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Co-methanation of carbon monoxide and carbon dioxide on supported nickel and cobalt catalysts prepared from amorphous alloys

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Abstract

The activity and durability of the catalysts prepared by the oxidation–reduction treatment of amorphous Co-15 at% Zr, Ni-40 at% Zr and Ni-30 at% Zr-10 at% Sm alloys have been investigated for simultaneous methanation of carbon monoxide and carbon dioxide. It has been found that the Ni–30Zr–10Sm catalyst shows the highest activity among the catalysts examined, and the activity of the Co–15Zr catalyst is lower than those of the nickel-based catalysts, in agreement with the activity for the solo methanation of carbon dioxide. On all the catalysts, carbon monoxide reacts preferentially with hydrogen, and is completely converted into methane at and above 523 K. The remaining hydrogen further reacts with carbon dioxide to form methane. The methanation rate in the H_2–CO–CO_2 mixed gas is higher than that in H_2–CO mixed gas without CO_2. This is probably related to the prevention of the formation of surface carbon by the disproportionation reaction of carbon monoxide due to the presence of carbon dioxide. The activity of the Ni–40Zr catalyst at 573 K gradually decreases with reaction time. It has been found that tetragonal ZrO_2, the presence of which is responsible for the high activity, is transformed to thermodynamically more stable monoclinic ZrO_2 during the catalytic reaction. In contrast to the Ni–40Zr catalyst, the Ni–30Zr–10Sm catalyst sustains the initial high activity, and no structural change is observed during the durability test regardless of the presence of a small amount of hydrogen sulfide.

Keywords: Co-methanation of CO and CO_2; Amorphous alloy catalyst; Nickel catalyst

1. Introduction

H_2–CO–CO_2 gas mixtures, produced by steam-reforming of hydrocarbons such as liquefied petroleum gas (LPG) and naphtha, have been widely used for town gas and synthesis of useful chemicals. Coal gasification processes also produce such gaseous mixtures. However, due to relatively low energy of the steam-reformed gas per volume and the presence of poisonous carbon monoxide, further transformation of the reformed gas into high energy gas, such as methane, is desired for use as a fuel. Since the main components of the reformed gas are hydrogen, carbon

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monoxide and carbon dioxide, methane can be formed by simultaneous hydrogenation of carbon monoxide and carbon dioxide as follows:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (1)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (2)$$

In order to transform the reformed gas into methane, tailoring of catalysts with high activity and durability for simultaneous methanation of carbon monoxide and carbon dioxide is needed.

Recently we have been studied the methanation of carbon dioxide on supported catalysts prepared by the oxidation–reduction treatment of amorphous iron group metal–valve metal alloys [1]. Among them we have found that the catalysts prepared from amorphous Co–Zr and Ni–Zr alloys have particularly high activity for the methanation of carbon dioxide [1]. From the examination of the compositional dependence of the catalytic behavior of the Ni–Zr alloy-derived catalysts, it has been found that Ni–Zr catalysts containing 40 or 50 at% zirconium show the highest methanation rate of carbon dioxide. The turnover number of the catalysts gradually increases with increasing nickel content, while the surface area decreases with increasing nickel content. Consequently, the Ni–Zr catalysts containing medium amounts of nickel show the highest activity [2]. Furthermore, we have found that the addition of sufficient amounts of rare earth elements, such as yttrium, cerium and samarium, to the Ni–Zr catalysts is effective in improving the methanation rate of carbon dioxide [3,4]. In particular, the addition of samarium is most effective in increasing the rate of methane formation due to an increase in the turnover number and surface area [4,5].

In contrast to the extensive studies of each hydrogenation of carbon dioxide or carbon monoxide on various solid catalysts, the investigation of simultaneous methanation of carbon monoxide and carbon dioxide is very limited [6]. In the present study, simultaneous methanation of carbon monoxide and carbon dioxide on catalysts prepared from amorphous Co–Zr and Ni–Zr and Ni–Zr–Sm alloys, which have been known to have high activity for methanation of carbon dioxide, has been examined. In addition to catalytic activity, the durability of the catalysts has been evaluated in an atmosphere containing a small amount of hydrogen sulfide, which often acts as a catalytic poison, in addition to hydrogen, carbon monoxide and carbon dioxide. In order to understand the catalytic behavior, temperature programmed desorption (TPD) and reaction (TPR) experiments of carbon monoxide and carbon dioxide have also been performed.

2. Experimental

2.1. Catalyst preparation

Ribbon-shaped amorphous Co-15 at% Zr, Ni-40 at% Zr and Ni-30 at % Zr-10 at% Sm alloys of about 1 mm width and 20–30 μm thickness were prepared by a single roller melt-spinning method. Prior to the catalytic reaction, these amorphous alloys were oxidized in air at 773 K for at least 5 h and subsequently reduced in flowing hydrogen at 573 K for 5 h. As a consequence of this pretreatment, the amorphous alloys were converted into cobalt or nickel catalysts supported on ZrO_2 or ZrO_2–Sm_2O_3 oxides.

