**1. Introduction**

Alloying is one of the most effective methodologies for modifying the catalytic performance of metal catalysts, and conventional methods have developed various useful catalysts containing solid solution alloys or intermetallic compounds. However, recent research has suggested that much more efficient catalysts using bimetallic materials is difficult, as there are limits to further improvement of activity and function based on only two metal elements. In this study, a series of multimetallic catalysts were developed for deNO\textsubscript{x} reactions and alkane dehydrogenation based on advanced catalyst design concepts using alloy materials. Two strategies based on pseudo-binary alloys and surface modification of intermetallic compounds were employed. Pseudo-binary alloy, in which a part of the constituent metal in a binary intermetallic compound is substituted with a third metal, allows construction of trimetallic active sites with flexibly optimized atomic ratio and catalytic characteristics. Surface modification of intermetallic compounds allows selective blocking of undesirable active sites catalyzing side reactions, and construction of a sterically hindered reaction environment for selective hydrogenation. High catalytic activity, selectivity, and stability were achieved by appropriately applying these materials and design concepts. Outstandingly high stability (almost no deactivation at 600 °C for a month) was achieved for propane dehydrogenation.

**Keywords**

Intermetallic compound, Pseudo-binary alloy, Surface modification, Dehydrogenation
We observed that this material was highly efficient for deNO\textsubscript{x} reactions as introduced in the following\textsuperscript{3,4).}

Our previous development of Pd-based bimetallic catalysts selective for low-temperature deNO\textsubscript{x} found that intermetallic PdIn supported on Al\textsubscript{2}O\textsubscript{3} showed high N\textsubscript{2} selectivity for the NO + CO reaction (model reaction of NO\textsubscript{x} removal in exhaust gas) at low temperatures (\textless 200 °C)\textsuperscript{3).} However, the catalytic activity (NO conversion) of PdIn was much lower than that of Pd/Al\textsubscript{2}O\textsubscript{3}. Therefore, both high catalytic activity and selectivity in the NO + CO reaction are highly desirable.

**Figure 2** shows the changes in the catalytic activity for the NO + CO reaction over Pd(In\textsubscript{1-x}Cu\textsubscript{x})/Al\textsubscript{2}O\textsubscript{3} catalysts. Catalyst with low Cu content (\(x = 0.33\)) showed improved NO conversion compared to PdIn, but high-temperature activity was not significantly improved. Therefore, the PdIn-like characteristics persist at low Cu content. The catalytic activity was further improved at higher Cu content (\(x = 0.5\) and 0.66), and the NO conversion at high temperatures was also enhanced. However, further increase in \(x\) resulted in drastic decreases in N\textsubscript{2} selectivity, which suggests that significant reduction in In content could not retain the selective deNO\textsubscript{x} character. Therefore, the optimum catalytic activity and selectivity were obtained with Cu content of \(x = 0.66\). The important point is that NO conversion was improved over a wide range of temperature without lowering the high N\textsubscript{2} selectivity, so that highly efficient low-temperature deNO\textsubscript{x} could be achieved using a pseudo-binary alloy\textsuperscript{3).}

