figure 4 Change in the conversion of carbon dioxide on the Ni/ZrO$_2$ and Ni/(Zr$_{0.9}$Sm$_{0.1}$)O$_{1.95}$ catalysts prepared by wet impregnation and by oxidation–reduction treatment of amorphous alloys[11] with the nickel content.

ZrO$_2$ and (Zr$_{0.9}$Sm$_{0.1}$)O$_{1.95}$ supports as well as a 30 mol% Ni/(Zr$_{0.9}$Sm$_{0.1}$)O$_{1.95}$ catalyst. ZrO$_2$ prepared from an aqueous sol solution consists of a monoclinic ZrO$_2$ phase, whereas (Zr$_{0.9}$Sm$_{0.1}$)O$_{1.95}$ is composed of tetragonal ZrO$_2$. Monoclinic ZrO$_2$ is a thermodynamically stable phase below about 1300 K and the tetragonal one is usually stable only at temperatures higher than 1300 K. However, as is well known, the tetragonal phase is stabilized by the addition of samarium.[13] In the X-ray diffraction patterns of ZrO$_2$ and (Zr$_{0.9}$Sm$_{0.1}$)O$_{1.95}$, each reflection is relatively broad, indicating the nanogranular nature of the oxides. From the full-width at half maximum of the reflections and the Scherrer equation,[14] the grain sizes of the ZrO$_2$ and (Zr$_{0.9}$Sm$_{0.1}$)O$_{1.95}$ were estimated to be 15 nm and 12 nm respectively. When nickel is supported on the (Zr$_{0.9}$Sm$_{0.1}$)O$_{1.95}$, reflections for a face-centered cubic nickel phase are found in addition to the tetragonal ZrO$_2$ pattern.

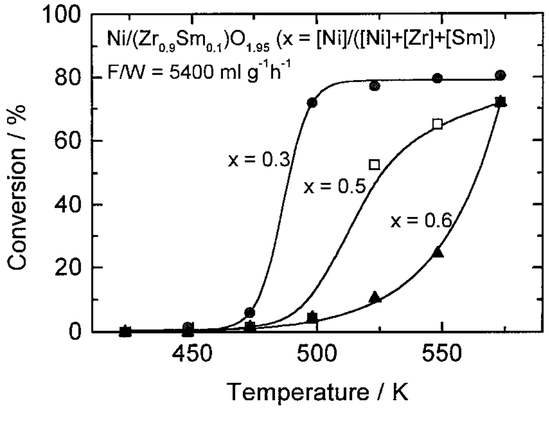

Figure 3 The conversion of carbon dioxide on the Ni/(Zr$_{0.9}$Sm$_{0.1}$)O$_{1.95}$ catalysts with various nickel contents as a function of reaction temperature.

Methanation of carbon dioxide on the present Ni/ZrO$_2$ and Ni/(Zr$_{0.9}$Sm$_{0.1}$)O$_{1.95}$ catalysts proceeds with a selectivity of almost 100%, which is similar to that on the catalysts prepared from amorphous nickel–Zirconium and nickel–Zirconium–samarium alloys. The change in the conversion of carbon dioxide on the 30 mol% Ni/ZrO$_2$ and Ni/(Zr$_{0.9}$Sm$_{0.1}$)O$_{1.95}$ catalysts with reaction temperature is shown in Fig. 2. The reaction on both the catalysts starts at about 448 K. Up to 573 K, the samarium-containing catalyst shows higher conversion than the samarium-free catalyst. At 573 K both the catalysts show a conversion of about 80%. This result indicates that the addition of samarium to the catalysts prepared by wet impregnation is effective in enhancing the catalytic activity between 448 and 548 K, similar to the amorphous alloy-derived catalysts.[10,11] Figure 3 shows the conversion of carbon dioxide on the Ni/(Zr$_{0.9}$Sm$_{0.1}$)O$_{1.95}$ catalysts with various nickel contents as a function of reaction temperature. The conversion decreases significantly with an increase in the nickel content at each temperature. Thus, the addition of excess amounts of nickel in the wet impregnated catalysts is detrimental to the activity of the catalysts. As shown in Fig. 4, the highest conversion at 523 K is obtained when 30 mol% nickel is contained in the catalyst prepared by wet

