Synthesis of Carbon-Supported Pd-Co Bimetallic Catalysts Templated by Co Nanoparticles for Selective Hydrogenation

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Abstract: Pd-Co bimetallic catalysts were prepared by the controlled synthesis of carbon-supported Co catalysts, ranging from single-sites to nanoparticles, followed by galvanic replacement with Pd^{2+} ions. Highly dispersed Pd-rich NPs containing a low concentration of Co species were formed retaining the original size of the Co NPs. These catalysts showed superior catalytic activity and selectivity in the selective hydrogenation of phenylacetylene than a monometallic Pd catalyst and a Pd-Co alloy catalyst. Furthermore, the electronic state of the Pd species was dependent on the size of the bimetallic NPs, and it played a crucial role in attaining high catalytic activity and selectivity.

Keywords: galvanic replacement • Pd-Co bimetallic catalyst • selective hydrogenation

1. Introduction

Bimetallic nanoparticles (NPs) have attracted much attention over the last several decades due to their potential applications as catalysts. Ligand and ensemble effects in bimetallic catalysts depend on the composition, size, morphology of the bimetallic species, and the preparation method is a crucial factor in determining the final structure of bimetallic NPs. The galvanic replacement (GR) method has been used over the last decade for the synthesis of bimetallic nanostructures. A pre-formed base metals, such as Co, Ni or Cu, and transition metal ions with a higher reduction potential, such as Pd^{2+}, Pt^{2+} or Au^{3+}, are used as precursors. The base metal is displaced by the transition metal ions due to the difference in ionization potential, and the second metal is redeposited onto the outer surface of the base metal. Various types of bimetallic nanostructures have been fabricated, including a core-shell structure, a hollow structure, and have recently been used for hydrogenation reaction, methane combustion and so on.

In this study, a series of carbon-supported Co species with different structures, ranging from single-sites to NPs, was used for the synthesis of Pd-Co by the GR method. Bimetallic nanoparticle catalysts prepared through the GR process usually exhibit core-shell or hollow/porous structures. In contrast, the Pd-Co NPs fabricated in this study are Pd-rich NPs with a low Co content that retain the size of the original Co NPs. Thus, the size of Pd-Co NPs can be controlled by the heat treatment temperature during preparation of the carbon-supported Co species. The electronic state of the Pd species was varied by changing the size of the Pd-Co nanoparticles, and the electron-rich Pd species was found to be most active and selective for the hydrogenation of phenylacetylene. In addition, the Pd-Co catalysts prepared by the GR method exhibited performance superior to that of monometallic Pd catalyst and Pd-Co alloy catalysts prepared by the conventional impregnation method.[1]

2. Experimental

A series of carbon-supported Co catalysts were synthesized thorough the process we previously reported.[2,3] Co(salen) complex (50 mg) was impregnated on the activated carbon (AC, 450 mg), followed by heat-treatment at different temperatures from 400 °C to 800 °C for 2 h under nitrogen atmosphere. The obtained powder was denoted as Co/AC-*T*, in which the T indicates the heat treatment temperature. Next, an aqueous solution of $NaBH_4$ was added to the Co/AC-*T* (100 mg) for reduction of Co^{2+} to Co^0. The product was dispersed in Ar-saturated ethanol/H_2O, and $Pd(NO_3)_2$ aqueous solution (140 μL, Pd 5 mg/mL) was added dropwise. Then, the reaction of $Pd^{2+} + Co^0 \rightarrow Pd^0 + Co^{2+}$ occurred, and Pd-Co NPs were formed by replacing Co species. Finally, the suspension was filtered and dried, and will be referred to as PdCo/AC-*T*.

The catalytic performance was evaluated in the selective hydrogenation of phenylacetylene. Prior to the catalytic reaction, the catalyst were pretreated with hydrogen at 200 °C for 1 h. The suspension containing methanol (5.0 mL), 1,4-dioxane (5.0 mL), phenylacetylene (1.0 mmol), biphenyl (0.5 mmol) as an internal standard and the catalyst (10 mg) were added into a glass reactor. The reaction was started by 10 mL/min hydrogen bubbling through the suspension under 30 °C.