We also performed multiple characterizations to confirm the structure of the Pd(In\textsubscript{0.66}Cu\textsubscript{0.33})/Al\textsubscript{2}O\textsubscript{3} catalyst. High-angle annular dark field-scanning transmission electron microscope-energy dispersive X-ray fluorescence spectrometer (HAADF-STEM-EDX) analysis revealed that small nanoparticles consisting of Pd, In, and Cu with 2-3 nm diameter were highly dispersed on the Al\textsubscript{2}O\textsubscript{3} support (**Fig. 3(a)**-**3(c)**). EDX mapping showed that the nanoparticles consisted of homogeneously dispersed Pd, In, and Cu (**Fig. 3(d) and 3(e)**). A high-resolution image of a single nanoparticle demonstrated the atomic arrangement of a CsCl-type crystal viewed along the [111] direction with interplanar distance of 2.11 Å (1 Å = 10\textsuperscript{-10} m) between the {110} planes (**Fig. 3(c)**). The observed interplanar distance is close to but slightly shorter than 2.30 Å of PdIn(110)\textsuperscript{5)}, suggesting that shrinkage of the PdIn crystal lattice by substitution of In with Cu had occurred. The theoretical shrinkage of the crystal lattice could be estimated as 8.4 % using Vegard’s law, which agrees with the experimental shrinkage observed in **Fig. 3(c)** (8.2 %) and supports the proposed formation of a Pd(In\textsubscript{0.3}Cu\textsubscript{0.67})
pseudo-binary alloy structure. Extended X-ray absorption fine structure (EXAFS) analysis was also performed to obtain the exact location of Cu in the lattice of the Pd-In-Cu catalysts. Pd K-edge EXAFS observed Pd-Cu and Pd-In bonds. K- and Cu K-edge EXAFS confirmed the corresponding Cu-Pd and In-Pd shells, respectively. However, our attempt to assume In-Cu scattering could not achieve a valid fitting. These results strongly support doping of Cu into the In locations and formation of the \( \text{Pd(In}_{1-x}\text{Cu}_x) \) pseudo-binary alloy structure. Detailed mechanistic study based on kinetic analysis and density functional theory (DFT) calculations revealed the functions of In and Cu. In accelerates decomposition of the \( \text{N}_2\text{O} \) by-product to \( \text{N}_2 \) to increase \( \text{N}_2 \) selectivity, but loses the ability of NO scission. In contrast, Cu recovers the reduced activity for NO activation.3

The Pd site can be replaced with other transition metals than In to form various (Pd\(_{1-x}\)M\(_x\))In type pseudo-binary alloys. We tried to improve the stability of the Pd(In\(_{0.33}\)Cu\(_{0.67}\))/Al\(_2\)O\(_3\) catalyst for deNO\(_x\) under lean conditions.4 Excess oxygen typically oxidizes base metals such as In or Cu, so the metallic state of the pseudo-binary alloy and its high catalytic performance can be no longer retained. Therefore, we introduced Pt to PdIn to form (Pd\(_{1-x}\)Pt\(_x\))In so that the oxidation resistance of In was greatly improved and deNO\(_x\) performance under lean conditions can be no longer retained. Therefore, we introduced Pt to PdIn to form (Pd\(_{1-x}\)Pt\(_x\))In so that the oxidation resistance of In was greatly improved and deNO\(_x\) performance under lean conditions was enhanced (Fig. 4).5 (Pd\(_{1-x}\)Pt\(_x\))In/Al\(_2\)O\(_3\) catalyst was tested for the NO-CO\(_2\) reaction at 350 \( ^\circ \)C with various O\(_2\) concentrations (Fig. 5(a), 0-7500 ppm; 0.75 \( \leq \lambda \leq 1.5 \)). Unlike monometallic Pd, Pt, and intermetallic PdIn, (Pd\(_{1-x}\)Pt\(_x\))In showed much higher NO conversion under significantly lean conditions (\( \lambda = 1.5 \)). Although NO conversion was low under rich conditions, but was remarkably enhanced by changing the catalyst support from Al\(_2\)O\(_3\) to CeO\(_2\) (Fig. 5(b)). (Pd\(_{1-x}\)Pt\(_x\))In/CeO\(_2\) catalyst also exhibited high NO conversion even under lean-rich cycles (Fig. 5(c)) and excellent catalytic performance even in the presence of the hydrocarbon (NO-CO\(_2\)-H\(_2\) reaction, as a model reaction of exhaust gas purification, Fig. 5(d))3). We also performed H\(_2\)- and CO-temperature-programmed reduction for PdIn/Al\(_2\)O\(_3\) and (Pd\(_{1-x}\)Pt\(_x\))In/Al\(_2\)O\(_3\), in which the reduction temperature of In\(^{3+}\) to In\(^0\) was significantly lowered by introducing Pt. Therefore, Pt promotes the reduction of In that was oxidized during the catalytic run by excess oxygen, and so enhances the oxidation tolerance as expected.