2.2. Catalytic reaction

Catalytic reaction was performed in a fixed bed flow glass reactor of 8 mm inner diameter. The amount of catalyst used was 0.5 g. A gas mixture of 14.4% CO, 13.3% CO_2, 5.4% N_2, 2.1% CH_4 and 64.8% H_2, the composition of which is almost the same as the composition of the steam-reformed gas, was passed continuously through the catalysts at 1 atm. For comparison catalytic reactions in a 80% H_2 and 20% CO_2 atmosphere and in a 75% H_2 and 25% CO atmosphere were also performed. In order to clarify the effect of the presence of water which was formed by the methanation reaction on the conversion into methane, a two-stage reaction using two reactors connected in series was also carried out; water vapor generated in the first reactor was removed by bubbling into water at room temperature between the first and second reactors. In this paper, however, unless otherwise noted, the catalytic reaction was carried out using a single reactor to evaluate the activity and durability of each catalyst. After reaction the gas mixture was analyzed using a Shimadzu GC-8A gas chromatograph equipped with a thermal conductivity detector. Except

methane, no carbon-containing compounds were detected, that is, the selectivity of methane formation was 100%. The durability of the catalysts was examined at 573 K in a gas mixture of 14.4% CO, 13.3% CO_2, 5.4% N_2, 2.1% CH_4 and 64.8% H_2 containing about 0.01 ppm of H_2S.

2.3. Catalyst characterization

The BET surface areas of the catalysts were measured using nitrogen physisorption at 77 K with a Belsorp 28SA automatic gas adsorption apparatus. Prior to the measurement, the catalysts were reduced in flowing hydrogen at 573 K for 2 h and then evacuated at the same temperature for 3 h. The temperature programmed desorption (TPD) and reaction (TPR) measurements were carried out using a Belsorp TPD-1-AT apparatus. After pretreatment in hydrogen at 573 K, about 100 mg of the catalyst was cooled in helium. Following adsorption of carbon monoxide or carbon dioxide at 313 K, the catalyst was heated at a constant rate of 10 K min^{-1} in helium or hydrogen for TPD or TPR measurements, respectively. The gas immediately passing through the catalyst was continuously analyzed by a quadrupole mass spectrometer. The *m/e* values used to detect methane, carbon monoxide and carbon dioxide were 16, 28 and 44, respectively.

The structure of catalysts was determined by X-ray diffraction using CuKα radiation. Furthermore, the surface morphology of the catalysts was observed by a scanning electron microscope (JEOL JSM-5400F).

3. Results and discussion

3.1. Catalytic activity

Methanation reaction in a gas mixture containing 14.4% carbon monoxide, 13.3% carbon dioxide and 64.8% hydrogen was carried out with F/W= 5400 ml g^{-1} h^{-1}. Temperature dependence of the conversion of carbon monoxide, carbon dioxide and hydrogen on the Co–15Zr, Ni–40Zr, and Ni–30Zr–10Sm catalysts is shown in Figs. 1-3, respectively. On all the catalysts, carbon monoxide reacts preferentially with hydrogen to form methane. The methanation of carbon dioxide occurs after almost all

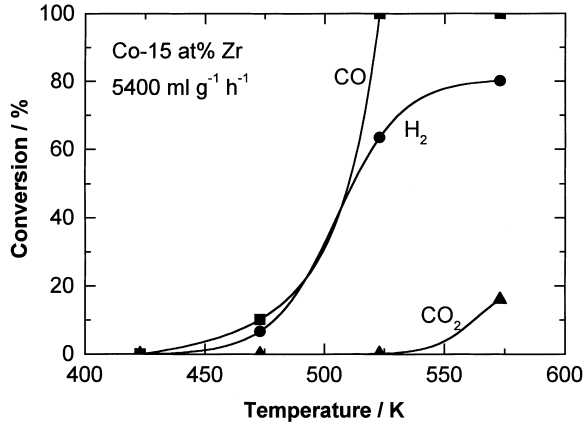

Fig. 1. Conversion of hydrogen, carbon monoxide and carbon dioxide on the Co–15Zr catalyst at F/W=5400 ml g^{-1} h^{-1} as a function of reaction temperature. Partial pressures of hydrogen, carbon monoxide and carbon dioxide are 0.648, 0.144 and 0.133 atm, respectively.

