Catalytic Properties of Heusler Alloys for Steam Reforming of Methanol

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ABSTRACT: Intermetallic compounds have attracted research attention in catalysis because of their unique catalytic properties. Recently, a group of intermetallic compounds, referred to as Heusler alloys (X2YZ), has been investigated as new catalysts. In this study, catalytic properties of 14 Heusler alloys with X = Fe, Co, Ni, or Cu; Y = Ti, Mn, or Fe; Z = Al, Si, Ga, Ge, or Sn for the steam reforming of methanol were examined. Co2TiAl and Ni2TiAl alloys exhibited relatively high H2 production rates because of the formation of fine particles via the selective oxidation of Ti. X2MnZ alloys exhibited high CO2 selectivity because of a water-gas shift reaction catalyzed by MnO that was formed during the reaction. Crystal phases, surface microstructures, and surface compositions of most alloys were changed because of the reaction, and the formation of fine particles possibly assisted in the observation of catalytic activity. Heusler alloys can be beneficial as catalyst precursors by the selection of appropriate elemental sets depending on target reactions.

1. INTRODUCTION

Intermetallic compounds exhibit unique atomic ordered structures and electronic structures, even at the surface, rendering unique catalytic properties. Currently, they are gaining increasing popularity as new catalysts. Almost all of the reported intermetallic catalysts are binary systems. However, ternary intermetallic compounds can render synergistic effects among three elements, which serve as novel catalysts different from ordinary binary catalysts. Heusler alloys (X2YZ) constitute a group of ternary intermetallic compounds with an L21 structure (other types are also present). Typically, the main element X belongs to groups 8–12, while subelements Y and Z belong to groups 3–8 and 13–15, respectively, which is similar to most of the intermetallic catalysts reported thus far. Various possible elemental sets of X, Y, and Z can afford new catalysts, and catalysis can be tuned by utilizing in-between compositions (e.g., X2YZ, X2Y0.5Z0.5). However, Heusler alloys have not been identified as catalysts until only recently. Typically, catalysts are prepared by a liquid process in a form of supported nanoparticles, which requires considerable trials and errors to establish preparation conditions for each elemental system. This fact makes it difficult to screen ternary intermetallic compounds, including Heusler alloys, as catalysts.

Most of the stable intermetallic compounds, even in ternary (or higher) systems, can be easily prepared by metallurgical methods such as arc-melting. By this method, Heusler catalysts in a form of unsupported powders have been screened by our group. Preceding the oxidation of carbon monoxide over Heusler catalysts revealed that X mainly exhibits catalytic activity and Y and Z modulate the activity and durability. Our group has also investigated the selective hydrogenation of alkynes and reported that unlike practical Pd-based catalysts, non-noble metal catalysts such as Co3(Mn or Fe)Ge exhibit high alkene selectivity, and catalysis can be systematically controlled by elemental substitution (Co2MnFe1−xGaxGe1−y). It would be desirable and beneficial to screen these emerging ternary intermetallic catalysts for other reactions to develop new catalysts and gain fundamental knowledge. Hence, the steam reforming of methanol (SRM) is conducted herein, for which intermetallic catalysts are typically applied. The reaction CH3OH + H2O → 3H2 + CO2 is one possibility for producing hydrogen from safe storage for use as a clean energy source in society. The catalytic properties of 14 Heusler alloys with X = Fe, Co, Ni, or Cu; Y = Ti, Mn, or Fe; Z = Al, Si, Ga, Ge, or Sn, which were easily prepared equilibrium phases, and structural changes occurring during the reaction were examined in this report.

2. RESULTS AND DISCUSSION

2.1. SRM with the Reactant CH3OH/H2O = 2:3. Figure 1 shows production rates of H2, CO, CO2, and CH4 for the SRM with the reactant CH3OH/H2O = 2:3 during heating and cooling processes. For Co2TiAl (Figure 1a), the H2 production rate started to significantly increase at 500 °C with the heating, but it decreased at 600 °C. A higher H2 rate was observed during cooling than during heating. Similarly, for Ni2TiAl, the H2 rate suddenly started to increase at 450 °C. Furthermore, the H2 production rate at ≤400 °C was greater during cooling than during heating. Studies reported that Ni3Al and Ni3(Si,Ti) form Ni fine particles on the surface because of the selective oxidation of Al and Si, respectively, during methanol decomposition, thereby exhibiting high activity. Similarly, 