We have also achieved similar functionalization for the dehydrogenation reaction. The target reaction is dehydrogenation of methylcyclohexane to toluene, which is used for hydrogen release from the hydrogen carrier. Higher efficiency of the catalytic process will reduce the hydrogen price by lowering the cost of the dehydrogenation process. High catalytic activity, selectivity, and durability are necessary for improved hydrogen production rate, higher purity of the carrier and hydrogen, and continuous hydrogen supply for long periods, respectively. To develop an efficient alloy catalyst for this reaction, we first surveyed a series of silica-supported Pt-based bimetallic alloys (Pt\(_3\)M/SiO\(_2\): M = Fe, Co, Cu, Zn, Ga, In, Sn, and Pb). Interestingly, we observed that PtFe showed higher TOF and stability than PtSn (Fig. 6(a) and 6(b)), which is a good catalyst for alkane dehydrogenation.6 Therefore, we ap-
Catalytic Performance of Pt-based Catalysts in MCH Dehydrogenation: (a) TOF at 300 °C and (b) MCH conversion at 400 °C. (c) HAADF-STEM image of Pt₃(Fe₀.75Zn₀.25)/SiO₂. (d) single unit cell of the crystal structure of Pt₃(Fe₀.75Zn₀.25)

Top view of this crystal (along the [100] direction) is shown right, which reflects the atomic arrangement of the nanoparticle shown in (c).

Fig. 6 Catalytic Performance of Pt-based Catalysts in MCH Dehydrogenation: (a) TOF at 300 °C and (b) MCH conversion at 400 °C. (c) HAADF-STEM image of Pt₃(Fe₀.75Zn₀.25)/SiO₂. (d) single unit cell of the crystal structure of Pt₃(Fe₀.75Zn₀.25)

The adsorption energies of toluene on the Pt site. Our DFT calculation showed that the adsorption energies of step-wise hydrogenation of carbon to methane (CH₃ + H → CₓHₓ₊₁; n = 0, 1, 2, and 3) were decreased if the catalyst contained Fe (Pt₃Fe and Pt₃(Fe₀.75Zn₀.25)). Thus, the combination of the two independent actions markedly enhanced the selectivity and stability of the catalyst for MCH dehydrogenation.

In summary, catalyst design based on pseudo-binary alloys enables the inclusion of multifunctional active sites that can be flexibly modified and additional activity is acquired by introducing an appropriate third metal. Highly efficient and improved catalysis is achieved by optimizing the combination and composition ratio of the elements. In particular, matching of the crystal structures between the parent intermetallic compound and the third metal-based compound, e.g., AₙBₘ and AₙCₘ, should be carefully considered. Identical structures result in high solubility of the third metal in the parent phase and a wide substitution range.

3. Surface Modification of Intermetallic Compounds

Heterogeneous catalysis generally occurs on the surface of a solid material. Therefore, modification of only the alloy surface will result in changes to the catalytic property. Moreover, surface modification strategy will remain effective even if a suitable third metal is unavailable for pseudo-binary alloys due to structural mismatching. This review introduces two examples of surface modification with Pb. Pb has a large atomic radius (1.8 Å), so doping Pb into an intermetallic compound consisting of atoms with smaller radius (typically 1.3-1.6 Å) is difficult, thus Pb doping requires location on the surface of the intermetallic compounds.

The first example is the Pb-modified PtGa catalyst for stable propane dehydrogenation. Propane dehydrogenation (PDH) is highly endothermic and so generally requires high reaction temperatures (typically > 600 °C) to achieve sufficient propane conversion. However, PDH at high temperatures often results in severe catalyst deactivation due to coke accumulation and/or irreversible aggregation of nanoparticles. Therefore, a truly stable catalyst for PDH will require high thermal stability and coke resistance. Since coke is typically formed by decomposition of the product propylene, achieving high propylene selectivity is the best way to inhibit coke formation.