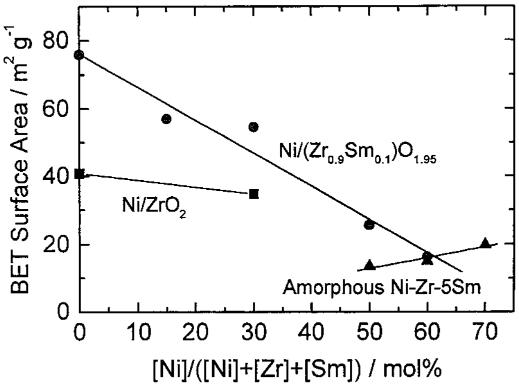

Figure 5 Change in the BET surface area of the Ni/ZrO_2 and $Ni/(Zr_{0.9}Sm_{0.1})O_{1.95}$ catalysts prepared by wet impregnation and by oxidation–reduction treatment of amorphous alloys with the nickel content.

impregnation. Although the conversion on the catalysts prepared from amorphous Ni–25Zr–5Sm alloy [15] (the number in an alloy formula denotes the content of the element in mole percent) is lower than those on the wet impregnated catalysts with the same nickel content, the conversion at 523 K on the catalysts prepared from amorphous Ni–Zr–5Sm alloys increases with an increase in the nickel content.[15] In particular, the nickel-rich catalysts prepared from amorphous alloys show a conversion of about 90%, which is higher than the highest conversion on the catalysts prepared by wet impregnation. Thus, it can be said that more-active catalysts for methanation of carbon dioxide are obtained from amorphous nickel–zirconium–samarium alloy precursors.

The compositional dependence of the activity of the catalysts prepared by wet impregnation and by the oxidation–reduction treatment of the amorphous alloys can be partly explained by the change in the surface area. As shown in Fig. 5, the BET surface area of the Ni/ZrO_2 and $Ni/(Zr_{0.9}Sm_{0.1})O_{1.95}$ catalysts decreases with an increase in the nickel content. In particular, when 50 mol% or more nickel is added, the BET surface area becomes less than 30 m^2 g^{-1}, suggesting that it is not easy to disperse large amounts of nickel finely on the oxide support by this method. By contrast, the BET surface area of the catalysts prepared from amorphous nickel–zirconium–samarium alloys increases with the nickel content,[15] although their areas are much smaller than those of the wet-impregnated catalysts containing $\leq$30 mol% nickel. Thus, it can be said that the catalysts prepared from amorphous alloys shows high activity in spite of the low surface area.

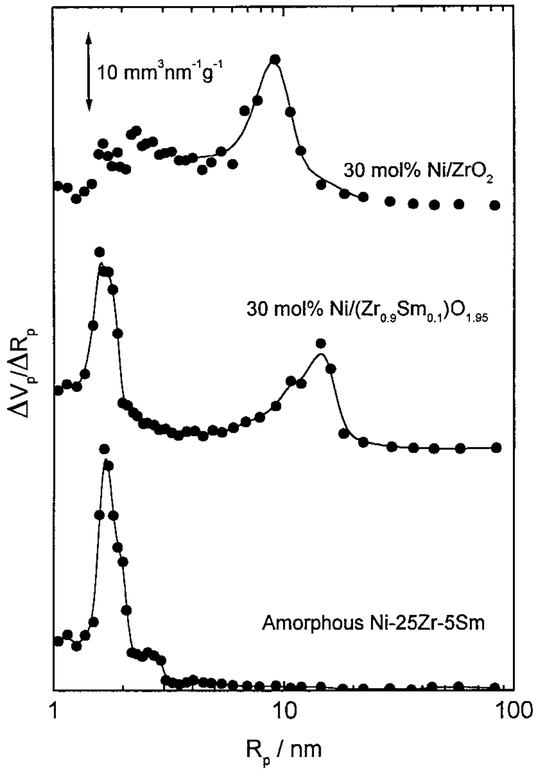

Figure 6 Pore size distribution of the 30 mol% Ni/ZrO_2 and 30 mol% $Ni/(Zr_{0.9}Sm_{0.1})O_{1.95}$ catalysts prepared by wet impregnation and the catalyst prepared from amorphous Ni–25Zr–5Sm alloy.[10].