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after SRM, Ni$_2$TiAl exhibited Ni fine particles, as can be observed by X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses (Figure 2a,b, respectively); these fine particles were probably formed because of the selective oxidation of Ti as revealed by X-ray photoelectron spectroscopy (XPS) analysis summarized in Table 1. The increased H$_2$ production rate at $\geq$ 450 $^\circ$C and the higher H$_2$ production rate at 400 $^\circ$C during cooling than during heating were attributed to the Ni fine particle formation. SEM images of Co$_2$TiAl after SRM mainly revealed a number of carbon nanofibers (CNF) with fine particles, while occasionally observed fine particles on the surface (Figure 2b). The crystal structure and composition of these fine particles were not observed by XRD (Figure 2a) and energy-dispersive X-ray spectrometry (EDX) analyses. However, the fine particles in Figure 2b (region 2) were probably Co precipitated via the selective oxidation of Ti; this precipitated Co could serve as active centers, which produced an increased amount of H$_2$ during cooling than during heating. This mechanism was deduced from Table 1 and the subsequent experiments discussed in the next section.

The decrease in the H$_2$ production rate at 600 $^\circ$C for Co$_2$TiAl was mainly related to the decrease in the methanol
feeding because of the blocking of the extensive growth of CNF (Figure 2b, region 1). Compared to Ni$_2$TiAl, Co$_2$TiAl exhibited a larger number of CNF, as indicated by the SEM images and by the higher surface area of Co$_2$TiAl ($3.26 \text{ m}^2 \text{ g}^{-1}$) than that of Ni$_2$TiAl ($0.32 \text{ m}^2 \text{ g}^{-1}$) after the reaction. Compared to Co$_2$TiAl, Ni$_2$TiAl exhibited a smaller decrease in methanol feeding (Figure 2c); therefore, the smaller H$_2$ production rate at 500 °C in the cooling phase than in the heating phase for Ni$_2$TiAl (Figure 1b) is related to the coarsening of Ni particles at ≥550 °C and not to the decrease in methanol feeding. Besides H$_2$, CO was the main product over these alloys, which was typical for pure Co and Ni.$^{13}$ Thus, H$_2$ is predominantly produced by methanol decomposition ($\text{CH}_3\text{OH} \rightarrow 2\text{H}_2 + \text{CO}$), and most of the methanol is consumed at ≥550 °C for both alloys as the H$_2$ rates almost reach their ideal maximum values (assuming decomposition) (Figure 2c). The increase in the CO$_2$ production rate at high temperatures confirms the growth of CNF via the disproportionation of CO ($2\text{CO} \rightarrow \text{CO}_2 + \text{C}$).

Conversely, Cu$_2$TiAl did not catalyze the reaction (Figure 1c). SEM images revealed homogeneously precipitated fine particles (Figure 3). However, XPS analysis revealed a very small surface composition of Cu (Table 1), indicating that active fine particles are not formed by selective oxidation. Co and Ni exhibited similar Gibbs energies of oxidation, but Cu exhibited a considerably more positive Gibbs energy (Table 2).$^{17}$ Fine particle formation by selective oxidation possibly depended on a balance of component oxidizability; thus, Cu is probably difficult to precipitate on the surface of alloy with Ti and Al.

In case of X$_2$TiSn, Fe$_2$TiSn exhibited extremely low activity (Figure 1d) and formed several phases after the reaction (Figure 4a). Co$_2$TiSn and Ni$_2$TiSn basically exhibited similar production rates although Ni$_2$TiSn was slightly active compared to Co$_2$TiSn (Figure 1e,f). In addition, Co$_2$TiSn and Ni$_2$TiSn exhibited similar structural changes, affording marginal X$_2$Sn$_2$ (Figure 4a), as well as similar SEM images revealing fine particles (Figure 4b) after the reaction. EDX analysis indicated that their alloy compositions are stoichiometric in most areas after the reaction. Similar to X$_2$TiAl, oxidizability (Fe > Co ≈ Ni; Table 2) likely played a role in the structural change through the reaction, consequently dominating the catalytic properties.

Similar to X$_2$TiSn, Co$_2$MnSn and Ni$_2$MnSn exhibited similar catalytic properties (Figure 1g,h). In addition, these alloys exhibited similar structural changes, affording marginal X$_2$Sn$_2$ and MnO (Figure 5a). SEM images after the reaction revealed fine particles in some parts of Co$_2$MnSn and all parts of Ni$_2$MnSn (Figure 5b). Even in the case of X$_2$MnSn, X = Co