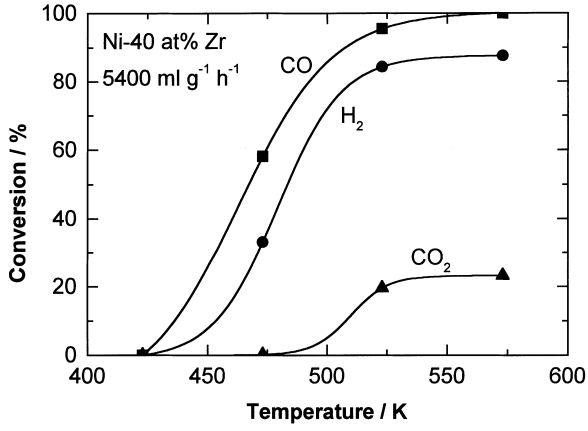

Fig. 2. Conversion of hydrogen, carbon monoxide and carbon dioxide on the Ni–40Zr catalyst at F/W=5400 ml g^{-1} h^{-1} as a function of reaction temperature. Partial pressures of hydrogen, carbon monoxide and carbon dioxide are 0.648, 0.144 and 0.133 atm, respectively.

carbon monoxide is consumed. Preferential methanation of carbon monoxide suggests stronger adsorption of carbon monoxide than carbon dioxide on the catalyst surface [6]. Clearly, the Ni–40Zr and Ni–30Zr–10Sm catalysts show higher activity for co-methanation than the Co–15Zr catalyst. The samarium-containing catalyst has particularly high activity, and the complete conversion of carbon monoxide is obtained

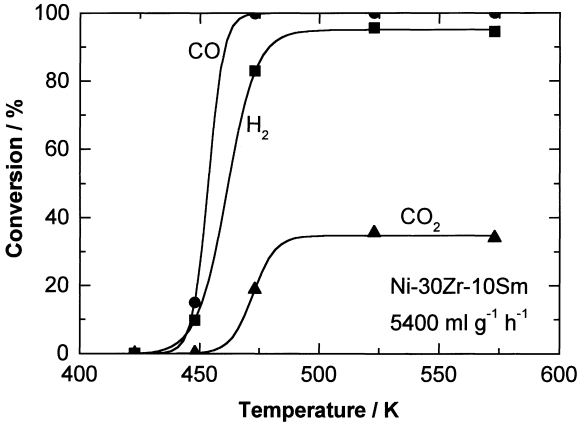

Fig. 3. Conversion of hydrogen, carbon monoxide and carbon dioxide on the Ni–30Zr–10Sm catalyst at F/W=5400 ml g^{-1} h^{-1} as a function of reaction temperature. Partial pressures of hydrogen, carbon monoxide and carbon dioxide are 0.648, 0.144 and 0.133 atm, respectively.

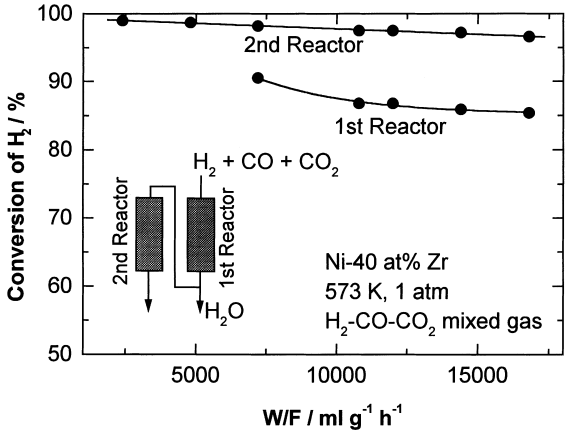

Fig. 4. Change in the conversion of hydrogen on the Ni–40Zr catalyst at 573 K with reactant gas flow rate after passing the first and second reactors. Before passing into the second reactor, water formed at the first reactor was removed. Partial pressures of hydrogen, carbon monoxide and carbon dioxide are 0.648, 0.144 and 0.133 atm, respectively.

even at 473 K. Since the Ni–Zr–Sm catalyst also shows higher activity for the methanation of carbon dioxide in a CO-free environment [4,5], the order of the activity of the present catalysts for the co-methanation is consistent with the activity for the methanation of carbon dioxide, even though carbon monoxide reacts preferentially with hydrogen during the co-methanation reaction. The conversion of carbon dioxide is apparently low even on the Ni–30Zr–10Sm catalyst, but this is mainly due to the deficiency of hydrogen which is necessary to convert both carbon monoxide and carbon dioxide. Under the condition of 100% conversion of carbon monoxide, the maximum conversion of carbon dioxide under the present reactant gas composition is about 35%.

3.2. Effect of water removal on the conversion into methane

In the methanation of carbon monoxide and carbon dioxide, a considerable amount of water is formed as reaction Eqs. (1) and (2) show clearly. It has been found that the use of two reactors connected in series, in which water formed in the first reactor was removed before passing into the second reactor, is effective in increasing the conversion of carbon dioxide into methane on the supported nickel catalysts prepared from amorphous Ni–40Zr and Ni–30Zr–10Sm alloys [3,4]. In this case, the conversion of carbon dioxide reaches 99% by using the two reactors.

