[Review Paper]

Selective Hydrogenation Catalyzed by Intermetallic Compounds

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Catalytic properties of intermetallic compounds for hydrogenation reactions are reviewed focusing on the differences in selectivity compared with monometallic catalysts. Intermetallic compound catalysts were prepared to form single phase particles of the target compound to clarify the specific catalytic properties. Pt3Ti showed higher activity than Pt for H₂ activation and ethylene hydrogenation. Various intermetallic compounds were found to be more selective than monometallic catalysts for the partial hydrogenation of alkyne into alkene. RhBi showed regioselectivity for the terminal C=CH₂ hydrogenation of trans-1,4-hexadiene. Combination of Pd₃Bi and RhSh gave trans-stilbene in the hydrogenation of diphenylacetylene through partial hydrogenation into cis-stilbene on Pd₃Bi and subsequent isomerization on RhSh. RhPb₂ exhibited higher activity and selectivity than Rh for the chemoselective hydrogenation of p-nitrostyrene into p-aminostyrene. The higher selectivity of intermetallic compounds than monometals is discussed based on their unique atom arrangement on the surface of intermetallic compounds originating from their regular crystal structures.

Keywords
Intermetallic compound, Selective hydrogenation, Rhodium, Palladium, Stilbene, Nitrostyrene

1. Introduction

Intermetallic compound (IMC) is classified as a specific type of alloy. Normal alloy consists of a solid solution between two metal elements, X and Y, where X and Y have similar characteristics such as neighboring elements in the periodic table. In contrast, IMC consists of two elements, X and Z, with significantly different characteristics, XnZm, in which n and m are usually small integers, typically 1, 2, and 3. The most characteristic difference of IMCs from normal alloys is the periodic regularity in atom alignment. In the solid solution of a normal alloy, Y atoms replace a significant portion of X atoms in a random arrangement (Fig. 1(a)), retaining the crystal structure of X. In IMCs, X and Z atoms usually form a new crystal structure, where the X and Z atoms are located in a regular arrangement (Fig. 1(b)).

Catalysis by solid materials is governed by the electronic and geometric structures of the active sites on the surface. Figure 2 illustrates the two-dimensional image of model alloy surfaces. On the solid solution alloy (a), islands will be formed through the accumulation of metal atoms of one component. Inside the X island, X atoms occur with no contact with Y atoms. On IMCs (b), every X atom has contacts with Z atoms. Therefore, the electronic structure of X atoms on IMCs will be greatly affected by the neighboring Z atoms compared with X atoms in the island of the normal alloy. In addition, the effect of the Z atoms would be almost equal on every X atom in the same plane. The random atomic alignment of the normal alloy does not create specific active sites homogeneously distributed on the surface, whereas active sites with uniform and homogeneous geometry will be occur in the IMC based on the specific crystal structure. Such structures never

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occur in normal alloys or in pure metals. Therefore, IMCs are great potential as highly active, selective and stable catalysts for specific reactions because of their unique electronic and geometric structures.

IMC phases have often been reported in bi-metallic catalysts. However, several phases co-existed on supports in most cases, such as pure metals, solid solution alloys, and pure and binary metal oxides, as well as IMCs with different compositions. Consequently, identification of the active species was uncertain. We previously studied unsupported and supported IMC particles consisting of pure IMC phase to clarify the catalytic properties of IMCs. We previously studied unsupported and supported IMC particles consisting of pure IMC phase to clarify the catalytic properties of IMCs. IMCs with specific compositions were prepared, and confirmed the phase purity by powder X-ray diffraction (XRD) before using the IMC in catalytic reactions.

This review describes catalysis by IMCs with a focus on reaction systems in which IMCs exhibited high catalytic activity and/or selectivity compared with pure metal particles.

2. Preparation of IMC Catalysts

2.1. Unsupported Catalyst

Unsupported IMC catalysts were prepared by arc melting a stoichiometric mixture of the component metals under argon atmosphere. The resultant ingot was crushed or ground in air and filtered into particles with diameters below 25 μm. The formation of the specific IMC as a single-phase crystal was confirmed by XRD.

