Screening of Ternary Intermetallic Catalysts Is Possible Using Metallurgical Synthesis: Demonstration on Heusler Alloys

Takayuki Kojima¹,², Satoshi Kameoka² and An-Pang Tsai²#
¹ Frontier Research Institute for Interdisciplinary Sciences (FRIS), Tohoku University, Japan
² Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Japan

Abstract
Intermetallic compounds are becoming hot materials as catalysts because they show unique catalytic properties that originate from a unique electronic structure and an atomic ordered surface. Ternary intermetallic catalysts have rarely been reported, which is likely due to the difficulty in synthesizing their supported nanoparticles, the typical form for catalysis research; however, there could be novel catalysts in ternary systems because they have much more elemental combinations than binary systems. They are expected to exhibit novel properties due to the synergy between three elements. Metallurgical methods, such as arc-melting, can easily synthesize intermetallic compounds even in ternary (or more) systems if they are thermodynamically stable. Thus, only metallurgical synthesis enables screening for ternary intermetallic catalysts. The catalyst screening of Heusler alloys, which are a group of ternary intermetallic compounds popular in other research fields, such as magnetics, has been conducted using metallurgical synthesis. The screening revealed fundamental catalytic properties of Heusler alloys for several reactions and identified good catalysts for the selective hydrogenation of alkynes. The systematic control of catalysis was also demonstrated by the substitution of fourth elements using a feature of Heusler alloys. This paper describes the importance of ternary intermetallic catalysts with practical examples of Heusler alloy catalysts and discusses future prospects.

Keywords: intermetallic catalyst, Heusler catalyst, intermetallic compound catalyst, Heusler alloy catalyst, ternary intermetallic compound, Heusler alloy

1. Introduction

A “catalyst” is defined as a material that promotes a chemical reaction but is not consumed and not irreversibly modified during the reaction. The mechanism of reaction promotion occurs when a reaction pathway changes into another pathway with a lower activation barrier, as illustrated in Fig. 1. The change in the pathway sometimes changes the product species, as shown in Fig. 1(b,c). Thus, catalysts are necessary to make a massive amount of products with a lower energy cost and fewer waste materials (unfavorable byproducts) and to remove harmful species. A chemical reaction, including elementary steps of a catalytic reaction, proceeds through an exchange of electrons. Therefore, an electronic structure of catalysts dominates a catalytic reaction. Obviously, a surface is also important for solid-state catalysts because the reaction proceeds on the surface.

Intermetallic compounds have a unique electronic structure completely different from a mixed state of component metals (Tsai A.P. et al., 2004; 2017) and have an atomic ordered structure even at the surface (Furukawa S. and Komatsu T., 2017). Thus, they are becoming hot materials for catalytic applications (Armbrüster M., 2014; Tsai A.P. et al., 2017; Furukawa S. and Komatsu T., 2017). Although almost all reports on intermetallic catalysts have discussed binary systems, there could be novel catalysts in ternary systems because there are much more potential elemental sets: 85,320 ternary and 3,240 binary compounds have been validated according to Dshemuchadse J. and Steurer W. (2015). Ternary intermetallic catalysts are also expected to exhibit novel properties due to the synergy between three elements. Catalyst research is mostly conducted by chemists, typically using nanoparticles supported by oxide fine particles; however, the synthesis of ternary intermetallic nanoparticles requires considerable efforts to identify the appropriate conditions.
The use of nanoparticles is impossible for the screening of ternary intermetallic catalysts with changing component elements. This is the reason for the lack of studies on ternary systems.

