

XANES Analysis of Zn species in Pd–Zn Alloy Nanoparticle Supported on Alumina

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1. Introduction

The supported Pd catalysts are widely used for many purposes because of their high performance. The generation of hydrogen is one of urgent demands of the modern society, and the Pd species is a good catalyst to convert the hydrocarbons to hydrogen by the steam reforming reaction. The selectivity of the supported Pd catalyst, however, is not high for the steam reforming reaction of methanol and it rather tends to selectively decompose methanol to generate carbon monoxide, which is a catalytic poison. It is found by Iwasa *et al.* that the Pd catalysts supported on ZnO shows remarkable improvement of the selectivity for the steam reforming reaction of methanol. The Pd–Zn alloy nanoparticle is considered to form in the catalyst, and the alloy is regarded to be a key species for the high selectivity. The evaluations of the formation and catalysis reaction mechanisms are essential to understand the performance of such Pd–Zn alloy catalyst and to improve the selectivity and the efficiency. The Zn component in the suggested alloy must be generated by the partial reduction of supporting material, and such redox behavior of the Zn species is thus a key issue for the production of the Pd–Zn alloy catalyst. In this study, the Pd and Zn species simultaneously supported on an inert medium of alumina have been prepared by the impregnation method using α -alumina and by the co-precipitation method, and the Zn species in the sample has been characterized by means of the X-ray absorption and diffraction techniques.

2. Experimental

The co-precipitates were prepared from an alkaline aqueous solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Pd}(\text{NO}_3)_2$, and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and were aged at pH 10 for 2 days at room temperature. The precipitates were collected by the filtration, washed by water, dried at 393 K, and calcined at 773 K in air for 3 h. The mol ratio of Pd and Zn was adjusted to be 1:1. The sample prepared by the co-precipitation method as described above was thus supported on γ -alumina because of the calcination temperature, and was reduced under the diluted hydrogen flow (4 vol.% balanced by Ar, 200 cm^3/min) at 773 K for 2 h. The aqueous solution of PdCl_2 and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ acidified by HCl was dried over α -alumina for the preparation by the impregnation method. The obtained powders were calcined at 773 K in air for 3 h, and were reduced under the H_2 flow as the same way to that prepared by the co-precipitation method.

The XAFS measurements were carried out at BL-4 of SR Center, Ritsumeikan University at the vicinity of the Zn K edge using the Ge(220) double crystal monochromator. The XRD patterns were measured using the laboratory-scaled X-ray diffractometer (RINT-2000, Rigaku).

3. Results and Discussion

The XANES spectra are compared in Fig. 1 for the prepared Pd–Zn catalysts with those of Zn metal and ZnO. The Zn species in the sample prepared by the co-precipitation method is chemically stable against the reduction, and the peak energy of the white line is higher than that of ZnO. Because the supporting material is γ -alumina, the zinc aluminate is concluded to form and the Pd–Zn alloy is not existed in the sample, which is also supported by the XRD pattern shown in Fig. 2(b), in which only the diffraction lines assigned to Pd are observed except for those of alumina. The formation of the aluminate species is similarly observed for the other first-row transition metals.

The XANES spectrum of the calcined sample prepared by the impregnation method is similar to that of ZnO. The diffraction lines of PdO are clearly appeared in Fig. 2(a) before the reduction. Thus the ZnO and PdO are coexisted on α -alumina before the reduction process of the catalyst prepared by the impregnation method. After the reduction, the absorption edge of the XANES spectrum is shifted to the lower energy, and the diffraction lines assigned to the Pd–Zn alloy are newly appeared in the XRD pattern. This clearly means that the co-supported ZnO and PdO species are reduced by hydrogen at 773 K to form the Pd–Zn alloy nanoparticle. Because the XRD lines of PdO are perfectly disappeared after the reduction, the Pd–Zn alloy are considered to form quantitatively.

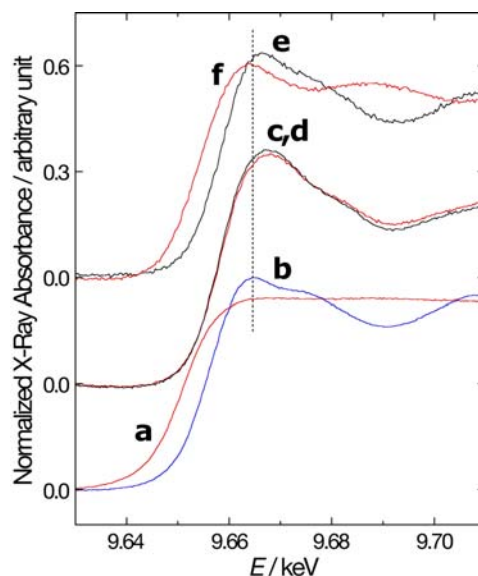


Fig. 1: XANES spectra at the Zn K edge of Zn metal (a), ZnO (b), calcined sample prepared by co-precipitation method (c, black) and its reduced sample (d, red), and calcined (e) and reduced (f) samples prepared by impregnation method on α -alumina.

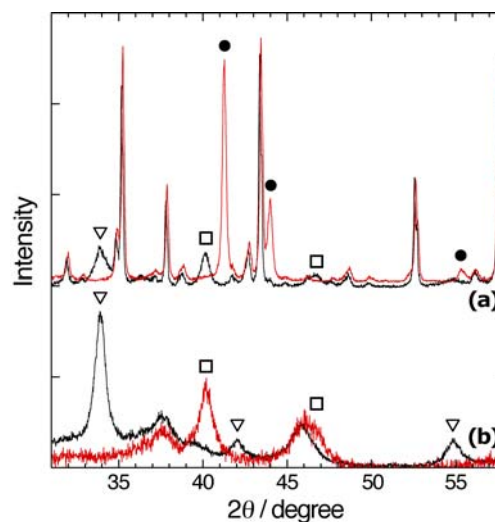


Fig. 2: XRD pattern of calcined (black) and reduced (red) samples prepared by impregnation method on α -alumina (a) and co-precipitation method (b). The observed peaks are assigned as Pd–Zn alloy (filled circles), Pd (squares), and PdO (inverted triangles).