2.2. Supported Catalyst

Unsupported ground particles of IMC had specific surface area smaller than 1 m² g⁻¹, which is too small for industrial application as well as basic research investigations such as adsorption measurement. Therefore, fine particles of IMCs were formed on the surface of silica gel (Cariact G6, Fuji Silysia). Support materials should be catalytically inert with appropriate interaction with metal species. Strong interaction will prevent metal species from dispersing on the surface to contact with other metal species to form the IMC. Weak interaction will form larger particles. We assigned the highest priority to obtain single-phase IMCs, so silica with weak interaction with metal species was used as the support.

To obtain an IMC with a specific composition, impregnation, liquid phase reduction, and chemical vapor deposition (CVD) were tried. In most cases, the impregnation procedure with pore-filling technique provided the single-phase IMC with the desired composition. XRD patterns of Pt-based IMCs prepared by impregnation showed diffraction peaks at different positions from those of Pt/SiO₂ (broken lines). Comparison with International Centre for Diffraction Data (ICDD) database and calculation using Scherer’s equation indicated particles with 4-8 nm diameter were obtained as almost single-phase IMC particles. Figure 4(a) shows the high resolution transmission electron microscopy (HR-TEM) image of Pd-Zn bimetallic particles supported on SiO₂ prepared by the impregnation procedure. Lattice fringes corresponding to (010) planes were clearly observed. The particle size distribution shown in Figure 4(b) shows the average particle diameter was 3.0 nm.
If impregnation resulted in a mixture of the desired IMC and undesirable phases, the other procedures were applied to obtain a single phase compound. For example, PtCu/Al₂O₃ was prepared by liquid phase reduction⁷. Pt(NH₃)₄(CH₃COO)₂ and Cu(acac)₂ dissolved in 2-propanol and γ-alumina were put into a flask. 2-Propanol containing NaBH₄ was added to the flask with agitation at 353 K. Metallic particles appeared immediately. The XRD pattern of the prepared catalyst showed the diffraction peaks of PtCu IMC.

Ni₃Sn/SiO₂ was prepared by the CVD method using Ni/SiO₂ and Sn(CH₃)₄⁸. Ni/SiO₂ was put in a flow reactor and dehydrated in helium flow. Then Sn(CH₃)₄ vapor was introduced with H₂ flow at a specific temperature and duration. Hydrogenolysis of Sn(CH₃)₄ was catalyzed by Ni particles on silica, resulting in deposition of Sn₀ and formation of methane predominantly on the Ni particles. Ni₃Sn particles were obtained after H₂ treatment at high temperature. The predominance of tin deposition on Ni was supported by Figure 5, where the same CVD procedure using silica instead of Ni/SiO₂ produced only a small amount of tin below ca. 500 K. Figure 5 further indicates that the amounts of tin deposited at 423, 448 and 498 K corresponded to the stoichiometry of Ni₃Sn, Ni₃Sn₂ and Ni₃Sn₄, respectively. Formation of these IMCs was confirmed by XRD. RuTi/SiO₂⁹ and PdFe/SiO₂¹⁰ were also obtained by the CVD procedure.

3. Hydrogenation Catalyzed by IMCs

3.1. Hydrogen Activation

Catalytic activities of IMCs for H₂-D₂ equilibration were studied to assess the activity of IMCs for the activation and dissociative adsorption of hydrogen molecules. Unsupported IMCs containing Pt and Ti were first evaluated¹¹. Pt₃Ti, Pt₃Ti and PtTi₃ are listed in the phase diagram, but PtTi was hard to prepare as a single-phase IMC. Pt₃Ti and PtTi₃ showed activity for HD formation only after pretreatment in atmospheric hydrogen flow at 873 K or higher, whereas Pt powder was active after hydrogen treatment at 573 K. White bars in Fig. 6 show the relative activity for HD formation based on the activity of pure Pt as unity. Clearly both IMCs exhibited much higher activity than Pt. We expected that both IMCs would also be more active than Pt for the hydrogenation of alkenes. Dark bars in Fig. 6 show the relative activity for ethylene hydrogenation. Pt₃Ti had higher activity than Pt as expected, but PtTi₃ was found to be inactive under the reaction conditions.