On the other hand, metallurgical methods, such as arc-melting, can easily synthesize most intermetallic compounds even in ternary (or more) systems if they are thermodynamically stable. Intermetallic compounds are usually brittle, being easily crushed into powder. Thus, the screening of ternary intermetallic catalysts is possible. We have investigated Heusler alloys as new catalysts using metallurgically synthesized samples (Kojima T. et al., 2017, 2018, 2019a, 2019b). Heusler alloys are a group of ternary intermetallic compounds described as \( X_2YZ \) with \( L_21 \) structure (body-centered cubic basis, called “full-Heusler” in a narrow sense), as shown in Fig. 2 (Kojima T. et al., 2018) (there are also other types, including \( XYZ \) with \( C1b \) structure, which lacks one of two \( X \) sites in the \( L_21 \) structure, called “half-Heusler”) (Kojima T. et al., 2019a). They are popular as magnetic (spintronic) (Graf T. et al., 2016), thermoelectric (Nishino Y. et al., 2001), and shape memory materials (Planes A. et al., 2009), and they have been studied as topological materials nowadays (Manna et al., 2018). Although their catalytic properties were unknown, we hypothesized that there are novel catalysts in the numerous elemental sets (Fig. 2). The abundant choice of elements also enables the substitution of various elements in a wide composition range (e.g. \( X_2YZ' \)), by which electronic structures can be fine-tuned. This tuning is a common practice in the aforementioned fields but is also applicable for the precise control of catalytic properties (called the ligand effect, Fig. 2). Obviously, the fourth element substitution changes the type of surface element, by which catalytic properties can be controlled (called the ensemble effect, Fig. 2). Considering these advantages of Heusler alloys, we have conducted the screening for various reactions to reveal their fundamental catalytic properties and to identify novel catalysts.

2. Sample preparation and characterization

Heusler alloy \( (X=\text{Fe, Co, Ni, or Cu}; \, Y=\text{Ti, Mn, or Fe}; \, Z=\text{Al, Si, Ga, Ge, or Sn}) \) ingots were prepared from pure metal pieces (purity: > 99.9 %) by arc-melting and were annealed in Ar atmosphere. For the annealing, the ingot was put on (into) an alumina piece (tube) or wrapped by a Ta or Mo foil in a quartz tube that was then sealed using a hydrogen gas burner after a cycle of evacuation and Ar purge. Although an annealing condition depends on alloys, we currently adopt 1000 \( ^\circ \text{C} \) for homogenizing followed by 600 \( ^\circ \text{C} \) for atomic ordering in many cases. The condition for each sample used in previous works has been described in Kojima T. et al. (2017) and (2018). The ingot was crushed using a pestle and mortar into powder that was then sieved to 20–63 \( \mu \text{m} \) for a catalytic reaction and < 20 \( \mu \text{m} \) for a structural evaluation using X-ray diffraction (XRD).

Before the XRD, a sample powder was annealed at 600 \( ^\circ \text{C} \) for 1 h to remove the strain. The XRD revealed that all the samples used in the published works (Kojima T. et al., 2017, 2018, 2019a, 2019b) were single-phase, as shown in Fig. 3. The XRD patterns were simulated by a peak fitting program, and the crystal structure was confirmed to be \( L_21 \) type.
Some Heusler alloys disorder their atomic arrangements by heating, transforming the phase from L2₁ to B2 (disordering between Y and Z atoms) followed by A2 (disordering between all atoms), which is referred to as “ordered alloys” rather than “intermetallic compounds” (Kojima T. et al., 2019a). Thus, a degree of ordering should be evaluated. A long-range order parameter is typically used for the evaluation, which is estimated from an XRD intensity ratio of a superlattice and fundamental peaks (Warren B.E., 1990). Webster’s model using parameters of $S$ and $\alpha$ is easily usable for Heusler alloys, where a high $S$ means a high ordering of $X$ atoms and a low $\alpha$ means a high ordering of $Y$ and $Z$ atoms (Webster P.J. and Ziebeck K.R.A., 1973). All the samples had high $S$ and low $\alpha$ (Kojima T. et al., 2017). Note that the superlattice peaks, such as 111 and 200 peaks, are essentially weak when the atomic numbers of the components are close, such as Co₂FeGe (Fig. 3), because an intensity in the superlattice peaks is proportional to the square of the difference of the atomic numbers.

A specific surface area of catalysts was estimated using the Brunauer-Emmett-Teller method for Kr adsorption isotherms at 77 K, which is a typical method for surface area estimation. Although the values per weight distributed from 0.047 to 0.13 m²·g⁻¹ depending on atomic weights, the values per volume were similar (4.0–8.3 × 10⁵ m⁻¹) due to the sieving into 20–63 μm, as shown in Table 1.