Similar to the methanation of carbon dioxide, conversion in the present gas mixture containing both carbon monoxide and carbon dioxide becomes higher by using two reactors connected in series, in which water formed in the first reactor is removed before being introduced into the second reactor, as shown in Fig. 4. The conversion of hydrogen at 573 K on the Ni–40Zr catalyst after passing the first reactor is about 90% or less in the flow rate range examined, but conversion after passing the second reactor is more than 97%, and at the low flow rates about 99% conversion is attained. Also on the Ni–30Zr–10Sm catalyst, conversion of about 99% was obtained at 573 K after passing the second reactor, and the high conversion was sustained even under the high flow rates. Since carbon monoxide is completely converted into methane in the first reactor on both the Ni–40Zr and Ni–40Zr–10Sm catalysts even under the high flow rate, only methanation of carbon dioxide occurs in the second reactor. Thus, the removal of water effectively enhances the conversion by using the two reactors even for co-methanation.

From a thermodynamic point of view, the equilibrium conversion of the reaction 2 at 573 K is esti-

mated to be about 95% under the presence of water formed by the reaction, when 0.20 atm of carbon dioxide and 0.80 atm of hydrogen react at atmospheric pressure. Even in the case of the present co-methanation conditions the equilibrium conversion of hydrogen does not reach 100%. Therefore, one of the reasons for increase in the conversion of carbon dioxide by using the two reactors is the shift of the thermodynamical equilibrium conversion to the product side by removing any water formed. However, even for solo-methanation of carbon dioxide on the Ni–40Zr and Ni–30Zr–10Sm catalysts [3,4], conversion at 573 K does not reach equilibrium conversion by using a single reactor. Since product water has been found to inhibit the rate of hydrogenation of carbon dioxide on $Cu/ZnO/Al_2O_3$ catalysts [7], it is also expected that solo-methanation of carbon dioxide and co-methanation of carbon monoxide and carbon dioxide on the Ni–Zr and Ni–Zr–Sm catalysts are slightly inhibited by the product water under high conversion.

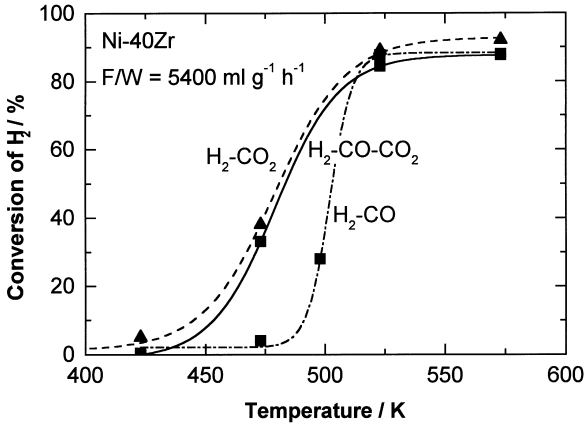

Fig. 5. Comparison of the conversion of hydrogen for co-methanation of carbon monoxide and carbon dioxide and solo-methanation of carbon monoxide and carbon dioxide on the Ni–40Zr catalyst at F/W=5400 ml g^{-1} h^{-1} as a function of reaction temperature. Partial pressures of hydrogen, carbon monoxide and carbon dioxide for the co-methanation are 0.648, 0.144 and 0.133 atm, respectively, those of hydrogen and carbon monoxide for the solo-methanation of carbon monoxide are 0.75 and 0.25 atm, respectively and those of hydrogen and carbon dioxide for the solo-methanation of carbon dioxide are 0.8 and 0.2 atm, respectively.

3.3. Comparison of the rates of solo-methanation and co-methanation of carbon monoxide and carbon dioxide

It has been reported that the rate of solo-methanation of carbon dioxide is generally higher than that of carbon monoxide on various catalysts [8–10]. As shown in Figs. 1–3, however, in the co-methanation of carbon monoxide and carbon dioxide, a preferential reaction of carbon monoxide with hydrogen occurs. This is probably due to the preferential adsorption of carbon monoxide on catalyst [6]. Fig. 5 shows the comparison of the conversion of hydrogen in the co-methanation and solo-methanation of carbon monoxide and carbon dioxide on the Ni–40Zr catalyst as a function of reaction temperature. At and above 523 K, conversion of about 90% is obtained for all the reactions. At temperatures lower than 523 K, conversion for the solo-methanation of carbon dioxide is higher than that for the solo-methanation of carbon monoxide, in agreement with previous reports[8–10]. Interestingly, conversion of hydrogen for co-methanation is higher than that for solo-methanation of carbon monoxide in spite of the fact that the predominant reaction during co-methanation is hydrogenation of carbon monoxide. Conversion of hydrogen for co-methanation is as high as that for the solo-methanation of carbon dioxide. Thus, the co-existence of carbon dioxide accelerates the rate of methanation of carbon monoxide.