| catalyst | reaction | chemical compositions [%] | chemical compositions [%] |
|----------|----------|----------------------------|----------------------------|
| Ni$_2$TiAl before reaction | all elements | 12.6 | 3.4 | 4.0 | 40.8 | 40.8 | 13.3 | 18.6 | 68.1 |
| Ni$_2$TiAl 2:3 SRM | 2:3 SRM | 12.6 | 3.4 | 4.0 | 40.8 | 40.8 | 13.3 | 18.6 | 68.1 |
| Ni$_2$TiAl MeOH deco | MeOH deco | 12.6 | 3.4 | 4.0 | 40.8 | 40.8 | 13.3 | 18.6 | 68.1 |
| Ni$_2$TiAl 2:1 SRM | 2:1 SRM | 2.5 | 2.5 | 2.5 | 4.0 | 4.0 | 2.5 | 2.5 | 2.5 |
| Ni$_2$TiAl O$_2$-pre SM | O$_2$-pre SM | 12.6 | 3.4 | 4.0 | 40.8 | 40.8 | 13.3 | 18.6 | 68.1 |
| Ni$_2$TiAl before reaction | XPS Analysis of the Chemical Compositions before and after SRM with Reactants of CH$_3$OH/H$_2$O = 2:3 and 2:1, Methanol Decomposition, and SRM with Oxygen Pretreatment |
| catalyst | reaction | chemical compositions [%] | chemical compositions [%] |
|----------|----------|----------------------------|----------------------------|
| Co$_2$TiAl before reaction | all elements | 12.6 | 3.4 | 4.0 | 40.8 | 40.8 | 13.3 | 18.6 | 68.1 |
| Co$_2$TiAl 2:3 SRM | 2:3 SRM | 12.6 | 3.4 | 4.0 | 40.8 | 40.8 | 13.3 | 18.6 | 68.1 |
| Co$_2$TiAl MeOH deco | MeOH deco | 12.6 | 3.4 | 4.0 | 40.8 | 40.8 | 13.3 | 18.6 | 68.1 |
| Co$_2$TiAl 2:1 SRM | 2:1 SRM | 2.5 | 2.5 | 2.5 | 4.0 | 4.0 | 2.5 | 2.5 | 2.5 |
| Co$_2$TiAl O$_2$-pret SM | O$_2$-pret SM | 12.6 | 3.4 | 4.0 | 40.8 | 40.8 | 13.3 | 18.6 | 68.1 |
| Co$_2$TiAl before reaction | XPS Analysis of the Chemical Compositions before and after SRM with Reactants of CH$_3$OH/H$_2$O = 2:3 and 2:1, Methanol Decomposition, and SRM with Oxygen Pretreatment |
| catalyst | reaction | chemical compositions [%] | chemical compositions [%] |
|----------|----------|----------------------------|----------------------------|
| Cu$_2$TiAl before reaction | all elements | 12.6 | 3.4 | 4.0 | 40.8 | 40.8 | 13.3 | 18.6 | 68.1 |
| Cu$_2$TiAl 2:3 SRM | 2:3 SRM | 12.6 | 3.4 | 4.0 | 40.8 | 40.8 | 13.3 | 18.6 | 68.1 |
| Cu$_2$TiAl MeOH deco | MeOH deco | 12.6 | 3.4 | 4.0 | 40.8 | 40.8 | 13.3 | 18.6 | 68.1 |
| Cu$_2$TiAl 2:1 SRM | 2:1 SRM | 2.5 | 2.5 | 2.5 | 4.0 | 4.0 | 2.5 | 2.5 | 2.5 |
| Cu$_2$TiAl O$_2$-pret SM | O$_2$-pret SM | 12.6 | 3.4 | 4.0 | 40.8 | 40.8 | 13.3 | 18.6 | 68.1 |
| Cu$_2$TiAl before reaction | XPS Analysis of the Chemical Compositions before and after SRM with Reactants of CH$_3$OH/H$_2$O = 2:3 and 2:1, Methanol Decomposition, and SRM with Oxygen Pretreatment |
In addition, the main byproduct of Co$_2$MnGe, Co$_2$MnGa, and CO$_2$ besides H$_2$, unlike (Co or Ni)$_2$TiAl and (Co or Ni)$_2$TiSn. However, Co$_2$MnSn and Ni$_2$MnSn mainly produced CO$_2$ with the reactant of CH$_3$OH/H$_2$O = 2:3. In (a), asterisks, “CS”, “NS”, “TO”, and “Un” represent X$_2$TiSn peaks, “CoGe?” peaks were likely CoGe with the C2/m space group, and “Un” peak was unknown, but possibly hcp-Co.