Catalytic tests were conducted using a flow reactor, as shown in Fig. 4. An appropriate amount of catalyst powders was set on quartz wool in a quartz tube. Before the reactions, the catalyst was heated at 600 °C for 1 h under H₂ gas flow to remove surface oxides and strain. A gaseous reactant was introduced from a mass flow controller with an inert carrier gas. A liquidous reactant was introduced using a plunger pump with the carrier gas, followed by evaporated using an electric furnace surrounding the quartz tube so that the reaction took place in the gas phase. Unreacted and produced gaseous species and their concentrations were analyzed using a gas chromatograph. When the amount of gas products was large (e.g. > 10 % of carrier gas), a flow meter was used for analysis along with

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area per weight [10⁻² m²·g⁻¹]</th>
<th>Surface area per volume [10⁵ m⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂TiSn</td>
<td>7.1</td>
<td>6.0</td>
</tr>
<tr>
<td>Co₂TiAl</td>
<td>11</td>
<td>7.3</td>
</tr>
<tr>
<td>Co₂TiGe</td>
<td>8.4</td>
<td>6.8</td>
</tr>
<tr>
<td>Co₂TiSn</td>
<td>7.0</td>
<td>5.9</td>
</tr>
<tr>
<td>Co₂MnSi</td>
<td>8.8</td>
<td>6.5</td>
</tr>
<tr>
<td>Co₂MnGa</td>
<td>6.1</td>
<td>5.1</td>
</tr>
<tr>
<td>Co₂MnGe</td>
<td>6.7</td>
<td>5.7</td>
</tr>
<tr>
<td>Co₂MnSn</td>
<td>5.6</td>
<td>5.1</td>
</tr>
<tr>
<td>Co₂FeGa</td>
<td>4.7</td>
<td>4.0</td>
</tr>
<tr>
<td>Co₂FeGe</td>
<td>5.4</td>
<td>4.7</td>
</tr>
<tr>
<td>Ni₂TiAl</td>
<td>13</td>
<td>8.3</td>
</tr>
<tr>
<td>Ni₂TiSn</td>
<td>9.5</td>
<td>7.9</td>
</tr>
<tr>
<td>Ni₂MnSn</td>
<td>8.9</td>
<td>7.7</td>
</tr>
<tr>
<td>Cu₂TiAl</td>
<td>12</td>
<td>7.4</td>
</tr>
</tbody>
</table>

![Fig. 3](image) XRD patterns for Ni₂TiAl (red) and Co₂FeGe (blue) powders. Intensity was normalized by the height of a 220 peak. Co₂FeGe showed a peak of a second phase, which was likely CoGe.

![Fig. 4](image) Schematic illustration of a catalytic reaction system. The illustration is highly simplified.
3. Oxidation of carbon monoxide

As a simple oxidation reaction, the oxidation of carbon monoxide (CO + 1/2O\textsubscript{2} → CO\textsubscript{2}) was conducted (Kojima et al., 2017), which is an important reaction for removal of harmful CO gas produced from combustors, including automobile engines. Co-based Heusler alloys showed higher activity than other alloys, as shown in Fig. 5 (higher activity means higher conversion (reaction rate) at lower temperature). A hierarchy of activity of X in X\textsubscript{2}TiSn, X\textsubscript{2}TiAl, and X\textsubscript{2}MnSn seemed roughly similar to that of pure Fe, Co, Ni, and Cu powders. This indicates that a main active element in Heusler alloys is X for CO oxidation. During a cycle of heating and cooling, the hysteresis of the activity was observed in most alloys, as shown in Fig. 6(a,b). This was due to the irreversible oxidation of catalysts, which was indicated by the excess consumption of O\textsubscript{2}; however, Co\textsubscript{2}TiSn showed very small hysteresis, as shown in Fig. 6(c) due to high resistivity to oxidation. These results indicate that not only activity but also durability can be controlled by choosing the appropriate X, Y, and Z.