We focused on intermetallic PtGa (space group: J. Jpn. Petrol. Inst., Vol. 65, No. 1, 2022
P2\textsuperscript{3,3} as a promising candidate material to satisfy these two requirements. PtGa contains single atom-like Pt\textsubscript{1} sites, which are isolated by Ga, on the most stable (111) surface (Fig. 7(a)). Such isolated Pt\textsubscript{1} sites are the most selective for PDH because undesirable side reactions (excessive C-H dehydrogenation and C-C cracking) occur at Pt-Pt ensemble sites. Moreover, PtGa has high thermodynamic stability ($\Delta H_f = -54$ kJ/mol), so has great resistance to sintering at high temperatures. However, PtGa also contains Pt\textsubscript{3} hollow sites on the (111) surface (Fig. 7(a)), which are more favorable for triggering undesirable side reactions and coking. Therefore, appropriate surface modification is necessary to disable the Pt\textsubscript{3} sites, but preserve the Pt\textsubscript{1} sites for catalysis.

Here, we used Pb as a third metal additive to enable this selective surface modification. The Pb atoms stably occupy the hollow site of Pt\textsubscript{3}, whereas the atop site of Pt\textsubscript{1} is geometrically unstable for capping (our DFT calculation supported this trend) as shown in Fig. 7(b). Interestingly, the Pb-modified PtGa/SiO\textsubscript{2} catalyst (PtGa-Pb/SiO\textsubscript{2}: Pb/Pt = 2) could be prepared by co-impregnation of Pt, Ga, and Pb salts, followed by H\textsubscript{2} reduction. Therefore, the surface modified PtGa intermetallic structure is thermodynamically stable, so undergoes self-organization during the reduction process even if the three metal precursors are impregnated simultaneously\textsuperscript{8}).

The prepared PtGa-Pb/SiO\textsubscript{2} (Pb/Pt = 2) catalyst was tested for PDH at 600 °C (Fig. 8). Unmodified PtGa/SiO\textsubscript{2} and conventional Pt\textsubscript{3}Sn/SiO\textsubscript{2} catalysts were deactivated within 10 h, reflecting the very harsh reaction conditions. Conversely, PtGa-Pb/SiO\textsubscript{2} catalyst showed no deactivation for at least for 50 h, demonstrating the remarkably high coke resistance and stability. Propylene selectivity was also the highest, with 99.6 % selectivity maintained during the catalytic run. Testing of the long-term stability of this catalyst under the same conditions observed almost no deactivation within 96 h. The deactivation constant ($k_d$) was 0.001 h\textsuperscript{-1}, which was the world record in this temperature region\textsuperscript{8}). We also performed a control experiment using Pt-Pb/SiO\textsubscript{2}, showing similar propane conversion to that of Pt/SiO\textsubscript{2},

Catalyst amount was adjusted so that the number of exposed Pt sites was identical (4.5 $\mu$mol): PtGa (9.0 mg), PtGa-Pb (15 mg), Pt\textsubscript{3}Sn (3.7 mg), and diluted with quartz sand (total 1.5 g). Gas feed: C\textsubscript{3}H\textsubscript{8} : H\textsubscript{2} : He = 3.9 : 5.0 : 40 mL min\textsuperscript{-1}. Temperature: 600 °C.

Fig. 8 Changes in Propane Conversion (left) and Propylene Selectivity (right) during PDH Catalyzed by PtGa/SiO\textsubscript{2}, PtGa-Pb/SiO\textsubscript{2} and Pt\textsubscript{3}Sn/SiO\textsubscript{2}

\textsuperscript{8} J. Jpn. Petrol. Inst., Vol. 65, No. 1, 2022
which indicates that Pb has negligible activity for PDH.

