The emergence of Heusler alloy catalysts

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ABSTRACT

For over a century, Heusler alloys \((X_2YZ; X, Y; \text{transition metals}, Z; \text{typical metals})\) have attracted attention as magnetic materials. Nowadays, they are also popular as thermoelectric and shape memory materials. However, until very recently, Heusler alloys had been almost unknown as catalysts. We conceived that they could be ideal candidates for catalysts because (1) they have so many elemental sets and (2) they can be partially substituted with other elements (e.g. \(X_2YZ, Z'_x\)) in many cases. We first investigated a variety of Heusler alloys as catalysts and then discovered effective catalysts without precious metals for the selective hydrogenation of alkenes based on the aforementioned feature (1) and demonstrated a systematic tuning of catalytic properties by applying the feature (2). Heusler alloy catalysts have also recently been studied by other groups; hence, this traditional alloy group is becoming a new stream in terms of catalysts. In this article, we review the current progress on Heusler alloy catalysts and describe their future prospects.

1. Introduction

The words ‘intermetallic compounds’ and ‘ordered alloys’ are often used synonymously. In a narrow sense, intermetallic compounds have no order–disorder transition temperature below a melting point and have a limited allowable composition range, while ordered alloys have the transition temperature and a relatively wide composition range, as shown in Figure 1(a,b) [1,2]. In an \(A-B\) alloy, an intermetallic compound with highly covalent bonds will form if the \(A-B\) bond is stronger than the \(A-A\) and \(B-B\) bonds, but an ordered alloy with a weakly covalent bonding will form if the \(A-B\) bond is moderately stronger. Thus, there are many intermetallic compounds in alloys consisting of transition metals and typical metals. However, many ordered alloys consist of only transition metals. Heusler alloys (Heusler compounds) \((X_2YZ)\) typically consist of transition metals in groups 8–12 for \(X\), 3–8 for \(Y\), and typical metals in group 13–15 for \(Z\), as shown in Figure 2 [3–5]. Depending on elemental sets of \(X, Y,\) and \(Z\), they are typical intermetallics, typical ordered alloys showing transitions of \(L2_1 \rightarrow B2 \rightarrow A2\) (body-centered cubic, bcc; Figure 3(a–c)), or in-between alloys only showing the \(L2_1 \rightarrow B2\) transition. Note that there are also \(D0_3\) phases with disordering between \(X\) and \(Y\) atoms, half-Heusler, inverse Heusler, and quaternary Heusler alloys, as shown in Figure 3(d–g).

Heusler alloys have great features. There are so many possible sets of \(X, Y,\) and \(Z\) (Figure 2). This feature predicts a discovery of new catalysts, and enables them to substitute each other (e.g. \(X_2YZ_{1-x}Z'_x\)). The substitution of Heusler alloys is common practice in other fields, especially because their electronic structures can be controlled in a rigid band-like fashion [6,7]. Thus, the substitution would be useful for tuning catalytic properties through controlling electronic structures (ligand effect) and also through changing surface elements (ensemble effect), as shown in Figure 2. However, Heusler alloys were almost unknown as catalysts even though they have been popular as magnetic (spintronic), thermoelectric, and shape memory materials.
materials [6–8]. Especially, they have attracted attention of magnetic researchers since the discovery of Cu$_2$MnAl over a century ago [9,10] because they display ferromagnetism without ferromagnetic elements. Focusing on these features, we started a study on Heusler alloys as new catalysts, and experimentally investigated their catalytic properties [11,12]. In this study, we roughly revealed the catalytic properties of Heusler alloys by investigating 12 alloys for the hydrogenation of propyne and the oxidation of carbon monoxide. Recently, we discovered effective catalysts without noble metals for the selective hydrogenation of alkynes and achieved a systematic control of catalytic properties by elemental substitution, by using the features of Heusler alloys [5]. In this article, we review our

![Figure 1](image1.png)

**Figure 1.** Phase diagrams of (a) Al-Pt system [1] forming intermetallic compounds and (b) Fe-Pt system [2] forming ordered alloys. The diagrams were traced from National Institute for Materials Science (NIMS) AtomWork <http://crystdb.nims.go.jp/> [1,2].