Table 2. Standard Gibbs Energies of Oxide Formation at 400 and 600 °C for the Reaction with 1 mol of O$_2$ (2m/nM + O$_2$ = 2/nM$_{2}$O$_x$) or 1 mol of H$_2$O (m/nM + H$_2$O(g) = 1/nM$_{m}$O$_n$ + H$_2$)

| element | oxide | ΔG$^\circ$ [kJ (O$_2$ 1 mol$^{-1}$)] | ΔG$^\circ$ [kJ (H$_2$O 1 mol$^{-1}$)] |
|---------|-------|----------------------------------|----------------------------------|
| Fe      | Fe$_2$O$_4$ | -444                            | -413                            |
| Co      | CoO    | -373                            | -344                            |
| Ni      | NiO    | -355                            | -320                            |
| Cu      | CuO    | -239                            | -209                            |
| Ti      | TiO$_2$ (rutile) | -821                            | -786                            |
| Mn      | MnO    | -665                            | -636                            |
| Al      | Al$_2$O$_3$ (α) | -976                            | -935                            |
| Si      | SiO$_2$ (quartz) | -788                            | -752                            |
| Ga      | Ga$_2$O$_3$ | -581                            | -537                            |
| Ge      | GeO$_2$ (hexagonal) | -437                            | -402                            |
| Sn      | SnO$_2$ | -442                            | -399                            |

Figure 4. (a) XRD patterns and (b) SEM images of X$_2$MnSn after SRM with the reactant of CH$_3$OH/H$_2$O = 2:3. In (a), asterisks, “CS”, “NS”, “TO”, and “Un” represent X$_2$TiSn, Co$_2$Sn$_2$, Ni$_2$Sn$_2$, TiO$_2$ (rutile), and unknown peaks, respectively.

Figure 5. (a) XRD patterns and (b) SEM images of X$_2$MnSn after SRM with the reactant of CH$_3$OH/H$_2$O = 2:3. In (a), asterisks, “CS”, “NS”, and “NS” represent X$_2$TiSn, Co$_2$Sn$_2$, and Ni$_2$Sn$_2$ peaks, respectively.

Table 3. CO$_2$ Selectivities at 550 and 600 °C for SRM with the Reactant of CH$_3$OH/H$_2$O = 2:3

| catalyst | 550 °C | 600 °C |
|----------|--------|--------|
| Co$_2$MnSn | 74.0    | 70.8   |
| Ni$_2$MnSn | 81.8    | 73.6   |
| Co$_2$MnGe | 81.5    | 74.9   |
| Co$_2$MnGa | 68.5    | 61.1   |
| Co$_2$MnSi | 83.9    | 78.5   |

Co$_2$MnSi was CO$_2$ (Figure 1i–k). All these Mn-containing alloys formed MnO during the reaction (Figure 6a). Especially, CO$_2$ selectivity (molar ratio of CO$_2$ in all byproducts) decreased with the increase in the temperature for Mn-containing alloys (Table 3).

Figure 6. (a) XRD patterns of Co$_2$MnZ after SRM with the reactant of CH$_3$OH/H$_2$O = 2:3 and (b) SEM image of Co$_2$MnGe after the reaction with atomic concentrations evaluated by EDX analysis of the represented image. In (a), asterisks represent X$_2$TiSn peaks, “CoGe?” peaks were likely CoGe with the C2/m space group, and “Un” peak was unknown, but possibly hcp-Co.

Figure 7. EDX analyses revealed that most of the surfaces are covered by inert TiO$_2$. The precipitation of small grains possibly greater than the stoichiometry even before the reaction (Table 1). These facts indicated that active sites are not formed on the surface covered by inert TiO$_2$.

Table 3. CO$_2$ Selectivities at 550 and 600 °C for SRM with the Reactant of CH$_3$OH/H$_2$O = 2:3

| catalyst | 550 °C | 600 °C |
|----------|--------|--------|
| Co$_2$MnSn | 74.0    | 70.8   |
| Ni$_2$MnSn | 81.8    | 73.6   |
| Co$_2$MnGe | 81.5    | 74.9   |
| Co$_2$MnGa | 68.5    | 61.1   |
| Co$_2$MnSi | 83.9    | 78.5   |

Co$_2$TiGe did not catalyze the reaction (Figure 1l). Fine particle formation was not observed by SEM (Figure 7b). Only this alloy clearly exhibited TiO$_2$ peaks in the XRD pattern (Figure 7a). The surface Ti composition was considerably greater than the stoichiometry even before the reaction (Table 1). These facts indicated that active sites are not formed on the surface covered by inert TiO$_2$.

Co$_2$FeGe exhibited an unusual change in the H$_2$ production rate: it increased with heating but decreased at 550 °C (Figure 1m). SEM revealed fine particles with diameters of ~400 nm (Figure 8a: region 1), and grains with diameters less than 100 nm are apparently precursors of the 400 nm particles (Figure 8a: region 2). The precipitation of small grains possibly increased the H$_2$ production rate at 450 °C. XRD and XPS analyses revealed that most of the surfaces are covered by Fe$_3$O$_4$ (Figure 8b and Table 1). Thus, the coarsening of the
grains and the formation of Fe$_3$O$_4$ possibly decrease the H$_2$ production rate at 550 °C.