The long-term stability of the PtGa-Pb/SiO2 catalyst was further improved by applying the “double decoration” strategy9). We expected the combination of electronic and geometric effects to enhance the selectivity and stability. The surface Pb-modification can be regarded as a geometric effect to block the undesired Pt sites. On the other hand, the electronic effect was achieved by introducing Ca as a strong electron donating agent to increase the electron density of the Pt sites. This modification promotes propylene desorption by electro-static repulsion, resulting in further increases in the selectivity and catalyst life. Ca has high ionization tendency, so is neither reduced nor alloyed with other metals, and remains as cations as the PtGa-Pb structure is formed. Detailed characterization revealed that Ca was present at the metal-support interface and on the support, but did not cover the Pt and Pt3 sites. Thus, the Pb- and Ca-modifications are mutually compatible.

The stability of PtGa/SiO2 catalysts with and without Pb- and/or Ca-modification for PDH is shown in Fig. 9(a). Note that the reaction was performed without co-feeding H2, which introduces more severe conditions than used in Fig. 8 (with H2). The Pb- and Ca-modifications not only individually exhibited promotional effects on the stability, but also showed synergy9). Coke accumulation on the catalyst also followed this trend (Fig. 9(b)). The long-term stability of PtGa-Pb-Ca/SiO2 for PDH was also tested with co-feed of H2 at 600 °C (Fig. 9(c)). Surprisingly, PtGa-Pb-Ca/SiO2 showed outstandingly high stability for a month during the first run. Importantly, the double decoration is only effective if Ca was used as the second modifier. We tested other alkali, alkaline earth, rare earth metals, and basic supports instead of SiO2 as the basic additive/material to donate electrons to PtGa, but none of them worked as efficiently as Ca. This indicates that these other modifications were less effective at occupation of the active Pt sites and/or reducing the electron density of Pt. Thus, Ca as the only second modifier is crucial for this enhancement9).

The second example is Pb-modified PdZn/SiO2 for selective hydrogenation of alkyne to alkene10). In this system, Pb was deposited on the outermost surface of the PdZn nanoparticles by galvanic replacement, in which reduced PdZn/SiO2 was added to an aqueous solution containing Pb2+. Since the reduction potential of Zn2+ (~0.762 V vs. SHE) is much lower than that of Pb2+ (~0.126 V vs. SHE)11), Pb2+ is reduced by Zn atoms at the surface of the PdZn (Pb2+ + Zn0 → Pb0 + Zn2+) and replaces the original Zn sites (Fig. 10(a)). The degree of Zn-Pb replacement can be controlled by changing the amount of Pb in the galvanic replacement procedure.

The prepared PdZn-Pb/SiO2 (Pb/Pd = 0.25) catalysts were tested for the semihydrogenation of phenylacetylene to styrene. PdZn-Pb/SiO2 showed greater suppression of undesirable overhydrogenation of styrene to ethylbenzene than PdZn. Importantly, PdZn-Pb/SiO2 also showed higher alkene selectivity and yield than Pd/Pb/SiO2 and a conventional Lindlar catalyst (Pd-Pb/CaCO3). Therefore, the Pd-Pb surface based on the PdZn structure is more suitable for selective semihydrogenation than the conventional Pd-Pb materials, which highlights the advantage of this catalyst design concept. Our DFT calculation revealed that the surface Pd sites
were sterically hindered after the Zn atoms were replaced with Pb, so the adsorption energy of ethylene as a model alkene was significantly decreased.

Our findings show that the surface modification strategy for alloys can construct specific and functional active metallic sites that cannot be spontaneously formed by single-phase materials. Further modification of these alloy materials also highlights the effectiveness of multimetallic materials for highly efficient catalysis.

4. Conclusion

This review summarizes the catalyst design concepts for multimetallic alloy materials with examples of catalysts developed in our research group. Pseudo-binary alloys allow the construction of multifunctional active sites with flexibly optimized composition ratios. Introducing a third metal element can both modify the catalytic performance of the parent active metals and provide new functionality for much more efficient catalysis of NO reduction and alkane dehydrogenation. Surface modification of intermetallic compounds allows selection of the specific active sites for selective and stable alkane dehydrogenation, and to introduce sterically hindered active sites for selective alkyne semihydrogenation. These strategies can be applied to other catalytic reactions and will guide further development of highly efficient catalytic systems.

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