![Figure 2](image2.png)

**Figure 2.** Schematic illustration of the elemental substitution of Heusler alloys ($X_2YZ$) [3] and typical components of $X$, $Y$, and $Z$ (highlighted in periodic table). Other elements such as lanthanoids and those in groups 1 and 2 are also possible components (see Ref [4]). The figure was excerpted from Ref [5], ©The Authors, some rights reserved; exclusive license American Association for the Advancement of Science. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC http://creativecommons.org/licenses/by-nc/4.0).
studies in Sections 2 and 3, and briefly refer to other studies on Heusler catalysts in Section 4 [13–15]. Finally, we summarize our studies and describe future prospects in Section 5.

2. Experimental details

Details are described in the previous papers [5,11,12]. Alloy ingots were prepared by arc-melting from pure metallic pieces (purity ≥ 99.9%). They were annealed in the Ar atmosphere for homogenizing compositions (typically 1000 °C) and ordering atomic positions (typically 500–600 °C) and then crushed using a mortar and pestle. The powders obtained were sieved to a particle size of 20–63 μm, and then used as catalysts. The sieving was necessary to exclude as many uncertain factors as possible. X-ray diffraction (XRD) was performed for a powder sieved to <20 μm after annealing at 600 °C for 1h to remove the defects introduced by crushing. The XRD confirmed that all samples were (almost) a single phase of the L2₁ structure with high order. The Brunauer–Emmett–Teller method for Kr adsorption isotherms at 77 K yielded the surface area of catalysts as 0.05–0.13 m² g⁻¹ mainly depending on atomic weights. Catalytic tests were conducted using a standard fixed-bed flow reactor built using Swagelok® parts made of 316 stainless steel. An appropriate amount of catalyst (typically 0.4 g) was placed into a quartz tube (4-mm internal diameter) and then inserted into an electric furnace. Before the reaction, gas lines, including gas regulators, were purged enough to remove air contamination accumulated due to a slight leakage at the joints, and the catalyst was heated at 600 °C for 1h under hydrogen flow for removing surface oxides and defects. After the introduction of a reaction gas at room temperature at a flow rate of 30 cm³ min⁻¹, heating was started to measure temperature dependence. Unreacted and produced gases were analyzed using a gas chromatograph.

3. Results and discussion

3.1. Oxidation of carbon monoxide [11,12]

The 12 Heusler alloys listed in Table 1 were investigated for the oxidation of carbon monoxide using a reactant of [1.2%CO/0.4%O₂/He balance], the concentration of which was CO rich to suppress an irreversible oxidation of catalysts. Figure 4 shows conversions of CO during continuous heating by 2.5 °C min⁻¹. In pure X, the hierarchy, Cu < Co < Ni < Fe, was observed of temperature, in which the

![Figure 3. Crystal structures for (a) L2₁ (full-Heusler, Fm–3m), (b) B2 (Pm–3m), (c) A2 (bcc, Ima–3m), (d) D0₁₃ (Fm–3m), (e) C1₁₃ (half-Heusler, F–43m, (f) Li₂AgSb or Hg₂CuTi (inverse Heusler, F–43m), and (g) LiMgPdSn (quaternary Heusler, F–43m) phases, where symbols in parentheses represent space groups [3]. In (b), the Y and Z atoms are mixed. In (c), all atoms are mixed. In (d), X and Y elements are mixed. In (e), half of X atoms are absent, so that the structure is called a half-Heusler (XYZ) in contrast to a full-Heusler (X₂YZ), in a narrow sense. In (f), additional Y atoms occupy the vacant sites of the half-Heusler. In (g), the fourth elements (A) occupy the vacant sites of the half-Heusler. (f) and (g) show the prototype names because their Strukturbericht symbols (like L2₁) are not commonly used. For (f), there are two prototype names for the same structure.](image-url)
CO conversion began to increase, while Co achieved a high conversion close to its limit (66.7%) at lower temperature than others, as shown in Figure 4(a). This temperature hierarchy of X and the high conversion of Co seemed to be basically followed by X in $X_2TiSn$, $X_2TiAl$, and $X_2MnSn$, as shown in Figure 4 (b–d), although the hierarchy of Fe and Ni in $X_2TiSn$ was opposite. This indicates that a main active element is X in $X_2YZ$ for CO oxidation.