The pore size distribution of the catalysts prepared by wet impregnation is also different from that of the catalysts prepared from amorphous alloys (Fig. 6). The catalyst prepared from amorphous Ni–25Zr–5Sm alloy has a major pore radius of about 1.8 nm.[10] The catalysts prepared from amorphous nickel–zirconium alloys without samarium have a similar pore size distribution. By contrast, the 30 mol% Ni/ZrO_2 catalyst prepared by wet impregnation has a main pore radius of about 9 nm, which is about eight times larger than that of the catalyst prepared from amorphous alloys. The 30 mol% $Ni/(Zr_{0.9}Sm_{0.1})O_{1.95}$ catalyst has two main pore radii: about 1.7 and 14 nm. In this manner, the pore size distribution of the catalysts changes great with the preparation method and presence of samarium.

These results suggest that the catalysts prepared by different methods are different from a micro-

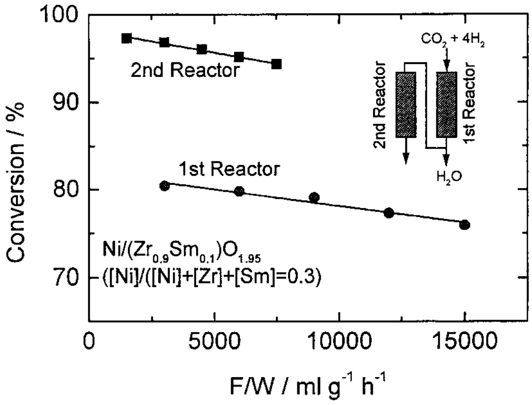

Figure 7 The conversion of carbon dioxide on the 30 mol% $Ni/(Zr_{0.9}Sm_{0.1})O_{1.95}$ catalyst using a single reactor and two reactors connected in series as a function of reactant gas flow rate. In the latter case, water was removed after passing the first reactor.

structural point of view, although the composition is similar. Thus, the performance of the catalysts prepared by different methods is different. As mentioned above, the catalysts prepared by wet impregnation show lower activity than the catalysts prepared from amorphous alloys. However, the conversion on the 30 mol% $Ni/(Zr_{0.9}Sm_{0.1})O_{1.95}$ catalyst at 573 K does not decrease great with an increase in the reactant gas flow rate. Additionally, when two reactors connected in series are used and when water produced in the first reactor is removed before introducing the reaction gas into the second reactor, the conversion is significantly increased, similar to the amorphous alloy-derived catalysts.[7,10] The increase in the conversion is mainly due to the removal of water, which inhibits the catalytic reaction.[16] A conversion of more than 94% is obtained, as shown in Fig. 7. Thus, although the activity of the wet impregnated catalysts is lower than that of the amorphous alloy-derived catalysts, even after the two-stage reaction, it may be said that the high conversion and high selectivity is obtained by using the $Ni/(Zr_{0.9}Sm_{0.1})O_{1.95}$ catalysts prepared by wet impregnation and by using two reactors connected in series.

CONCLUSIONS

(1) A $(Zr_{0.9}Sm_{0.1})O_{1.95}$ oxide with tetragonal ZrO_2 structure is formed from ZrO_2 aqueous solution containing $Sm(NO_3)_3$.

(2) The $Ni/(Zr_{0.9}Sm_{0.1})O_{1.95}$ catalyst prepared by wet impregnation shows higher activity for methanation of carbon dioxide than the similarly prepared Ni/ZrO_2 catalyst, in which ZrO_2 has a monoclinic ZrO_2 structure. The beneficial role of the formation of tetragonal ZrO_2, observed for the catalysts prepared from amorphous nickel–zirconium–samarium alloys is again confirmed for the present catalysts prepared by wet impregnation.

(3) However, the activity of the $Ni/(Zr_{0.9}Sm_{0.1})O_{1.95}$ catalysts prepared by wet impregnation is lower than those prepared from amorphous nickel–zirconium–samarium alloys. Additionally, the activity of the former catalysts decreases with increasing nickel content, mainly due to a decrease in the surface area.

(4) When two reactors connected in series are used and when water generated in the first reactor is removed before passing into the second reactor, a conversion of more than 94% is obtained even on the $Ni/(Zr_{0.9}Sm_{0.1})O_{1.95}$ catalyst prepared by wet impregnation at 573 K up to a reactant gas flow rate of 7500 ml g^{-1} h^{-1}.

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