To clarify the reason for this considerable difference between Pt₃Ti and PtTi₃, hydrogenation of ethylene was carried out with a mixture of H₂ and D₂ in a closed circulation system (Fig. 7). On Pt₃Ti (a), the total pressure (solid line) decreased from the initial stage and became constant after about 20 min reaction, indicating that hydrogen was consumed to hydrogenate ethylene totally into methane. The fraction of HD in hydrogen (broken line) also increased from the initial stage. Therefore, both hydrogenation and equilibration proceeded simultaneously on the Pt₃Ti surface, suggesting that hydrogen is adsorbed on the surface in an adequate amount for both reactions. On Pt (b), HD formation did not occur at first but started to proceed just after most of the ethylene was converted into ethane. At that time, HD formation proceeded with a very high reaction rate. These observations suggest that adsorption of ethylene must be stronger than that of hydrogen to cover most of the surface. Dissociated hydrogen will hydrogenate ethylene immediately because all neighboring species are ethylene. PtTi₃ (c) showed no formation of HD or ethane, although HD formation rate was 6 times higher than that on Pt without ethylene as already shown in Fig. 6. Therefore, adsorption of ethylene would be too strong to allow hydrogen to be adsorbed. These results suggest that the formation of IMC changes the adsorption property of monometallic catalyst, thus leading to the creation of novel catalysts superior to monometal and solid solution alloy cata-

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**Fig. 5** Effect of CVD Temperature on the Amount of Deposited Tin on Ni/SiO₂ (■) and SiO₂ (○)

**Fig. 6** Relative Activity of Pt-Ti IMCs for H₂-D₂ Equilibration at 195 K and Hydrogenation of Ethylene at 251 K, Assuming the Activity of Pt as Unity
lysts.

IMCs containing an early transition metal, such as PtTi3, were hard to reduce into the metallic state on silica surfaces. Therefore, we have concentrated mainly on IMCs between a transition metal and a typical element. However, H2-D2 equilibration proceeded with reaction rates much lower on these IMCs than on the pure component transition metal. For example, Pt3Ge required the reaction temperature of 523 K to obtain comparable HD formation rate on Pt at 298 K12).

### 3.2. Partial Hydrogenation of Alkyne into Alkene

The lower activity for hydrogen dissociation suggests that IMCs may be effective catalysts for partial-, regio- and chemo-selective hydrogenations. Hydrogenation of acetylene was carried out to clarify the selectivity of IMCs for partial hydrogenation into ethylene. Table 1 shows the ethylene selectivity at almost full conversion of acetylene as observed on supported and unsupported IMCs8,13–16. Values in parentheses in the last column show ethylene selectivity of parent transition metal catalysts measured under similar acetylene conversion. All IMCs gave much higher ethylene selectivity than the parent metals. In the case of Pd:Bi/SiO2, the reaction was carried out using a continuous flow system with cofeed of excess ethylene, C2H2/C2H4/H2 = 1/16/2. High selectivity (80 %) suggests that Pd:Bi could achieve excellent performance in commercial ethylene purification process. Other research groups have also reported high ethylene selectivity for Pd-Ga IMCs17,18. Therefore, formation of IMCs between transition and typical elements can provide selective catalysts for the partial hydrogenation of alkyne to alkene.

### 3.3. Chemoselective and Regioselective Hydrogenation of Dienes

Chemoselective (partial) hydrogenation of 1,3-butadiene is sometimes observed on bimetallic catalysts19,20. We applied Pt-Ge IMCs as catalyst for 1,3-butadiene hydrogenation12). Figure 8(a) shows the selectivity to each product obtained on unsupported Pt powder plotted against butadiene conversion. From the initial stage of reaction, at the lowest conversion, butane was formed as well as 1-butene, and trans- and cis-2-butene. The selectivity to 1-butene decreased with higher conversion. A steep increase in butane selectivity was observed as the conversion approached 100 %. Finally, the selectivity to butane reached 100 % at full conversion. On the other hand, unsupported Pt3Ge gave only butenes at the initial stage, with 1-butene selectivity maintained above 60 % up to 95 % conversion (Fig. 8(b)). Isomerization of 1-butene into 2-butenes was slightly detected but little butane was produced at full conversion, resulting in 96 % selectivity for partial hydrogenation. This result again indicates the high selectivity of IMC for partial hydrogenation.