Figure 5 shows CO conversions during cycles of heating and cooling between 80 and 600 °C for catalysts with a total surface area of 0.027 m$^2$. Most Heusler alloys exhibit a hysteresis as Fe$_2$TiSn and Ni$_2$TiSn, as shown in Figure 5 (a,b). This was due to the irreversible oxidation of catalysts, which was revealed by estimating an excess consumption of O$_2$ from a consumption ratio of CO and O$_2$. In contrast, Co$_2$TiSn showed a small hysteresis, as shown in Figure 5(c). This was due to high oxidation resistance, which was indicated by a small excess O$_2$ consumption and by a tiny XRD peak of oxide even after the reaction under O$_2$-rich conditions. These results indicate that we can control an activity by choosing X and a durability by Y and Z.

3.2. Hydrogenation of propyne [11,12]

The alloys listed in Table 1 were investigated for the hydrogenation of propyne ($C_3H_4$) using a reactant of [1%C$_3$H$_4$/55%H$_2$/He balance]. Figure 6 shows conversions of $C_3H_4$ for catalysts with a total surface area of 0.027 m$^2$. Most Heusler alloys showed a too small conversion, as well as Co$_2$TiSn. This small conversion was indicated due to residual surface oxides and/or segregated Sn at the surface, because most alloys contain elements having very stable oxides such as Al, Si, and Ti, and because Sn atoms tend to segregate at the
surface [11,12]. Co₂FeGe, Co₂MnGe, and pure Co showed a certain conversion, as shown in Figure 6, whereas pure Fe, Mn, and Ge revealed almost no activity. This indicates that a main active element was X for C₃H₄ hydrogenation as well as for CO oxidation. The conversion for Co₂FeGe (50%Co) was larger than that for pure Co (100%Co). This indicates that a new electronic structure formed by the alloying of Co, Fe, and Ge was more suited for the C₃H₄ hydrogenation than pure Co. These results indicate that we can control an activity by choosing not only the main active element, X, but also sub-elements, Y and Z, through the creation of new electronic structures.

3.3. Selective hydrogenation of alkynes [5]

3.3.1. High alkene selectivity

The investigation in Section 3.2 indicated that only Co₂MnGe and Co₂FeGe had an activity for the hydrogenation of hydrocarbons in the alloys listed in Table 1. Thus, we further investigated them for selective hydrogenation of alkynes, focusing on selectivity. This reaction is important for removing alkyne impurities from alkene feedstocks because the impurities inhibit the polymerization process of alkenes [16,17]. In industry, Pd-based catalysts have been used for selective hydrogenations of ethyne (C₂H₂) in ethene (C₂H₄) and propyne (C₃H₄) in propene (C₃H₆) [16–18]. We found that non-noble metal catalysts, Co₂MnGe and Co₂FeGe, had a high alkene selectivity with these reactions.

Figures 7(a–c) present results on the C₃H₄ conversion and the C₃H₆ selectivity for C₃H₄ hydrogenation using a reactant of [0.1%C₃H₄/40%H₂/He balance]. For Co₂FeGaₐ₋₇₅Ge₀.₇₅ in Figure 7(c), the selectivity was high when the conversion was low, decreasing as the conversion increased, which is typical behavior for ordinary catalysts because of the strong adsorption of alkynes inhibiting re-adsorption of alkenes [19–21]. In contrast, Co₂MnGe and Co₂FeGe showed a high selectivity even when conversion was at 100%, as shown in Figure 7(a,b). Figure 7(d–f) show a C₃H₆ conversion for C₃H₄ hydrogenation without C₃H₆ using a reactant of [0.1%C₃H₄/40%H₂/He balance]. Co₂FeGa₀.₇₅Ge₀.₇₅ converted C₃H₆ to C₃H₄ in 100% even at room temperature, while Co₂MnGe and Co₂FeGe showed only a small conversion in the whole temperature. Thus, Co₂MnGe and Co₂FeGe do not have the ability to hydrogenate alkenes to alkanes, which can be called ‘intrinsic selectivity,’ unlike Pd-based catalysts that need precise controls of reaction conditions to ensure the selectivity [16,17].