All of the alloy powders changed their colors after the catalytic reaction, but the metallic gray color of Co$_2$FeGa did not change, although the color of the bottommost region (ca. 10 vol %) of the catalyst bed changed to black. XRD (Figure 9a), SEM, and EDX results did not reveal changes in structures and compositions of the metallic gray powders during the reaction, except for the presence of minute CNFs in some areas of SEM images (Figure 9b). However, XPS analysis revealed that most of the surfaces are covered by Ga oxides (Table 1). Although studies on the SRM and methanol decomposition over Ga oxides at high temperatures of greater than 500 °C have not been reported, studies revealed that Ga oxides strongly interact with methanol molecules at a lower temperature. Thus, the H$_2$ production over Co$_2$FeGa is likely related to the presence of surface Ga oxides. The SEM image of the bottommost black powders revealed a significant growth of CNF (Figure 9b). As these black powders were obtained at the bottommost region and the H$_2$ production rate only exhibited a marginal difference between the heating and cooling processes, the fine particles on CNFs did not contribute to the H$_2$ production.

### 2.2. Further Investigation on Co$_2$TiAl, Ni$_2$TiAl, Co$_2$FeGe, and Co$_2$FeGa

Co$_2$TiAl and Ni$_2$TiAl apparently exhibited high activity for methanol decomposition, which corresponded to the first step of SRM, because of the fine particle formation. Pure Co and Ni powders sieved to 20–63 μm exhibited low activity (Figure 10), possibly related to the large particle size for methanol decomposition that is structure-sensitive. To validate the importance of fine particle formation, effects of steam and oxygen were investigated. Figure 11 shows the results of methanol decomposition using CH$_3$OH as the reactant without H$_2$O, the SRM using CH$_3$OH/H$_2$O = 2:1 as the reactant, and the SRM using CH$_3$OH/H$_2$O = 2:3 as the reactant after the oxygen pretreatment at 500 °C. For Co$_2$TiAl, a H$_2$ production rate for 2:1 SRM was greater than that for methanol decomposition (Figure 11a,b), but it was less than that for 2:3 SRM (Figure 11c), indicating that active fine particles are formed via oxidation by H$_2$O. The highest H$_2$ production rate was observed for 2:3 SRM after the oxygen pretreatment (Figure 11c), indicating that fine particle formation is considerably enhanced by O$_2$ instead of H$_2$O. Ni$_2$TiAl exhibited a similar tendency with Co$_2$TiAl (Figure 11d–f), although similar results were obtained for 2:1 and 2:3 SRM reactions (Figures 11e and 1b).

Figure 12 shows SEM images after these reactions. Co$_2$TiAl exhibited significant CNF growth in all reactions, where almost all areas were covered by CNF in the case of the methanol decomposition and 2:1 SRM. In case of the surface after...
oxygen-pretreated SRM, fine particle formation was occasionally observed, which was likely enhanced by O₂ pretreatment (Figure 12d), although the structure of fine particles was not observed by XRD analysis (Figure 13a). As indicated by SEM and XPS analyses, significant CNF growth likely increased in the order of methanol decomposition > 2:1 SRM > 2:3 SRM without and with oxygen pretreatment (Table 1), but the H₂ production rate followed the reverse order. Thus, the active centers of Co₂TiAl are likely fine particles formed by the selective oxidation of Ti, not the fine particles on CNF. For Ni₂TiAl, only methanol decomposition afforded an excess growth of CNF (Figure 12e). After 2:1 and 2:3 SRM, similar surfaces (Figures 12f and 2b) as well as catalytic properties (Figures 11e and 1b) were observed. After oxygen-pretreated SRM, the surface clearly exhibited large numbers of fine particles (Figure 12g), which was verified by XRD analysis, with the strongest intensity peaks observed for Ni in the series (Figure 13b). The H₂ production rate clearly depended on the number of fine particles, indicating that the active centers are fine particles formed by the selective oxidation of Ti as well as in Co₂TiAl. Note that the topmost region (ca. 20 vol %) of the catalyst bed changed the color to black after SRM with oxygen pretreatment and revealed significant CNF growth (Figure 12h, Table 1). However, our conclusion was not altered as
CNFs were apparently not grown at 400 °C during heating, while a higher H₂ production rate was observed during heating than during cooling at this temperature. Jang et al. reported that the activation of Ni₃Al catalysts by the selective oxidation of Al is enhanced by the addition of some steam (CH₃OH/H₂O = 10:1) in methanol decomposition, but it is significantly suppressed by the addition of more steam (CH₂OH/H₂O = 2:1 and 1:1). The activation of Ni,TiAl was more enhanced by the addition of more steam and using more severe oxidant (O₂). As Ni fine particle formation required the selective oxidation of Ti in the presence of Al, more severe oxidation conditions were likely preferred.