4. Hydrogenation of alkynes

4.1 Catalytic properties

As a simple reduction reaction, the hydrogenation of alkynes (C\textsubscript{n}H\textsubscript{2n−2} + aH\textsubscript{2} → bC\textsubscript{n}H\textsubscript{2n} + (a−b)/2C\textsubscript{n}H\textsubscript{2n+2}) was conducted (Kojima et al., 2017, 2018); such hydrogenation of hydrocarbons is important in various fields, including petrochemical industry. For propyne (C\textsubscript{3}H\textsubscript{4}) hydrogenation, most Heusler alloys showed very low activity (Kojima et al., 2017). This is likely due to the residual surface oxides of Al, Si, and Ti and due to the surface segregation of Sn. Co\textsubscript{2}(Mn or Fe)(Ga or Ge) alloys were active. Interestingly, Co\textsubscript{2}MnGe and Co\textsubscript{2}FeGe showed high alkene selectivity (fraction of alkene in products: C\textsubscript{n}H\textsubscript{2n}/(C\textsubscript{n}H\textsubscript{2n}+C\textsubscript{n}H\textsubscript{2n+2})) (Kojima et al., 2018). Fig. 7 shows alkyn e conversion (percentage of reacted alkyn e) and alkene selectivity during the hydrogenation of alkynes (C\textsubscript{3}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{2}) in the presence of...
A large amount of alkenes (C$_3$H$_6$, C$_2$H$_4$). In general, alkene selectivity decreases with an increase in alkyne conversion as Co$_2$FeGa (Fig. 7c1,c2), which is due to the promotion of alkene adsorption along with the consumption of strongly adsorbed alkyne molecules. In contrast, Co$_2$MnGe and Co$_2$FeGe kept high selectivity even when the conversion was high enough (Fig. 7a1–b2).

Fig. 7 Alkyne conversion and alkene selectivity in the reaction using the reactant of (a1,b1,c1) [0.1% C$_3$H$_4$ / 10% C$_2$H$_2$ / 40% H$_2$ / 49.9% He] or (a2,b2,c2) [0.1% C$_3$H$_4$ / 10% C$_2$H$_2$ / 40% H$_2$ / 49.9% He] for (a1,a2) Co$_2$MnGe, (b1,b2) Co$_2$FeGe, and (c1,c2) Co$_2$FeGa. After Ref. (Kojima et al., 2018) licensed under CC BY-NC (http://creativecommons.org/licenses/by-nc/4.0).

The selective hydrogenation of alkenes in alkene feedstocks is a crucial process to remove alkyne impurities that hinder the polymerization of alkenes in the process to produce polyalkenes, such as polyethylene (Borodziński A. and Bond G.C., 2006, 2008). In industry, the selective hydrogenation is achieved by the precise control of reaction conditions, including temperature, pressure, H$_2$ concentration, and the introduction of CO gas as an inhibitor because Pd-based practical catalysts do not have essential selectivity. Therefore, these Heusler alloy catalysts would be useful in terms of replacing noble metals.

4.2 Elemental substitution effects

The effects of elemental substitution were investigated for C$_3$H$_4$ hydrogenation using Co$_2$FeGa$_{0.75}$Ge$_{0.25}$ catalysts (Kojima et al., 2018). Fig. 9 shows the results of the Mn and Ga substitutions for Fe and Ge, respectively, of Co$_2$FeGe. The reaction rate and the selectivity systematically changed with the amount of the substitution (Fig. 9a). The Mn substitution increased the reaction rate while maintaining high selectivity. The Ga substitution significantly increased the reaction rate but decreased selectivity. An experimental apparent activation energy ($E_a$)
change of a $d$ band center ($\varepsilon_d$) calculated for bulk states (Fig. 9b). $\varepsilon_d$ means an average energy of $d$ states, dominating a strength between adsorbates and metals; that is, higher (lower) $\varepsilon_d$ makes higher (lower) energy levels of the adsorbates, resulting in lower (higher) occupation of anti-bonding states. Thus, $\varepsilon_d$ affects relevant energy quantities in elementary steps, such as adsorption energy and activation energy (Nørskov J.K, et al, 2011). The good correlation between $E_a$ and $\varepsilon_d$ in Fig. 9(b) proves that the electronic modification by elemental substitution certainly affected the elementary steps. Actually, the fine modification of electronic structures was achieved in good accordance with the calculated results, which was indicated by photoelectron spectroscopy and first-principles calculation, as shown in Fig. 10. These results indicate that a precise control of catalytic properties through the fine-tuning of electronic structures is possible by elemental substitution of Heusler alloys.