Owing to this property, they also showed high selectivity even for the hydrogenation of alkyne impurities in alkene feedstocks using a reactant of [0.1%C₃H₄ or C₂H₂/10%C₃H₆ or C₂H₂/40%H₂/He balance], as shown in Figure 8(a,b), in contrast to the example for Co₂FeGa shown in Figure 8(c). An excessive H₂ concentration in the reactants, alkyne:H₂ = 1:400, also indicated the great selectivity, because the alkyne:H₂ ratio is usually 1:10–20 in other reports, including the reports on binary intermetallic compounds [16,20,22,23].

3.3.2. Control of catalytic properties by elemental substitution

We investigated a change in catalytic properties by elemental substitution (Co₂MnₓFe₁₋ₓGaₓGe₁₋ₓ).
Figure 8. Alkyne conversions and alkene selectivities in alkyne hydrogenations in the presence of alkenes for (a) Co₂MnGe, (b) Co₂FeGe, and (c) Co₂FeGa. The reactant was [0.1%C₃H₄ or C₆H₆/10%C₃H₄ or C₆H₆/40%H₂/He balance]. After Ref [5], © The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC, http://creativecommons.org/licenses/by-nc/4.0).

Figure 9 summarizes the effects due to substitutions of Mn for Fe and Ga for Ge in Co₂FeGe, using [0.1%C₃H₄/40%H₂/He balance] in reaction. For Mn substitution, the C₆H₆ selectivity showed no change, while the C₃H₄ reaction rate increased with Mn substitution, as shown in Figure 9(a). On the other hand, Ga substitution significantly decreased the selectivity, while increasing the reaction rate. In Figure 9(b), we can see a strong correspondence between the apparent activation energy (Eₐ) estimated from the rate, and a d-band center (ε_d) estimated from the density-of-state (DOS) curves calculated for bulk states. This means that the change in electronic structures affected the elementary steps of the reaction. Hard X-ray photoelectron spectroscopy confirmed that actual specimens had valence band structures corresponding to the calculated DOSs, which means that both the sample preparations and the calculations were well conducted. Note that the bulk ε_d can be used for relative comparison among the alloys, with the same structure consisting of similar elements because the change in DOSs, from bulk to surface, originates from the symmetry breaking at the surface [24]. In addition, Mn substitution for Fe in Co₂FeGa and Ga substitution for Ge in Co₂MnGe showed similar changes in catalytic properties to those in Figure 9(a), which indicates that the effects of Mn-Fe and Ga-Ge substitutions are independent of each other.

3.3.3. Possible mechanisms of substitution effects

The Mn substitution certainly changed the electronic structures, increasing ε_d and causing the monotonic decrease in E_a with the Mn composition, but not causing the monotonic increase in the reaction rate, as shown in Figure 9. We built a hypothesis that this lack of correspondence between E_a and rate was due to the enthalpy-entropy compensation [25]. For H₂ adsorption, the increase in ε_d strengthens the bond between H and catalyst atoms, which decreases (negatively increases) not only the adsorption enthalpy (ΔH₁₂_ads), but also the adsorption entropy (ΔS₁₂_ads) due to the reduction of freedom. This phenomenon is the compensation effect [25]. In the Arrhenius equation of the reaction rate, r = Aexp(−E_a/RT), the apparent frequency factor (A) and the E_a have the relations: A ∝ exp(ΔS/RT) and exp(−E_a/RT) ∝ exp(−ΔH/RT), where ΔS and ΔH are entropy and enthalpy changes for related elementary steps. Thus, if a reaction mechanism is fixed with a change in ε_d, a reduction in E_a with ε_d should originate from a reduction in ΔH, which diminishes

Figure 9. Elemental substitution effects on (a) C₃H₄ reaction rate at 50 °C and C₆H₆ selectivity at 200 °C, and (b) experimental E_a and calculated ε_d in Mn substitution (Co₀MnₓFe₁₋ₓ Ge) and Ga substitution (Co₀FeₓGa₁₋ₓ Ge) for Co₂FeGe. The rate is per surface area and relative to that of Co₂FeGe. The figure was remade using the data in Ref [5], ©The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC, http://creativecommons.org/licenses/by-nc/4.0).
ΔS, and eventually A. We believe that such compensation was the reason why the rate did not increase monotonically with the reduction in $E_a$. See [5] for details.

