Surface modification of PdZn intermetallic compound via galvanic replacement reaction and their catalytic properties for phenylacetylene hydrogenation

Masayoshi Miyazaki,[a] Tomoaki Takayama,[a] Shinya Furukawa,[b] Takayuki Komatsu[a,]*

[a] *Department of Chemistry, Tokyo Institute of Technology, Meguro-ku, 152-8551, Japan*

[b] *Institute for Catalysis, Hokkaido University, Sapporo, 001-0021, Japan*

**Corresponding author: 03-5734-2758, komatsu.t.ad@m.titech.ac.jp*

Abstract: In order to improve performance of a PdZn intermetallic catalyst, replacement of the second metal with third metal via galvanic replacement reaction (GR) was investigated. A partial replacement of Zn with noble metals resulted in high activity for phenylacetylene hydrogenation compared to the pristine PdZn. Replacement of Zn with Pb and Bi was effective for suppressing consecutive hydrogenation into ethylbenzene. The Pb-substituted catalyst showed superior activities and selectivities compared to the ordinary alloy, having the same composition. The modification of the PdZn intermetallic catalyst via GR with third metals is effective for improving the performance.

Keywords: Intermetallic compounds, Galvanic replacement, Selective hydrogenation.

1. Introduction

Intermetallic compounds exhibit superior catalytic performance to monometal in various reactions such as selective hydrogenation of acetylene and aerobic oxidation of amine. The origin of these properties would be their specific crystal structures, namely high-ordered surface atomic arrangements and electronically modified bimetallic surfaces.[1] However, since the crystal structures of the intermetallic compounds are uniquely determined by their elements and compositions, it usually is difficult to independently control the surface structures and electronic states by substitution of third elements.

Galvanic replacement reaction[2] (GR) is one of the promising candidates for a solution to the above problem. For example, it has been reported that metallic Fe atoms constituting binary Pt-Fe nanoparticles are selectively replaced with metallic Ru atoms via the GR.[3] The driving force of the replacement is attributed to the differences in the reduction potentials between such exchangeable metal elements. Therefore, GR will lead to the development of the methodology for selective replacement of the specific metals in the surface of the intermetallic compound-based catalysts with third metals.

In this research, we attempted to partially replace metallic Zn atoms in the surface of PdZn-based catalysts, which showed relatively high activity and selectivity for hydrogenation of phenylacetylene,[4, 5] with third metals via the GR. The influence of this modification on their performance for the phenylacetylene hydrogenation and the surface and crystal structures of the catalysts were investigated.

2. Experimental

PdZn intermetallic catalysts were prepared on silica supported by pore-filling co-impregnation and subsequent reduction at 1073 K. The amount of Pd metal loaded and the atomic ratio of Pd/Zn were adjusted to 3 wt% and 1, respectively. The prepared catalyst was pretreated in a three-necked flask under flowing H_2 at 673 K for 30 min. After cooling and replacing the flask with argon, GR was carried out by the subsequent addition of third metal precursor solutions. Phenylacetylene hydrogenation was conducted in a three-necked flask reactor. The catalyst (10 mg) was reduced under flowing H_2 at 403 K for 30 min in the reactor followed by cooling to room temperature. The reaction was initiated by adding a tetrahydrofuran (THF) solution (5 mL) of phenylacetylene (0.5 mmol) into the reactor under 1 atm of H_2 gas at room temperature.

3. Results and discussion

To evaluate activities for phenylacetylene hydrogenation quantitatively, the reaction rate of phenylacetylene hydrogenation at conversion lower than 30% and that of styrene hydrogenation just after the conversion reached 100% were obtained and expressed as R_1 and R_2, respectively. Figure 1 shows R_1 and R_2 of a pristine PdZn catalyst and a series of PdZn-based catalysts added third metals via GR. Adding Cu, Ru, Rh, Ag, Ir, and Au as third metals were effective for improving the R_1 and R_2. In particular, when Rh and Au were employed, the R_1 and R_2 values were nearly twice as compared with those of the pristine PdZn catalyst. In contrast, the addition of Bi and Pb, which have negligible hydrogen dissociation ability, gave the high styrene yields at conversion above 99%, while both those R_1 and R_2 values decreased. The GR catalyst utilizing Pb as the third metal exhibited the highest styrene yield of 94%.

To verify the effects of the amount of the third metals, GR catalysts with different amount of added Pb were prepared. Figure 2 shows R_1 and R_2 of the GR catalysts that are described as PdZn + x Pb (x = 0.1-0.4 molar equivalent to Pd). An increase in the amount of Pb caused the decrease in both R_1 and R_2. On the other hand, the ratio of the reaction rates, R_1/R_2, increased with the increase in the amount of Pb, indicating that hydrogenation of styrene was suppressed. Therefore, it is suggested that Pb caused steric hindrance on the catalyst surface to suppress sequential hydrogenation.

In addition, the difference between the GR catalysts and usual alloy was examined by means of the alloy catalyst that had the same composition as GR catalysts. The alloy catalyst exhibited poor activity compared to the GR catalyst, resulting in lower styrene yield. Moreover, when the GR catalyst was reduced at 673 K under H_2 flow, the catalytic performance was almost the same as that of the alloy catalyst. Therefore, Pb atoms, which were introduced by galvanic replacement, were present in the surface region of PdZn nanoparticles and thermal treatment might lead to the formation of the alloy of PdZn and the Pb atoms.

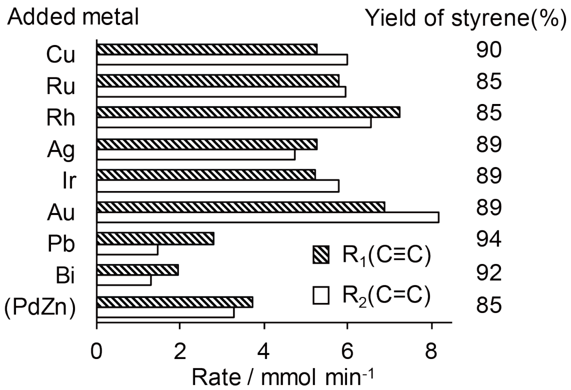

Figure 1. Phenylacetylene hydrogenation on PdZn and a series of GR catalysts. The amount of added metal were 0.25 molar equivalent to Pd.

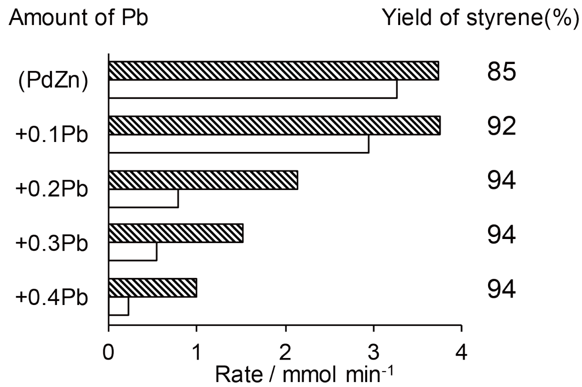

Figure 2. Effects of the amount of Pb on phenylacetylene hydrogenation.

4. Conclusions

The PdZn intermetallic compound modified with third metals via galvanic replacement reaction was used as the catalysts for hydrogenation of phenylacetylene to styrene. The rate of phenylacetylene hydrogenation was significantly improved when the Zn atoms in the catalyst surface were partially replaced with Au or Rh atoms. Moreover, the replacement of Zn with Pb resulted in suppression of styrene hydrogenation and high yield of styrene. The amount of added Pb and thermal treatment of the GR catalysts were important factors affecting the surface structures and catalytic properties.

References

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