As a result of further experiments and analyses, including the estimation of reaction orders and the deduction of reaction mechanisms, the Mn and Ga substitution effects were concluded to be mainly ligand and ensemble effects (Fig. 2), respectively (Kojima et al, 2018). In other words, Mn substitution changes catalysis through the modification of the whole electronic structure, while Ga substitution changes catalysis through the replacement of surface Ge atoms by Ga atoms that have a greater ability to adsorb molecules. In addition, Mn-Fe substitution and Ga-Ge substitution affect catalysis independently. For example, Mn substitution for Co$_2$FeGa caused a similar change in catalysis to that for Co$_2$FeGe, while Ga substitution for Co$_2$MnGe caused a similar change in catalysis to that for Co$_2$FeGe (Kojima et al, 2018). Therefore, the fine-tuning of catalysis is possible depending on the target reaction by (1) choosing a main active element $X$ and sub-elements $Y$ and $Z$, (2) substituting $Y$ to optimize electronic structures, (3) and substituting $Z$ to optimize surface ensembles. Furthermore, this precise controllability would be useful to reveal a general relation between electronic structures and catalysis, which are only partially understood thus far.

5. Steam reforming of methanol

The steam reforming of methanol (SRM: CH$_3$OH + H$_2$O →3H$_2$ + CO$_2$) is a candidate to produce hydrogen from a safe hydrogen carrier, which is often studied using intermetallic catalysts (Tsai A.P, et al, 2004, 2017; Armbrüster M. et al., 2014; Furukawa S. and Komatsu T., 2017). As another type of reaction different from those mentioned above, SRM was used to investigate Heusler alloy catalysts (Kojima et al., 2019b). Among the 14 Heusler alloys listed in Table 1, most alloys did not produce H$_2$ at a low temperature of ≤ 450 °C, as shown in Fig. 11(a–d). Several alloys did not produce H$_2$ even at 600 °C, as shown in Fig. 11(e). Surface microstructural changes, such as the formation of fine particles, were observed in most alloys that showed a certain activity, as shown in Fig. 12(a–d). In many catalysts consisting of group 8–10 metals, the first step of SRM is the decomposition of methanol (CH$_3$OH →2H$_2$ + CO) (Sá S. et al., 2010). This reaction is structure sensitive; that is, larger particles show a lower reaction rate per surface area. Thus, the diameter of 20–63 μm was likely too large, while the precipitation of fine particles yielded activity.

In particular, Ni$_5$TiAl exhibited high activity due to the formation of Ni fine particles, as shown in Fig. 13(a,b). A higher activity at 400 °C during cooling than heating implies fine particle precipitation at ≥ 450 °C (Fig. 13a). A Ni$_5$Al catalyst is known to precipitate Ni fine particles during methanol decomposition through the selective oxidation of Al (Chun et al., 2006). On the other hand, Ni$_5$TiAl likely precipitates Ni fine particles through the selective oxidation of Ti, as shown in Table 2. Co$_2$TiAl showed a similar change in catalytic properties along with fine particle precipitation (Kojima et al., 2019b). In contrast, Cu$_4$TiAl did not form Cu fine particles as indicated by the decrease in the surface Cu composition after the reaction.
Fig. 11  Production rates of \( \text{H}_2 \) and byproducts (CO, CO\(_2\), CH\(_4\)) in the reaction using a reactant mixture of CH\(_3\)OH and H\(_2\)O (molar ratio 2:3) fed at 0.07 g min\(^{-1}\) corresponding to 20 \( \mu \text{mol s}^{-1} \) of CH\(_3\)OH. After Ref. (Kojima T. et al., 2019b), reproduced with permission by ACS (https://pubs.acs.org/doi/abs/10.1021/acsomega.9b01837). Further permissions related to the material excerpted should be directed to the ACS.

Fig. 12  Surface microstructures after the SRM reaction observed by scanning electron microscopy for (a) Co\(_2\)MnSn, (b) Ni\(_2\)MnSn, (c) Co\(_2\)TiSn, and (d) Ni\(_2\)TiSn.
Table 2. Surface composition [%] of X, Y, and Z in X_2YZ before and after SRM reaction analyzed by X-ray photoelectron spectroscopy.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni_2TiAl</td>
<td>Before</td>
<td>8</td>
<td>19</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>13</td>
<td>36</td>
<td>51</td>
</tr>
<tr>
<td>Co_2TiAl</td>
<td>Before</td>
<td>13</td>
<td>19</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>23</td>
<td>46</td>
<td>31</td>
</tr>
<tr>
<td>Cu_2TiAl</td>
<td>Before</td>
<td>13</td>
<td>11</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>4</td>
<td>41</td>
<td>56</td>
</tr>
</tbody>
</table>

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Table 3. Standard Gibbs energy of oxide formation (ΔG°) [kJ (O_2 mol⁻¹)] at 400 °C.