However, the increase in the rate due to Ga substitution seemed reasonable. In addition, the selectivity significantly decreased, unlike in Mn substitution. These results can be explained by assuming that Ga atoms contribute to molecular adsorption, but Ge atoms do not. The high selectivity of Pd-based catalysts is believed to originate from small active sites surrounded by poisonous species, which sterically inhibit the adsorption of larger molecules, alkenes, but allow the adsorption of smaller molecules, alkynes [16,17]. Figure 10(a) shows schematic illustrations of (110) surfaces for Co$_2$FeGe, Co$_2$FeGa$_{0.5}$Ge$_{0.5}$, and Co$_2$FeGa. These indicate that the size of adsorption sites is small for Co$_2$FeGe, while it is enlarged by Ga substitution, if Ge atoms have no ability for molecular adsorption but Ga atoms do. Thus, Co$_2$FeGe should have a high alkene selectivity, while Ga substitution should decrease the selectivity. In Figure 10(a), we can also see an increase in the number of sites available for adsorption due to Ga substitution, which indicates an increase in the reaction rate. We believe that this hypothesis was the reason for the Ga substitution effects.

We verified the difference of adsorption ability between Ga and Ge. Figure 10(b) shows local partial 4p DOSs of Ga and Ge at (110) surfaces for Co$_2$FeGa and Co$_2$FeGe, respectively. We can see that the Ga band has higher energy than the Ge band, which indicates that Ga atoms have a higher ability for molecular adsorption than Ge atoms. In addition, theoretical calculations have indicated that typical metals gain the adsorption ability through the hybridization of their $p$-bands with the $d$-bands of transition metals in intermetallic compounds [26,27].

### 4. Other research

There is a catalytic study on Cu$_2$MnAl published in 1935 [13]. We did not know the existence of this paper, written in German, until the recent appearance of a patent on Heusler alloy catalysts [14], which mentioned that 1935 work. Hedvall had intensively investigated the relationship between ferromagnetism and catalysis, and reported in this paper that an increase in CO$_2$ yield over Curie temperature was observed in the catalytic reaction of 2CO $\rightarrow$ CO$_2$ + C by Cu$_2$MnAl, as well as in the hydrogenations of CO and C$_2$H$_4$ by Ni [13].

The patent was filed by BASF [14], which claimed the supported fine-particle catalysts of Heusler alloys with $X = $ Mn, Fe, Co, Ni, Cu, and Pd; $Y = $ V, Mn, Cu, Ti, and Fe; $Z = $ Al, Si, Ga, Ge, In, Sn, and Sb. Hereafter, we will only mention the experimental data described in the patent. Table 2 lists the catalysts, which were prepared by impregnation using fumed silica or gamma alumina as a support, and methanol or water as a solvent, followed by annealing under a gas flow of pure H$_2$, 5%H$_2$/N$_2$, or 10%H$_2$/N$_2$. The XRD indicated that most samples consisted of A2 (bcc) main phase and A1 (face-centered cubic, fcc) secondary phase. The formation of L2$_1$ and B2 phases could not be monitored because their fingerprint peaks were hidden by the halo peak of amorphous silica. The XRD patterns for Samples 12 and 13 are likely from the A1 single phase. We cannot evaluate the phases of the catalysts supported on the alumina because the XRD patterns
were mostly from the aluminas. The distribution of particle size was evaluated for Sample 8. Figure 11(a) shows the size distribution for smaller particles (mainly < 400 nm) observed by high-angle annular dark field scanning transmission electron microscopy. The median particle size was evaluated as 86.6 nm in these particles. Figure 11(b) shows the size distribution for larger particles (mainly > 400 nm) observed by backscattered electron images from scanning electron microscopy, and indicates that the size was distributed around 800 nm for the particles of > 400 nm.