Catalysts for the hydrogenation of symmetrical dienes, e.g. 1,3-butadiene, into monoenes do not need to differentiate the two C=C bonds in the molecule. However, hydrogenation of asymmetrical trans-1,4-hexadiene into 2-hexene requires the catalyst to possess regioselectivity for the hydrogenation of terminal C=C bond instead of the inner C=C bond, and chemoselectivity for the partial hydrogenation into hexenes instead of complete hydrogenation into hexane. We examined monometallic catalysts, Pt, Pd, Rh or Ni supported on silica under reaction conditions of temperature 298 K.

| Catalyst | Reaction temperature [K] | C2H2 conversion [%] | C2H4 selectivity [%] | Ref. No. |
|----------|--------------------------|---------------------|---------------------|---------|
| CoGe     | 573                      | 100                 | 88 (0)              | 13      |
| Ni3Sn    | 523                      | 100                 | 69 (2)              | 14      |
| Ni3Sn/SiO2 | 448                   | 100                 | 96 (-)              | 8       |
| PtGe/SiO2 | 573                     | 99                  | 72 (17)             | 15      |
| Pd3Bi/SiO2 | 343                    | 95                  | 80 (0)              | 16      |

Table 1 Partial Hydrogenation of Acetylene on Supported and Unsupported IMCs

![Fig. 7](image-url) Change in HD Proportion (○) and Total Pressure (●) in Hydrogenation of Ethylene with a Mixture of H2 and D2 on Unsupported Pt (a), Pt3Ti (b), and PtTi3 (c) Catalysts at 251 K
and atmospheric pressure hydrogenation. Rh/SiO₂ had the highest selectivity for the formation of trans-2-hexene through terminal C=C bond hydrogenation. Then supported IMCs containing Rh and a second element M (Fe, Zn, Ga, Sn, In, Sb, Pb or Bi) with Rh/M atomic ratio of 1.0 were examined to identify selective catalysts for the terminal hydrogenation. **Figure 9** demonstrates the selectivity of IMC catalysts for trans-2-hexene corresponding to the terminal selectivity. Except for IMCs with Fe and Zn, IMC catalysts had higher trans-2-hexene selectivity than monometallic Rh. RhBi exhibited the highest selectivity of 90%, where no formation of 1-hexene was observed.

RhBi IMC represents a novel catalyst with extremely high chemoselectivity and complete regioselectivity for the hydrogenation of trans-1,4-hexadiene. Hydrogen atoms will diffuse only one-dimensionally on the Rh row, and the large Bi atoms will sterically hinder adsorption of the inner C=C bond. These two geometric effects combine to accelerate hydrogenation of the terminal C=C bond and suppress subsequent hydrogenation into hexane.

### 3.4. Diphenylacetylene Hydrogenation into trans-Stilbene

Partial hydrogenation of diphenylacetylene (DPA) yields cis- and trans-stilbene (ST) and deep hydrogenation yields diphenylethane (DPE) as illustrated in **Fig. 11**. trans-ST is in high demand for the production of liquid crystal devices, so we tried to obtain selective IMC catalysts for the formation of trans-ST through the hydrogenation of DPA. Previously, only homogeneous catalysts have been effective for alkyne hydrogenation into trans-alkene. We found that Pd₃Bi/SiO₂ has high selectivity for the partial hydrogenation of acetylene into ethylene. Therefore, we first examined Pd₃Bi/SiO₂ for the DPA hydrogenation. Deep hydrogenation into DPE was effectively sup-
pressed, but cis-ST was mainly formed. We then examined monometallic catalysts. Rh/SiO\textsubscript{2} gave the highest trans-ST selectivity of 19\%\textsuperscript{24).} Rh\textsubscript{2}Sb gave much higher selectivity of 70\% at 89\% conversion of DPA. However, deep hydrogenation was accelerated after full conversion, resulting in lower trans-ST selectivity.