<table>
<thead>
<tr>
<th>Element</th>
<th>Oxide</th>
<th>ΔG°</th>
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<tbody>
<tr>
<td>Fe</td>
<td>Fe_3O_4</td>
<td>–444</td>
</tr>
<tr>
<td>Co</td>
<td>CoO</td>
<td>–373</td>
</tr>
<tr>
<td>Ni</td>
<td>NiO</td>
<td>–355</td>
</tr>
<tr>
<td>Cu</td>
<td>Cu_2O</td>
<td>–239</td>
</tr>
<tr>
<td>Ti</td>
<td>TiO_2 (rutile)</td>
<td>–821</td>
</tr>
<tr>
<td>Mn</td>
<td>MnO</td>
<td>–665</td>
</tr>
<tr>
<td>Al</td>
<td>Al_2O_3 (α)</td>
<td>–976</td>
</tr>
<tr>
<td>Sn</td>
<td>SnO_2</td>
<td>–442</td>
</tr>
</tbody>
</table>

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(Table 2), thus not gaining activity. Standard Gibbs energies of oxide formation (ΔG°) are similar between Co and Ni but fairly different between them and Cu, as shown in Table 3. This is likely the reason for the difference in the structural change. Co_2MnSn and Ni_2MnSn showed similar structural changes (Fig. 11a,b) (Kojima et al., 2019b). Co_2TiSn and Ni_2TiSn also showed similar structural changes (Fig. 11c,d), but Fe_2TiSn showed a different change, likely due to the difference of ΔG° between Co, Ni, and Fe (Kojima et al., 2019b). These results indicate that the tendency of structural changes through oxidation is determined by a balance of the oxidizability of components. The activity of Ni_2TiAl was enhanced by preheating under [1 %O_2/99 %He] flow at 500 °C for 1 h before the reaction due to the enhancement of the Ni fine particle precipitation, as shown in Fig. 13(c,d). Co_2TiAl showed similar results by O_2 preheating (Kojima et al., 2019b).

Many alloys mainly produced CO as a byproduct, meaning that methanol decomposition predominantly occurred.

In contrast, all the alloys containing Mn mainly produced CO_2 as a byproduct (Fig. 11a,b). During the reaction, all these alloys formed MnO (Kojima et al., 2019b), which catalyzes a water-gas shift reaction (CO + H_2O→H_2 + CO_2), eventually achieving SRM by converting CO that was produced by methanol decomposition. This study revealed a variety of structural changes through oxidation, which suggests a development of multi-functional catalysts consisting of several phases using Heusler alloys as a...
precursor. Intermetallic compounds are atomically homogeneous in essence, even in ternary systems. This is an advantage of being used as a precursor of catalysts with less inhomogeneity.

Co$_2$FeGe was active for methanol decomposition using a pure methanol reactant without steam, as shown in Fig. 14. Interestingly, the initial metallic state was likely active because a certain activity appeared even at ≤ 400 °C and because a significant structural change was not observed after the reaction at 600 °C (Kojima et al., 2019b). A specific electronic structure or a specific reaction field created by atomic ordered structures might be suited to this reaction. The origin of the activity is attractive to be studied.

6. Perspectives

For other reactions, we are currently investigating the dehydrogenation of 2-propanol and the methanation of carbon monoxide. Screening for the dehydrogenation of methylocyclohexane (MCH) and its reverse reaction, the hydrogenation of toluene, was also conducted; however, no activity was observed in the tested alloys. These molecules, which have a six-membered ring, are highly stable, and most studies on MCH dehydrogenation have used Pt-based nanoparticles (Nakano A. et al., 2017). Thus, the diameter of 20–63 μm (surface area: ca. 0.1 m$^2$·g$^{-1}$) was considered too large to exhibit activity. Aside from an extreme case, such as MCH dehydrogenation, even ammonia synthesis, which must break a very stable triple bond of N$_2$, can be attractive for intermetallic nanoparticles.

Interestingly, the initial metallic state was likely active because a certain activity appeared even at ≤ 400 °C and because a significant structural change was not observed after the reaction at 600 °C (Kojima et al., 2019b). A specific electronic structure or a specific reaction field created by atomic ordered structures might be suited to this reaction. The origin of the activity is attractive to be studied.