The selectivity of methane formation in the H_2–CO_2 mixture is almost 100% on the present catalysts [1,4]. However, in the H_2–CO atmosphere carbon dioxide as well as methane was also formed on the Ni–40Zr catalyst, and the selectivity of carbon dioxide was about 10% at and above 523 K. In the H_2–CO atmosphere carbon dioxide can be formed by the water gas shift reaction 3 or the disproportionation reaction 4:

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (3)$$

$$2CO \rightarrow CO_2 + C \quad (4)$$

In reaction 3, water produced by the methanation reaction 1 can be used to form carbon dioxide. The possibility of the disproportionation reaction 4 has been confirmed by the TPD measurements, as shown in Fig. 6. Carbon monoxide was pre-adsorbed on the Ni–40Zr catalyst surface, and then the catalyst was

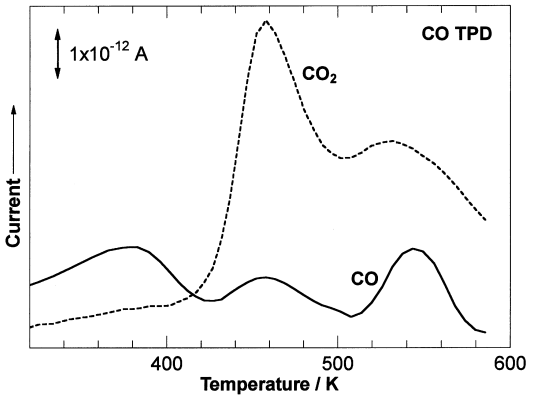

Fig. 6. TPD spectra of carbon monoxide and carbon dioxide for carbon monoxide adsorption on the Ni–40Zr catalyst. Heating rate was 10 K min^{-1}. The vertical axis corresponds to ionic current detected by a quadrupole mass spectrometer. The *m/e* used for carbon monoxide, carbon dioxide detection is 28 and 44, respectively.

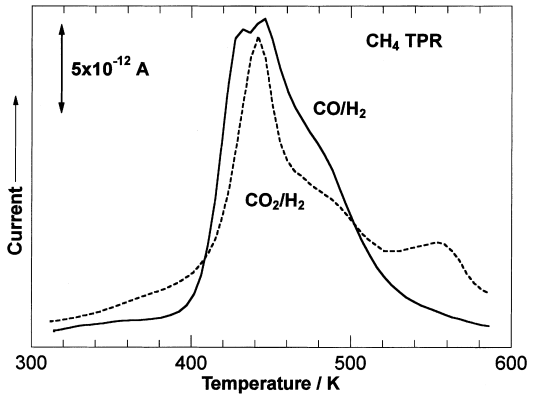

Fig. 7. Methane spectra of TPR for adsorbed carbon monoxide and carbon dioxide with hydrogen on the Ni–40Zr catalyst. Heating rate was 10 K min^{-1}. The vertical axis corresponds to ionic current detected by a quadrupole mass spectrometer. The *m/e* used for methane detection is 16.

heated with a rate of 10 K min^{-1} in a flowing dry helium atmosphere. It is clear from Fig. 6 that carbon dioxide is formed under the atmosphere without the presence of water vapor, and the amount of carbon dioxide formed is larger than that of the carbon monoxide desorbed. This implies that the disproportionation reaction occurs during the solo-methanation of carbon monoxide. Furthermore, in order to compare the reactivity of adsorbed carbon monoxide and carbon dioxide with hydrogen, TPR measurements were also performed on the Ni–40Zr catalyst. The results are shown in Fig. 7. Although the steady-state methanation rate of carbon monoxide is slower than that of carbon dioxide below 523 K (Fig. 5), the formation of methane from adsorbed carbon monoxide occurs at temperatures as low as or even lower than that from the adsorbed carbon dioxide. This suggests that the carbon monoxide adsorbed on the Ni–40Zr catalyst possesses essentially high reactivity similarly to carbon dioxide adsorbed on the same catalyst, and the slower steady-state methanation rate of carbon monoxide is probably due to the presence of inhibitive species, that is probably carbon deposited on the catalyst by the disproportionation reaction 4 during the catalytic reaction on active sites of the catalyst.

From these results, it is clear that carbon is formed by the disproportionation reaction of carbon monoxide during methanation of carbon monoxide in the atmosphere without carbon dioxide. Thus, methane can be formed in the atmosphere by the reaction of carbon monoxide with hydrogen as well as by the reaction of carbon and carbon dioxide, formed by the disproportionation reaction, with hydrogen. It is well known that the disproportionation reaction, leading to the carbon deposition on catalysts, is related to the deactivation of Ni catalysts [8]. The carbon deposited on the catalyst by the disproportionation reaction is also known to be converted into methane by reaction with hydrogen, as follows.

$$C + 2H_2 \rightarrow CH_4 \quad (5)$$

However, the methanation reaction of carbon is relatively slow [11]. Consequently, carbon is accumulated on the catalyst surface, and the intrinsic high activity of the catalyst cannot be sustained during the methanation reaction of carbon monoxide, thus the steady-state methanation rate in the H_2–CO atmosphere becomes lower than that in the H_2–CO_2 atmosphere. However, under the presence of carbon dioxide, the disproportionation reaction of carbon monoxide should be suppressed, because carbon dioxide is a product of the disproportionation reaction. Thus, the formation of carbon is highly reduced, and the intrinsic high activity is sustained during the co-methanation of carbon monoxide and carbon dioxide, as shown in Fig. 5.