In terms of application, the activity of oxygen-pretreated Ni,TiAl is herein compared to those of reported catalysts. The turnover frequency (TOF) is often evaluated to compare the activity. TOF values have been reported for many transition-metal-supported catalysts, however, strongly depending on surface areas and dispersion of metals. Thus, activities cannot be compared by TOF between supported small catalysts and our unsupported large catalysts. A H₂ production rate per catalyst weight is crucial for applications. Supported Cu catalysts exhibited H₂ production rates of ∼200 μmol g⁻¹ s⁻¹ at ∼250 °C and ∼300 μmol g⁻¹ s⁻¹ at ∼300 °C. In our previous study, Raney Pd exhibit a H₂ production rate of 87 μmol g⁻¹ s⁻¹ at 300 °C. However, herein, Ni,TiAl exhibited a H₂ production rate of 8.6 μmol g⁻¹ s⁻¹ at 300 °C. Considering that the size of Ni fine particles was up to 400 nm and that their precursors were powders sieved to 20–63 μm, a considerably higher H₂ production rate is expected by using, for example, precursor powders with a diameter of ∼2 μm or foils with a thickness of ∼2 μm.

Co₂FeGe and Co₂FeGa exhibited relatively high H₂ production rates for 2:3 SRM (Figure 1m,n). As the main byproduct was CO, H₂ was supposedly produced by methanol decomposition. Actually, these catalysts were active for the methanol decomposition without steam (Figure 14). For Co₂FeGe, rather than fine particle formation, only surface roughening was observed in the SEM images (Figure 15a). XPS analysis indicated that the chemical composition among metals is not changed (Table 1). As H₂ was produced in the low-temperature region of ≤400 °C, metallic Co₂FeGe was considered to be active for methanol decomposition. Lower H₂ production rates observed at ≤400 and ≥550 °C for 2:3 SRM than those for methanol decomposition (Figures 1m and 14a) were likely related to the oxidation by H₂O at ≤400 °C and to the significant formation of Fe₃O₄ at ≥550 °C. Metallic Co₂FeGe with a diameter of 20–63 μm was active for the structure-sensitive reaction possibly due to the specific electronic structure or a specific reaction field constructed by atomic ordered structures. For Co₂FeGa, the H₂ production rate was slightly less for the methanol decomposition than that for 2:3 SRM. SEM only revealed surface roughening, not fine particle formation (Figure 15b). XPS analysis revealed an increase in the composition of Ga among metals (Table 1). However, it was less significant than that observed for 2:3 SRM. Thus, Ga oxides are considered to play a key role in catalysis of methanol decomposition. By the comparison of all results, secondary phases that might be FeO for Co₂FeGe and Co₃C for Co₂FeGa (Figure 15c) were not likely to contribute to the methanol decomposition without steam.

3. METHODS

Heusler alloy ingots were prepared by arc-melting and subsequent annealing, the conditions of which were described previously. First, the ingots were crushed using a mortar and pestle. Second, the obtained powders were sieved to 20–63 μm for catalytic measurements. The alloys were (almost) a single phase with a highly ordered L₂₁ Heusler structure, which was examined by XRD for powders with a size of less than 20 μm post-annealed at 600 °C for removing strains.

A catalytic reaction was conducted in the gas phase using a fixed-bed flow reactor. A powder catalyst was held on quartz wool fixed in a quartz tube with an internal diameter of ~7.5 mm. Considering formula weights, catalyst amounts were 0.60, 0.75, and 0.90 g for alloys with Z = Al, Si; Z = Ga, Ge; Z = Sn, respectively, so that the catalyst layer height was ~5 mm. The catalyst was preheated at 600 °C for 1 h under H₂ flow for removing surface oxides and strains introduced because of crushing. A reactant mixture of CH₃OH and H₂O with a molar ratio of 2:3 was fed using a plunger pump at a constant rate of 0.1 mL min⁻¹, where the actual measured rate was typically 0.07 g min⁻¹ corresponding to 0.08 mL min⁻¹ and a liquid hourly space velocity (LHSV) of ~20 h⁻¹. In addition to the reactant, 30 mL min⁻¹ of N₂ carrier gas was introduced during the reaction. The reaction temperature was controlled using an electric furnace surrounding the reactor. Gaseous products (H₂, CO, CO₂, and CH₄) were analyzed by gas chromatography.
raphic (Shimadzu GC 14A). Their production rates were estimated from the analyzed concentrations and downstream flow rate measured at room temperature using a flow meter. These analyses were performed 30 min after achieving the measurement temperatures from every 50 °C from 300 °C when heating up to 600 °C and every 100 °C when cooling down to 300 °C.