3. Results and discussion

PdCo/AC-*T* catalysts provided no peaks arising from Co species in their XRD patterns, unlike their Co/AC-*T* precursors, indicating the atomic-scale replacement with Pd during GR process. In the TEM images, PdCo/AC-*T* contained distinct NPs and their size was similar to those of their Co/AC-*T* counterparts, suggesting that Co NPs are replaced by Pd species while maintaining the size of the original Co NPs. Moreover, XAFS, HAADF-STEM and EDX mapping results showed that the formed Pd-Co NPs in PdCo/AC-*T* were mainly composed of partially crystallized Pd species, with Co species present at low concentration. From the above characterization results, size-controlled carbon-supported Pd-Co bimetallic NP catalysts were synthesized using GR method templated by Co NPs (Fig. 1).

To investigate the catalytic activity, PdCo/AC-*T* were tested in the selective hydrogenation of phenylacetylene. PdCo/AC-600 showed the highest conversion and selectivity among the PdCo/AC-*T* samples: 92% selectivity and 93% conversion after 75 min reaction (Fig. 2). The selectivity of PdCo/AC-600 was higher than that of monometallic Pd catalyst and its activity was higher than that of a Pd-Co alloy catalyst. Moreover, the electronic state of the Pd species was varied by changing the size of the Pd-Co nanoparticles, and the electron-rich Pd species was found to be effective for selective hydrogenation of phenylacetylene.

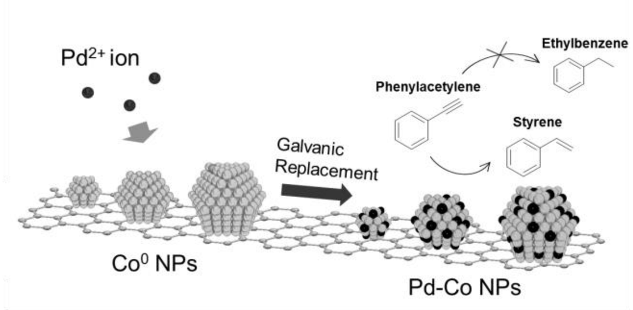

Figure 1 Structural transformation from Co NPs to Pd-Co NPs by galvanic replacement method.

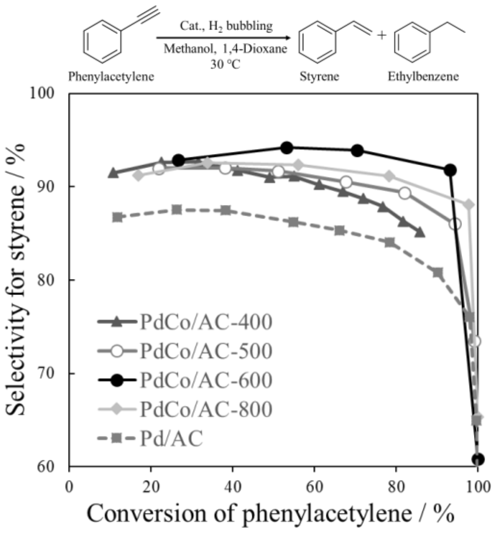

Figure 2 Conversion-selectivity relationship in the hydrogenation of phenylacetylene over PdCo/AC-*T* and Pd/AC.

4. Conclusions

We adopted the GR method for the synthesis of Pd-Co NP catalysts using Co NPs with various sizes and tested their catalytic performance in the selective hydrogenation of phenylacetylene. The correlation was observed between the electronic state of the Pd species and catalytic activity/selectivity in the selective hydrogenation of phenylacetylene: PdCo/AC-600, possessing the most electron-rich Pd species, showed the best catalytic performance, which was higher than that of pure Pd catalyst and Pd-Co alloy catalyst.

References

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