3.4. Durability of the catalysts

The durability of catalysts is an important factor for the practical use of catalysts. Thus, durability tests were performed in the H_2–CO–CO_2 gas mixture with and without a small amount of hydrogen sulfide, which often leads to deactivation of the catalyst. The concentration of hydrogen sulfide is almost the same as that expected in practical catalytic environments using steam-reformed gas of LPG as a reactant gas. Conversion of carbon monoxide and carbon dioxide on the Co–15Zr catalyst in hydrogen sulfide-free gas mixtures decreased significantly within several hours. By contrast, nickel catalysts prepared from amorphous alloys showed higher durability. Fig. 8 shows changes in the conversion of carbon monoxide, carbon dioxide and hydrogen on the Ni–40Zr catalyst in hydrogen sulfide-containing gas mixture at 573 K during the co-methanation of carbon monoxide and carbon dioxide with reaction time. After 8 and 24 h the catalytic reactor was cooled to room temperature for several hours, and then heated again to 573 K. The periods of cooling are eliminated from the reaction times in Fig. 8. From Fig. 8 it is found that the catalyst shows lower conversion of hydrogen just after the temperature is re-raised to 573 K, although the conversion is recovered gradually. Initially, carbon monoxide is completely consumed by the reaction, but after the second cooling conversion of 100% is not attained. Furthermore, after showing an almost steady-state conversion up to 200 h, it decreases gradually with reaction time. After the reaction for 400 h, it was found that metallic nickel was deposited on the inner wall of the glass reactor. This indicates the formation of a volatile nickel-containing compound, likely to be $Ni(CO)_4$, and its decomposition during this durability test.

$$Ni + 4CO \rightarrow Ni(CO)_4 \rightarrow Ni + 4CO \quad (6)$$

It is known that the nickel–carbonyl complex is formed below 423 K, and decomposes over this temperature. Therefore, the complex should be formed mainly during the cooling of the reactor. Evaporation of nickel by the formation of this complex may be the main reason for lower conversion just after re-heating the reactor.

The structure of the Ni–40Zr catalyst is largely changed by the reaction for 400 h. Fig. 9 shows the X-ray diffraction patterns of the Ni–40Zr catalyst specimens before and after the reaction for 400 h. The amorphous Ni–40Zr alloy is converted to a nickel catalyst supported on zirconia by the oxidation–reduction pretreatment [3]. Thus, the X-ray diffraction pattern of the catalyst before the reaction shows the reflections of fcc metallic nickel and two types of ZrO_2, that is, monoclinic and tetragonal ZrO_2. From the methanation reaction of carbon dioxide the presence of tetragonal ZrO_2, which is generally stable

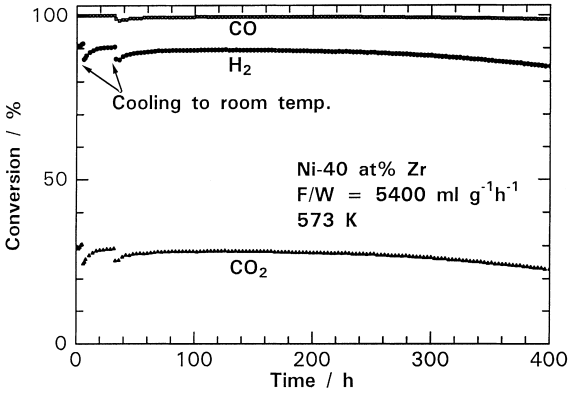

Fig. 8. Change in the conversion of carbon monoxide, carbon dioxide and hydrogen on the Ni–40Zr catalyst at 573 K and F/W=5400 ml g^{-1} h^{-1} with reaction time. Partial pressures of hydrogen, carbon monoxide and carbon dioxide are 0.648, 0.144 and 0.133 atm, respectively. After the reaction for 8 and 24 h, the reactor was cooled to room temperature for several hours.

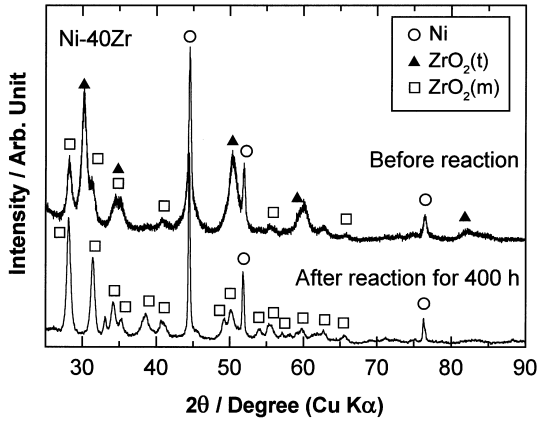

Fig. 9. X-ray diffraction patterns of the Ni–40Zr catalyst before and after reaction of co-methanation at 573 K for 400 h.