For selected samples, the effect of steam was investigated by the SRM using the reactant CH3OH/H2O = 2:1 and 1:0 (methanol decomposition), with a methanol feeding rate of 0.04 g min−1, corresponding to that in the SRM with the reactant CH3OH/H2O = 2:3. In addition, the effect of oxygen pretreatment was investigated by the addition of a heating process at 500 °C for 1 h under a 100 mL min−1 flow of [1% O2/He balance] gas before the reaction.

The surface area was determined by the Brunauer–Emmett–Teller (BET) method with Kr adsorption (BELSORP-max volumetric adsorption instrument, MicrotracBEL); the BET surface area was 0.05–0.13 m² g−1 before the reaction, mainly depending on formula weights. Structural changes occurring because of the reaction were examined by XRD (Ultima IV diffractometer, Rigaku), SEM (field-emission type, SU6600, Hitachi) equipped with EDX (INCA x-act, Oxford Instruments), and XPS (PHI 5600, ULVAC-PHI).

4. CONCLUSIONS

Fourteen Heusler alloy catalysts were examined for SRM. Depending on elemental sets, various catalytic properties were observed because of structural changes occurring during the reaction; these structural changes apparently depended on a balance of component oxidizability. The H2 production rates over Co2TiAl and Ni2TiAl significantly increased because of the formation of fine particles via the selective oxidation of Ti during the reaction, although most of H2 was produced by methanol decomposition. H2 production was enhanced by oxygen pretreatment, promoting fine particle formation. All of the Mn-containing alloys formed MnO, which catalyzed the water-gas shift reaction and produced CO2 from CO generated by methanol decomposition. Co2FeGa apparently exhibited activity for methanol decomposition because of the formation of Ga oxides. By choosing appropriate elemental sets, Heusler alloys can be good precursors of catalysts that exhibit high activity and desirable selectivity. On the other hand, Co2FeGa apparently catalyzed methanol decomposition in the initial metallic states, possibly related to its unique electronic structure or a unique atomic ordered reaction field.

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Notes

The authors declare no competing financial interest. An-Pang Tsai passed away on May 25, 2019.