Samples 1–10 (probably also 11) were tested for the Knoevenagel condensation using benzaldehyde and malononitrile. The fumed silica support showed a certain activity. Samples denoted 'Up' in Table 2 showed a higher activity than the pure fumed silica. Especially, CoFeAl showed the highest activity, while the inventors considered that it was due to the high activity of Al for this reaction. Samples 12–17 were tested for the selective reduction of NO using a reactant of [0.05%NO/0.05%NH3/5%H2/10%H2O/N2] balance. Samples 12 and 13 showed a moderate activity for reducing NO and produced a certain amount of N2O. Samples 14–17 showed a high activity with almost no production of N2O.

In addition, a thesis exists on the first-principles calculation for NH3 dissociation on Ni3MnGa and Co3CrGe surfaces [15]. The author, Senanayake, considered that a higher DOS at the Fermi energy would result in a lower activation energy for the dissociation, and explored such materials in Heusler alloys. The Co3CrGe surface had a high DOS, lowering the activation energy to 0.862 eV. The Ni3MnGa surface lowered it to only 1.309 eV, while calculations on 105 kinds of Ni-Mn-Ga compositions revealed that the Ni3Mn11Ga surface had a high DOS, lowering it to 0.575 eV. Although the Ni3Mn11Ga can no longer be called ‘Heusler alloy’ and the preparation is probably impossible, the value was lower than 0.73 eV for pure Fe.

**Figure 11.** Size distribution for (a) smaller particles (mainly < 400 nm) and (b) larger particles (mainly > 400 nm) in Sample 8 listed in Table 2. The figure was excerpted from Ref [14], with slight rearrangement. See Ref [14], for details of how to estimate the minimum diameter.

### Table 2. List of Heusler catalysts with preparation conditions, including phases indicated by XRD and catalytic properties in Ref [14]. 'Up' and 'Down' for Knoevenagel condensation means that activity was higher or lower than that for SiO2 support without Heusler catalysts, respectively. Phases in samples 14–17 were not determined (n.d.).

| No. | Alloy | Support | Solvent | Annealing atmosphere | XRD | Activity for Knoevenagel condensation | Selective reduction of NO |
|-----|-------|---------|---------|----------------------|-----|--------------------------------------|--------------------------|
| 1   | CoFeGa | SiO2    | Methanol | H2                   | A2 + A1 | Down                                 | –                         |
| 2   | CoFeAl | SiO2    | Methanol | H2                   | A2 + A1 | Up                                   | –                         |
| 3   | CoFeSi | SiO2    | Methanol | H2                   | A2 + A1 | Down                                 | –                         |
| 4   | CoFeIn | SiO2    | Methanol | H2                   | A2 + little A1 | Down                     | –                         |
| 5   | CoFeGa | SiO2    | Water    | H2                   | A2 + A1 | Down                                 | –                         |
| 6   | CoFeAl | SiO2    | Water    | H2                   | A2 + little A1 | Up                       | –                         |
| 7   | CoFeSi | SiO2    | Water    | H2                   | A2 + little A1 | Up                       | –                         |
| 8   | CoFeGa | SiO2    | Water    | 5%H2/N2              | A2 + A1 | Up                                   | –                         |
| 9   | CoFeSi | SiO2    | Water    | 5%H2/N2              | A2 + A1 | Up                                   | –                         |
| 10  | CoFeIn | SiO2    | Water    | 5%H2/N2              | A2 + little A1 | Down                     | –                         |
| 11  | CoFeIn | SiO2    | Methanol | 5%H2/N2              | A2 + little A1 | Probably down | –                         |
| 12  | CuFeAl | SiO2    | Water    | 5%H2/N2              | A1    | –                                    | Moderately active, N2O produced |
| 13  | CuFeSi | SiO2    | Water    | 5%H2/N2              | A1    | –                                    | Moderately active, N2O produced |
| 14  | Fe3MnGa | Al2O3  | Water    | 10%H2/N2             | n.d.  | –                                    | Highly active, no N2O        |
| 15  | Fe3MnSi | Al2O3  | Water    | 10%H2/N2             | n.d.  | –                                    | Highly active, no N2O        |
| 16  | Co2CuAl | Al2O3  | Water    | 10%H2/N2             | n.d.  | –                                    | Highly active, no N2O        |
| 17  | Fe2TiGa | Al2O3  | Water    | 10%H2/N2             | n.d.  | –                                    | Highly active, no N2O        |