only at high temperatures of more than 1300 K, is closely related to the high activity of this catalyst [2]. However, in the X-ray diffraction pattern of the catalyst after reaction for 400 h the reflections corresponding to the tetragonal ZrO_2 are completely missing, due to the transformation of the tetragonal phase to the more stable monoclinic phase. This transformation should be one of the reasons for the gradual decrease in the conversion shown in Fig. 8. In the Ni–40Zr catalyst prepared from amorphous alloy, tetragonal ZrO_2 is formed as a result of stabilization by the presence of nickel as well as the formation of nano-grained crystals [12]. Evaporation of nickel by the formation of the carbonyl complex may therefore lead to the transformation of tetragonal ZrO_2 to monoclinic ZrO_2 during the durability test.

The morphology of the Ni–40Zr catalyst also changed significantly during the reaction for 400 h, as can be clearly seen in the scanning electron micrographs (Fig. 10). Compared with the specimen before the reaction, the surface of the specimen after the reaction is clearly more rough. In fact, the BET surface area changes from 8.5 $m^2\ g^{-1}$ to 61.0 $m^2\ g^{-1}$ by the reaction for 400 h. Increase in the surface area of the catalyst is usually beneficial, due to the increase in the number of active sites, but in the present Ni–40Zr catalyst the disappearance of the tetragonal ZrO_2 is more significant for catalytic activity and hence a decrease in conversion is observed during the catalytic reaction at 573 K.

From these results, the formation of $Ni(CO)_4$ during cooling of the reactor seems to have a large influence on the durability of the Ni–40Zr catalyst. In fact, continuous durability test without cooling the reactor did not show an obvious decrease in the conversion on the Ni–40Zr catalyst up to 550 h. However, even in this case, similar structural and morphological changes of the catalyst were found to occur partially after the 550 h reaction. Therefore, it is predicted that deactivation of this catalyst occurs even in the continuous durability test after prolonged reaction, although deactivation is delayed. It is well known that nickel catalysts for methanation of carbon monoxide and carbon dioxide deactivate under the presence of sulfur compounds [13]. In this case, carbon deposition on catalysts has often been observed. However, for the present Ni–40Zr catalyst, no carbon deposition was observed on the catalyst surface even after the

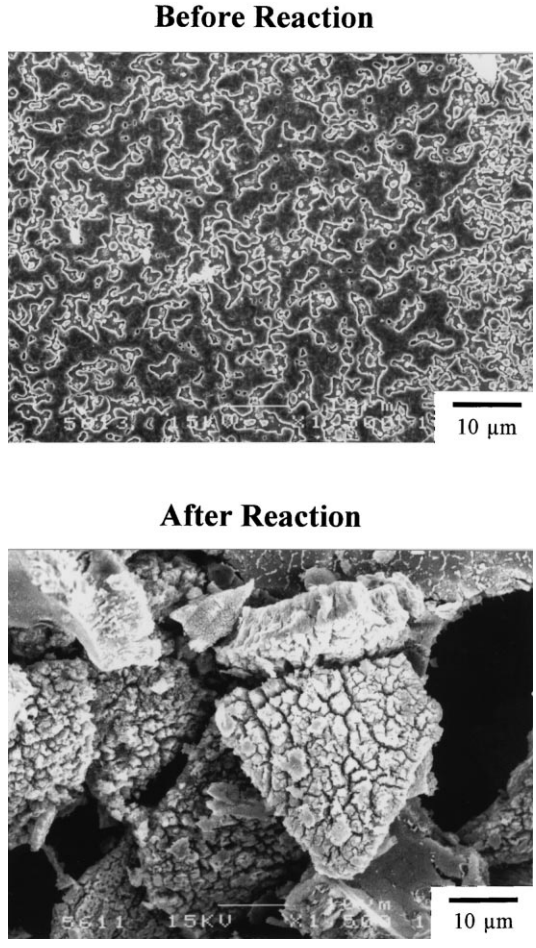

Fig. 10. Scanning electron micrographs of the Ni–40Zr catalyst surface before and after reaction of co-methanation at 573 K for 400 h.

decrease in conversion into methane. This may suggest that the small amount of hydrogen sulfide, being present in the reaction environment, does not contribute much to the deactivation of the catalyst.