Aside from our studies, there are few early studies on Heusler alloy catalysts: the theoretical calculation for ammonia dissociation by Ni$_2$MnGa and Co$_2$CrGe (Senanayake N.M., 2016) and the screening of supported Heusler alloy catalysts (Mueller U. et al., 2018). BASF did not obtain a sufficient quality of samples in the latter study but then succeeded in the development of the aforementioned Cu$_2$NiSn nanoparticles (Ernst S. et al., 2019). Recently, experimental studies have been conducted on methanol synthesis using Ni$_2$FeGa (Smitshuysen T.E.L., et al., 2020) and on ammonia dissociation using Co$_2$CrGe (Chao H. et al., 2019). For other ternary intermetallic catalysts, aforementioned RTX (R: rare earth, T: transition metal, X: p-block element) compounds (LaCoSi, LaRuSi) have been recently reported on ammonia synthesis, which were prepared by arc-melting (Gong Y. et al., 2018; Wu J. et al., 2019). In these catalysts, the property as an electride, the ability for hydrogen storage, and an electron transfer from La to active elements (Co, Ru) play key roles. Thus, ternary systems exhibit novel catalytic properties that are not realized in binary systems. The screening of ternary intermetallic catalysts would be accelerated for the potential discovery and development of novel catalysts.
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References


Borodziński A., Bond G.C., Selective hydrogenation of ethyne in ethene-rich streams on palladium catalysts. part 1. effect of changes to the catalyst during reaction, Catalysis Reviews, 48 (2006) 91–144. DOI: 10.1080/01614940500364909


Furukawa S., Komatsu T., Intermetallic compounds: Promising inorganic materials for well-structured and electronically modified reaction environments for efficient catalysis, ACS Catalysis, 7 (2017) 735–765. DOI: 10.1021/acscatal.6b02603


Kojima T., Kameoka S., Tsai A.P., Heusler alloys: a group of novel catalysts, ACS Omega, 2 (2017) 147–153. DOI: 10.1021/acsomega.6b00299


Kojima T., Kameoka S., Tsai A.P., Catalytic properties of Heusler alloys for steam reforming of methanol, ACS Omega, 4 (2019b) 21666–21674. DOI: 10.1021/acsof.9b01837


Nørskov J.K., Abild-Pedersen F., Studt F., Bligaard T., Density functional theory in surface chemistry and catalysis, Pro-


Senanayake N.M., Exploring Heusler alloys as catalysts for ammonia dissociation, master’s thesis for Bowling Green State University, USA (2016).


Authors’ Short Biographies

Takayuki Kojima

Dr. Kojima majored in materials science during his student career (2001–2006: Kurume National College of Technology; 2006–2013: Tohoku University for bachelor, master, doctoral). He researched magnetic material thin-films when he was a graduate student. He then came up with the idea of using Heusler alloys as catalysts, which are popular as magnetic materials, inspired by Prof. A.P. Tsai’s lecture on “like electronic structure, like catalysis”, and began conducting catalytic studies in Tsai’s group in 2014. He is currently researching catalysts and functional materials, including magnetic materials, through an interdisciplinary approach as an Assistant Professor of FRIS.
Authors' Short Biographies

Satoshi Kameoka

Dr. Kameoka is an Associate Professor at the Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University. He received his PhD from University of Tsukuba in 1996. In 2004, he moved to IMRAM as a Research Associate. His research interests are catalysis by metals and alloys. He has performed collaborative research with Prof. Tsai and Dr. Kojima in studies on the metallurgy for advanced catalysis materials since 2002 and 2014, respectively.

An-Pang Tsai

Dr. Tsai was an outstanding researcher who is well-known for the first discoveries of a stable quasicrystal and a binary quasicrystal. Most quasicrystals were discovered by him. He received his PhD from Tohoku University and many honors, including the Medal of Honor with Purple Ribbon (Japan), and was elected as a member of Academia Sinica (Taiwan). He became a Professor of IMRAM in 2004 after working at the Institute for Materials Research of Tohoku University and the National Institute for Materials Science (NIMS). He began research on catalysis from a metallurgical viewpoint about 20 years ago. He passed away on May 25, 2019 (age 60).