We considered that the combination of partial hydrogenation catalyst and isomerization catalyst may provide a highly effective catalytic system for the production of trans-ST if both catalysts possess low activity for deep hydrogenation. The candidate for the former catalyst was Pd\textsubscript{3}Bi, and solid acid for the latter catalyst. In fact, trans-ST yield reached 74\% on Pd\textsubscript{3}Bi/SiO\textsubscript{2} mixed with H-USY zeolite\textsuperscript{23).} However, the reaction rate was suppressed significantly because diffusion of the reactant and product molecules was inhibited drastically inside the zeolite pores. cis-trans isomerization of alkene proceeds in the presence of hydrogen on some metallic catalysts. Rh-based IMCs were tested for the isomerization of cis-ST into trans-ST\textsuperscript{24).} RhSb/SiO\textsubscript{2} showed the highest selectivity to trans-ST (93\%) at cis-ST conversion of 35\%. Figure 12 shows the time course of conversion and selectivity using the mixture of Pd\textsubscript{3}Bi and RhSb catalysts for the hydrogenation of DPA. cis-ST was first produced as a primary product and abruptly converted into trans-ST at the conversion of ca. 85\%. A small amount of DPE was simultaneously formed, but the trans-ST yield reached 88\%.

The high trans-ST selectivity of RhSb in the isomerization of cis-ST was further investigated through crystallographic data and DFT calculations\textsuperscript{25).} Isomerization of cis-ST and cis-β-methylstyrene (cis-MS) was carried out on various Rh-based IMCs. IMCs with the orthorhombic Pnma structure exhibited higher selectivity to the trans-isomer than IMCs with the hexagonal and cubic structures, suggesting that the trans-isomer selectivity is governed by geometric effects. RhSb with the highest trans-isomer selectivity in both reactions was further investigated. HR-TEM observations, DFT calculations, and IR spectra of adsorbed CO revealed that the surface of the RhSb crystallite consists of (211), (020), and (013) planes. The (211), (020), and (013) planes have unique geometric structures similar to the (110) plane of RhBi mentioned above (3, 3.). This stripe-like structure (Fig. 13) has one-dimensionally aligned Rh atoms separated by wide rows of Sb atoms. The activation barriers were calculated for a hydrogen atom adsorbed on Rh in RhSb (020) to diffuse on the surface. The barrier is 32-52 kJ mol –1 for hydrogen diffusion along the Rh row. Therefore, hydrogen atoms adsorbed on surface Rh atoms would diffuse predominantly along the Rh row, and will approach the cis-ST molecule adsorbed on Rh from only the two opposite directions.

Density functional theory (DFT) calculations were carried out for cis-trans isomerization on the RhSb (020) plane using cis- and trans-2-butenes as model molecules. The mechanism of selective formation of trans-ST on RhSb can be extrapolated as described below (Fig. 14). A cis-ST molecule is adsorbed on a Rh row. A surface hydrogen atom attacks one of the carbon atoms at the C=C bond from one direction along the row. The cis-ST molecule is converted into a half-hydrogenated intermediate species bound through a C-Rh bond (1,2-diphenylethylrhodium). Deep
hydrogenation into DPE needs a second hydrogen attack on the other C atom. However, this hydrogen attack is restricted to one direction along the Rh row, so steric hindrance of the phenyl group will hinder the second hydrogen attack. 

β-Hydrogen elimination from the intermediate after C–C single bond rotation generates the trans-ST molecule.

3.5. Catalytic Transfer Hydrogenation

Catalytic transfer hydrogenation (CTH) is the reaction between hydrogen donor and acceptor molecules consisting of dehydrogenation of the former and hydrogenation of the latter. CTH of p-nitrostyrene (NS) proceeds in parallel through intermediate products, p-aminostyrene (AS) and p-ethylnitrobenzene (ENB), into the completely hydrogenated product, p-ethylaniline (EA) as illustrated in Fig. 15. Among these products, AS is used industrially as raw materials for various chemicals. The surface of IMC, XnZm (Fig. 1), consists of two metal elements, where one X-atom contacts several Z-atoms. If the hydrogen donor and acceptor molecules are adsorbed on X and Z, respectively, most of the surface would act as active sites for the CTH.