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■ REFERENCES

(1) Armbrüster, M.; Schlögl, R.; Girn, Y. Intermetallic compounds in heterogeneous catalysis—a quickly developing field. Sci. Technol. Adv. Mater. 2014, 15, 034803.
(2) Furukawa, S.; Komatsu, T. Intermetallic Compounds: Promising Inorganic Materials for Well-Structured and Electronically Modified Reaction Environments for Efficient Catalysis. ACS Catal. 2017, 7, 735–765.
(3) Tsai, A. P.; Kameoka, S.; Nozawa, K.; Shimoda, M.; Ishii, Y. Intermetallic: A Pseudoelement for Catalysis. Acc. Chem. Res. 2017, 50, 2879–2885.
(4) Kojima, T.; Kameoka, S.; Tsai, A.-P. The emergence of Heusler alloy catalysts. Sci. Technol. Adv. Mater. 2019, 20, 445–455.
(5) Kojima, T.; Kameoka, S.; Tsai, A.-P. Heusler Alloys: A Group of Novel Catalysts. ACS Omega 2017, 2, 147–153.
(6) Kojima, T.; Kameoka, S.; Fujii, S.; Ueda, S.; Tsai, A.-P. Catalysis-tunable Heusler alloys in selective hydrogenation of alkenes: A new potential for old materials. Sci. Adv. 2018, 4, No. eaat6063.
(7) Tsai, A. P.; Kameoka, S.; Ishii, Y. PdZn = Cu: Can an Intermetallic Compound Replace an Element? J. Phys. Soc. Jpn. 2004, 73, 3270–3273.
(8) Friedrich, M.; Teschner, D.; Knop-Gericke, A.; Armbrüster, M. Surface and Subsurface Dynamics of the Intermetallic Compound ZnNi in Methanol Steam Reforming. J. Phys. Chem. C 2012, 116, 14930–14935.
(9) Hago, Hofer, A.; Büttler, K.; Gigrasdi, F.; Teschner, D.; Knop-Gericke, A.; Schlögl, R.; Ruppertesh, G. In situ study of the formation and stability of supported Pd, Ga methanol steam reforming catalysts. J. Catal. 2012, 286, 13–21.
(10) Bobadilla, L. F.; Palma, S.; Ivanova, S.; Domínguez, M. I.; Romero-Sarria, F.; Centeno, M. A.; Odriozola, J. A. Steam reforming of methanol over supported Ni and Ni–Sn nanoparticles. Int. J. Hydrogen Energy 2013, 38, 6646–6656.
(11) Atzenha, C. S. R.; Mateos-Pedrero, C.; Queirós, S.; Concepción, P.; Mendes, A. Innovative ZrO2-supported CuPd catalysts for the selective production of hydrogen from methanol steam reforming. Appl. Catal., B 2017, 203, 400–407.
(12) Palo, D. R.; Dagle, R. A.; Holladay, J. D. Methanol Steam Reforming for Hydrogen Production. Chem. Rev. 2007, 107, 3992–4021.
(13) Sá, S.; Silva, H.; Brandão, L.; Sousa, J. M.; Mendes, A. Catalysts for methanol steam reforming—A review. Appl. Catal., B 2010, 99, 43–57.
(14) Chun, D. H.; Xu, Y.; Demura, M.; Kishida, K.; Oh, M. H.; Hirano, T.; Wee, D. M. Catalytic properties of NiAl foils for methanol decomposition. Catal. Lett. 2006, 106, 71–75.
(15) Chun, D.; Xu, Y.; Demura, M.; Kishida, K.; Wee, D.; Hirano, T. Spontaneous catalytic activation of NiAl thin foils in methanol decomposition. J. Catal. 2006, 243, 99–107.
(16) Kaneno, Y.; Kondo, T.; Fujimoto, Y.; Tsuda, H.; Xu, Y.; Demura, M.; Iwai, H.; Hirano, T.; Takasugi, T. Catalytic Properties of Cold-Rolled Ni5(Si,Ti) Intermetallic Foils for Methanol Decomposition. Mater. Trans. 2010, 51, 1002–1010.
(17) Kracke, O.; Kubaschewski, O.; Hesselmann, K. Thermochromic Properties of Inorganic Substances, 2nd ed.; Springer-Verlag, Verlag Stahleisen: Berlin, New York, Düsseldorf, 1991.
(18) Tanaka, Y.; Utaka, T.; Kukuchi, R.; Takeuchi, T.; Sasaki, K.; Eguchi, K. Water gas shift reaction for the reformed fuels over Cu/MS catalysts prepared via spinel-type oxide. J. Catal. 2003, 215, 271–278.
(19) Morales, F.; Desmit, E.; Degroot, F.; Visser, T.; Weckhuysen, B. Effects of manganese oxide promoter on the CO and H2 adsorption.
properties of titania-supported cobalt Fischer–Tropsch catalysts. J. Catal. 2007, 246, 91–99.
(20) Johnson, G. R.; Werner, S.; Bell, A. T. An Investigation into the Effects of Mn Promotion on the Activity and Selectivity of Co/SiO$_2$ for Fischer–Tropsch Synthesis: Evidence for Enhanced CO Adsorption and Dissociation. ACS Catal. 2015, 5, 5888–5903.
(21) Ratnasamy, C.; Wagner, J. P. Water Gas Shift Catalysis. Catal. Rev. 2009, 51, 325–440.
(22) Haghofer, A.; Ferri, D.; Föttinger, K.; Rupprechter, G. Who Is Doing the Job? Unraveling the Role of Ga$_2$O$_3$ in Methanol Steam Reforming on Pd$_2$Ga/Ga$_2$O$_3$. ACS Catal. 2012, 2, 2305–2315.
(23) Mihaylov, M.; Tsoncheva, T.; Hadjiivanov, K. Structure sensitivity of methanol decomposition on Ni/SiO$_2$ catalysts. J. Mater. Sci. 2011, 46, 7144–7151.
(24) Jang, J. H.; Xu, Y.; Chun, D. H.; Demura, M.; Wee, D. M.; Hirano, T. Effects of steam addition on the spontaneous activation in Ni$_3$Al foil catalysts during methanol decomposition. J. Mol. Catal. A: Chem. 2009, 307, 21–28.
(25) Iwasa, N.; Mayanagi, T.; Ogawa, N.; Sakata, K.; Takezawa, N. New catalytic functions of Pd-Zn, Pd-Ga, Pd-In, Pt-Zn, Pt-Ga and Pt-In alloys in the conversions of methanol. Catal. Lett. 1998, 54, 119–123.
(26) Matsumura, Y.; Ishibe, H. Suppression of CO by-production in steam reforming of methanol by addition of zinc oxide to silica-supported copper catalyst. J. Catal. 2009, 268, 282–289.
(27) Yang, H.-M.; Liao, P.-H. Preparation and activity of Cu/ZnO-CNTs nano-catalyst on steam reforming of methanol. Appl. Catal., A 2007, 317, 226–233.
(28) Kameoka, S.; Kimura, T.; Tsai, A. P. A Novel Process for Preparation of Unsupported Mesoporous Intermetallic NiZn and PdZn Catalysts. Catal. Lett. 2009, 131, 219–224.
(29) Kameoka, S.; Okada, M.; Tsai, A. P. Preparation of a Novel Copper Catalyst in Terms of the Immiscible Interaction Between Copper and Chromium. Catal. Lett. 2008, 120, 252–256.