In contrast to the Ni–40Zr catalyst, no deactivation is observed for the Ni–30Zr–10Sm catalyst up to the reaction for 400 h (Fig. 11) and no structural and morphological changes are detected either. As shown in Fig. 12, the Ni–30Zr–10Sm catalyst consists of fcc metallic nickel and tetragonal ZrO_2. As a consequence of the stabilization of the tetragonal ZrO_2 structure by the formation of ZrO_2–Sm_2O_3 solid solution, no reflections corresponding to the monoclinic ZrO_2 can be observed. Even after reaction for 400 h, no

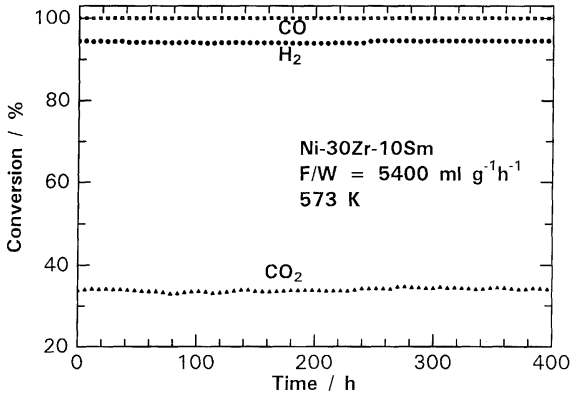

Fig. 11. Change in the conversion of carbon monoxide, carbon dioxide and hydrogen on the Ni–30Zr–10Sm catalyst at 573 K and F/W=5400 ml g^{-1} h^{-1} with reaction time. Partial pressures of hydrogen, carbon monoxide and carbon dioxide are 0.648, 0.144 and 0.133 atm, respectively.

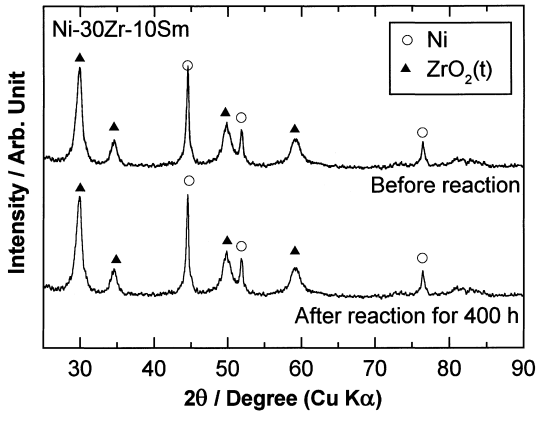

Fig. 12. X-ray diffraction patterns of the Ni–30Zr–10Sm catalyst before and after reaction of co-methanation at 573 K for 400 h.

structural change is seen from Fig. 12. Accordingly, the Ni–30Zr–10Sm catalyst prepared from amorphous alloy possesses very high durability for the co-methanation of carbon monoxide and carbon dioxide under the presence of a small amount of hydrogen sulfide, as well as high catalytic activity.

4. Conclusions

For the transformation of H_2–CO–CO_2 mixed gas, which is formed by steam-reforming of hydrocarbons into methane with higher energy per volume, the simultaneous methanation of carbon monoxide and carbon dioxide has been examined on the supported cobalt and nickel catalysts prepared by the oxidation–reduction treatment of amorphous Co–15Zr, Ni–40Zr and Ni–30Zr–10Sm alloys. The following conclusions have been drawn.

1. Nickel-containing catalysts show higher activity than the Co–Zr catalyst. In particular, the Ni–30Zr–10Sm catalyst has remarkably high activity for the simultaneous methanation of carbon monoxide and carbon dioxide. Carbon monoxide is completely converted into methane at and above about 473 K on the Ni–30Zr–10Sm catalyst. Furthermore, by using two reactors connected in series, in which water formed in the first reactor is removed between the two reactors, 99% conversion of hydrogen is also obtained on the Ni–40Zr and Ni–30Zr–10Sm catalysts at 573 K.
2. On all catalysts carbon monoxide reacts preferentially with hydrogen, possibly due to stronger adsorption of carbon monoxide than carbon dioxide on the catalysts. Conversion of carbon dioxide occurs after almost all carbon monoxide is converted into methane.
3. The rate of methanation during the co-methanation of carbon monoxide and carbon dioxide on the Ni–40Zr catalyst is higher than that during the solo-methanation of carbon monoxide, in spite of the preferential reaction of carbon monoxide during co-methanation. The suppression of carbon deposition, which occurs by the disproportionation reaction of carbon monoxide, by the presence of carbon dioxide prevents deactivation of the catalyst.
4. Catalytic activity of the Ni–40Zr catalyst gradually decreases with reaction time at 573 K in the H_2–CO–CO_2 atmosphere containing a small amount of hydrogen sulfide. Transformation of tetragonal ZrO_2, the presence of which is responsible for high activity, to thermodynamically more stable monoclinic ZrO_2 during the reaction is attributed to the decrease in the activity. However, the transformation includes the surface roughening of the catalyst. Thus, decrease in the activity is suppressed as a result of increase in the number of active sites for co-methanation.
5. In contrast to the Ni–40Zr catalyst, no degradation of Ni–30Zr–10Sm catalyst is observed, and

complete conversion of carbon monoxide and high conversion of hydrogen are sustained at 573 K in the H_2–CO–CO_2 atmosphere containing a small amount of hydrogen sulfide.

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