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5. Summary and future prospects

5.1. Our studies

Catalytic properties of many Heusler alloys were investigated. The results indicated that X is the main active element, and Y and Z have roles that can change the activity, selectivity, and durability. Especially for the selective hydrogenation of alkynes, non-noble metal catalysts with a great selectivity were discovered, based on the feature that there are so many sets of X, Y, and Z. In addition, the systematic control of catalytic properties by elemental substitution was demonstrated based on the feature that substitution is possible with various elements in a wide composition range. In Co2(Mn,Fe)(Ga,Ge) for the selective hydrogenation, the Mn-Fe and Ga-Ge substitutions brought the ligand and ensemble effects, respectively, and they were independent of each other. Thus, we expect that the catalytic properties can be fine-tuned for specific target reactions. Aside from the practical benefit, this tunability would be useful for investigating general mechanisms of catalysis by intermetallic compounds, because the effects originating from electronic structures and surface elements can be investigated independently and systematically under the same crystal structure.

Since many Heusler alloys contain easily oxidizable elements, as shown in Figure 2, it is difficult to predict which elemental sets are suited for the reactions involving oxygen. Actually, we have also confirmed the metallurgical and microstructural changes due to oxidation in ongoing studies on the steam reforming of methanol, and the dehydrogenation of 2-propanol. However, some alloys show unique properties depending on the elemental set, like the Co2TiSb for CO oxidation, which showed high oxidation resistance. Therefore, we believe that there is great promise in using Heusler alloys for various reactions.

5.2. Beyond our studies

Materials informatics could be relevant when seeking effective Heusler catalysts [28]. This method usually requires a large number of data sets, especially in the application of catalysts where the properties vary strongly depending on experimental processing conditions [29]. Heusler alloys are a well-defined platform where the components and compositions can be changed without structural change. This would decrease the number of descriptors, reducing data sets required. Recently, predictions using materials informatics from only several tens to hundreds of data sets were achieved even for catalysts [30]. Thus, effective Heusler catalysts could be found using the informatic approach with catalytic experiments under the same reaction conditions.

There have only been a few studies on Heusler catalysts, since their potential was only recently discovered. However, certain researchers have considered the application of catalysts as mentioned in Section 4, and we succeeded in spotlighting the potential of Heusler alloy catalysts. Thus, more researchers will start to study Heusler catalysts. For practical applications, the patent seems to have not succeeded in developing ‘good Heusler catalysts’ because the L2 phase single phase and a small average particle size (e.g. < 50 nm) with the sharp size distribution were not obtained, and because the properties were not compared to those of practical catalysts.

On the other hand, a certain number of groups have tried to prepare Heusler nanoparticles, however, not for catalytic application. The studies published before 2014 were summarized in the review paper by Felser’s group [31]. L21-Co2FeGa nanoparticles with an average particle size of around 20 nm were successfully synthesized on fumed silica supports by impregnation, although a relatively small amount of extra phases existed in addition to the L2 phase [32–35]. The synthesis was also achieved by impregnation into facile carbon nanotubes [36]. The synthesis of L21-Co2FeAl nanoparticles was also reported [37,38]. In addition, Fe2CoGa nanoparticles were synthesized, while the structure was Li2AgSb or Hg2CuTi type, the so-called ‘inverse Heusler’ (Figure 3(f)) [39]. To our knowledge, for other L21-Heusler nanoparticles, the size was not small enough, or there was not sufficient information on the size distribution or no proof of the L21 phase, like Co2FeSn [40] and Ni2MnIn [41].

There are still only a few reports of successful, high-quality preparation of Heusler nanoparticles. However, this seems to reflect a scarcity of attempts at synthesis, because the applications have been considered limited. Now, we have a big application for catalysts. Therefore, we believe that many researchers will start developing a variety of Heusler nanoparticles as catalysts.

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Disclosure statement

The authors are inventors on a patent application related to this work filed by Tohoku University (JP patent application no. 2017–220616, filed on 16 November 2017).
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