We examined Pd- and Rh-based IMC catalysts for CTH of NS using 4-methyl-1-cyclohexene or methanol as the hydrogen donor. Table 2 shows the NS conversion and selectivity to three products obtained with a batch reactor at 343 K for 1 h. Monometallic Pd had high activity, but no formation of the target AS was observed. Pd-IMCs had lower activity than Pd. However, the selectivity depended strongly on the second element, as IMCs with Ga and Zn predominantly gave ENB, whereas IMCs with Pb, Bi and Fe mainly gave AS. Pd13Pb9 gave AS with the highest selectivity of 93 %. Pure Rh was almost inactive, but Rh-IMCs exhibited much higher conversion. In addition, all Rh-IMC catalysts tested produced AS with very high selectivity.

Conversion over RhPb2, RhPb and Rh3Pb2 IMCs decreased from 94 to 15 % with higher Rh content. This is a unique result because in most reactions we have examined, the activity of IMC increased with higher content of precious metal. The inverse correlation observed here for Rh–Pb IMCs implies that the combination of Rh and Pb atoms generates superior active sites for AS formation. RhPb2 was revealed to be the most effective catalyst, with high AS selectivity of 93 % at 94 % conversion. RhPb2 and Pd13Pb9 were also active and selective for CTH of various nitroaromatic compounds, such as 4-nitrostilbene and nitroindole isomers.

Figure 16 shows the influence of the electronegativity of the second elements on the formation rate of AS and ENB. AS formation rate increased with electronegativity on both Rh and Pd catalysts. Electron poor Pd or Rh generated by electron transfer to the second elements would accelerate AS formation. This electronic effect of the surface atoms was confirmed by IR spectra of adsorbed CO. Peak top of linear CO appeared at higher wavenumber on Pd13Pb9 than on Pd/SiO2, indicating that the lower electron density of Pd atoms is preferable for AS formation in accord with Fig. 16. Crystal structure of Pd13Pb9 would lead to specific alignment of the Pd and Pb atoms to enhance electron transfer to Pb. The high activity and selectivity of Pd13Pb9 and RhPb2 for the CTH reaction would...
be generated through the electronic effect improved by the regular geometric structure.

4. Conclusions

Several hundred IMCs consisting of two metal elements are known, but the catalytic properties have never been studied in detail with a few exceptions. As discussed in this review, a significant number of IMCs possess high catalytic activity and selectivity for partial, regioselective and chemoselective hydrogenations. These high catalytic activities and selectivities originate from the electronic and geometric effects resulting from the formation of crystalline compounds. In some cases, these effects are similar to those in normal solid solution alloy catalysts. However, the specific crystal structures of IMCs sometimes form geometrically unique ensemble sites on the surface, which result in the high catalytic activities and selectivities. Only IMCs can form such ensemble sites homogeneously dispersed on the support surface. Typical examples are one-dimensionally aligned Rh sites on RhSb and RhBi as mentioned in this review. Further investigation of the catalytic properties of IMC may reveal the importance of IMCs as catalytic materials.

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要  旨

選択的水素化反応に対する金属間化合物の触媒作用

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水素化反応に対する金属間化合物の触媒作用について、純金
属との選択性の違いを中心に検討した。金属間化合物そのもの
の触媒特性を明らかにするため、目的化合物の単一相からなる
触媒を調製した。水素分子の活性化に対し Pt3Ti は Pt より高活
性を示した。アルキンの部分水素化に対しては、多くの金属間
化合物が金属単体より高いアルケン選択性をもつことが明らか
となった。1,4-ヘキサジェンの水素化において RhBi は、内部
C=C と比べ末端 C=C を優先的に水素化する高い位置選択性
を示した。ジェフェニルアセチレンの水素化において、部分水素
化能をもつ Pd2Bi と異性化能をもつ RshB と組み合わせること
により、trans-スチルベンを高収率で得た。さらに、p-ニトロ
スチレンの水素化においては、RhPhB2 が高い官能基選択性を示
し、ニトロ基のみが水素化された p-アミノスチレンを高収率
で与えた。単金属との選択性の差について金属間化合物表面の
規則的原子配列を基に考察した。