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Novel Pd–Zn/C catalyst for selective alkyne hydrogenation: evidence for the formation of Pd–Zn bimetallic alloy particles

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The formation of Pd–Zn alloy was revealed in a highly selective Pd–Zn/C catalyst for acetylene hydrogenation prepared *via* the heterobimetallic PdZn(OAc)$_4$(OH$_2$) complex.

The selective hydrogenation of acetylene to ethylene is a commercially important process used to remove trace acetylene from ethylene feed for the production of polyethylene because acetylene is a poison for the polymerization catalyst.[1] High selectivity to ethylene is particularly desired for the process.[2] The liquid-phase hydrogenation of mono- or disubstituted acetylenes is widely used in the industrial synthesis of fine chemicals and pharmaceuticals.[3]

Pd-supported catalysts are routinely employed for this process due to their high activity.[4] However, they suffer from insufficient selectivity for ethylene at high acetylene conversions because of undesired ethylene hydrogenation. The addition of metal (M = Ag, Zn, Cu and Co) promoters improves the performance of a Pd catalyst due to Pd–M alloy formation.[5–7] However, the formation of homogeneous Pd–M alloy nanoparticles is difficult to achieve. Previously, the heterobimetallic lantern complex PdZn(OAc)$_4$(OH$_2$) was found the most promising precursor for the preparation of a selective Pd–Zn supported catalyst for gas-phase and liquid-phase hydrogenation of alkynes.[8] The process of PdZn(OAc)$_4$(OH$_2$) transformation was studied in detail by Murzin and co-authors by XANES and XRD methods.[9] In this study, we carried out a detailed investigation into Pd–Zn/C catalysts synthesized *via* the PdZn(OAc)$_4$(OH$_2$) complex[†] by catalytic tests in selective acetylene hydrogenation and characterized it by transmission (TEM) and scanning (SEM) electron microscopy in combination with energy dispersive X-ray spectrometry (EDS)[‡] analysis to reveal Pd–Zn alloy formation.

The catalytic performance in selective acetylene hydrogenation was studied in a temperature range of 30–120 °C at atmospheric pressure and a total gas flow rate of 150 ml min^{-1} (H$_2$: C$_2$H$_2$ = 2 : 1). The catalyst sample weight was 6 mg. The catalyst was thoroughly mixed with 1 g of SiC in order to minimize the reaction heat effect. The feedstock contained ~1.3% acetylene in ethylene. Note that the experimental conditions were similar for all catalysts. The reaction products were analyzed using on-line gas chromatography.

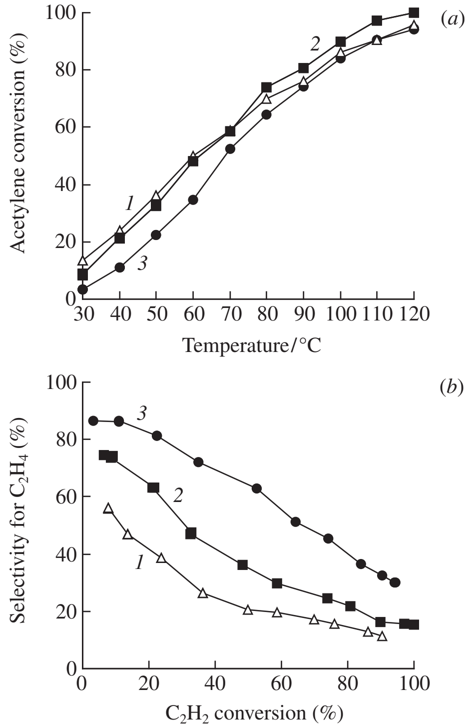

Figure 1 Dependence of (*a*) acetylene conversion on temperature and (*b*) selectivity for C$_2$H$_4$ on C$_2$H$_2$ conversion. Performance of (*1*) Pd/C, (*2*) Pd–Zn/C *via* Pd(OAc)$_2$ and Zn(OAc)$_2$OH$_2$ and (*3*) Pd–Zn/C *via* **1** in acetylene hydrogenation. *T* = 30–120 °C; *P* = 1 atm; H$_2$: C$_2$H$_2$ = 2 : 1.

[†] The catalysts were prepared using a Sibunit mesoporous carbon carrier (BET specific surface area, 332 m^2 g^{-1}; total pore volume, 0.45 cm^3 g^{-1}). The reference monometallic Pd catalysts [0.9 wt% Pd in accordance with inductively coupled plasma (ICP) analysis] was prepared by the incipient-wetness impregnation of the carrier with a methanol solution of Pd(OAc)$_2$. Bimetallic catalysts (0.9 wt% Pd and 0.59 wt% Zn in accordance with ICP analysis) were prepared by (1) incipient-wetness impregnation using complex PdZn(OAc)$_4$(OH$_2$) **1** and (2) co-impregnation with aqueous solutions of individual Pd(OAc)$_2$ and Zn(OAc)$_2$·2H$_2$O. The synthesis of complex **1** was described elsewhere.[10] The catalysts were dried in an Ar flow (80 °C, 2 h) and reduced in H$_2$ (250 °C, 1 h) before experiments. The ICP-OES analysis was performed on a Perkin Elmer Optima 3000 instrument.

[‡] Reduced samples were analyzed by TEM on a Philips CEM200 instrument operated at 200 kV. The samples were crushed, ultrasonically dispersed in ethanol, and dropped on a 200 mesh copper grid for TEM analysis. SEM images were acquired using a Philips XL30 ESEM-FEG microscope operating at 10 keV, spot size 3 and using the backscattered electron signal. The samples were crushed, and fixed on a sample holder using carbon tape. Qualitative chemical analyses of the samples were made by EDS. For the analysis of nanoparticle size, the Digital Micrograph software[11] was used.

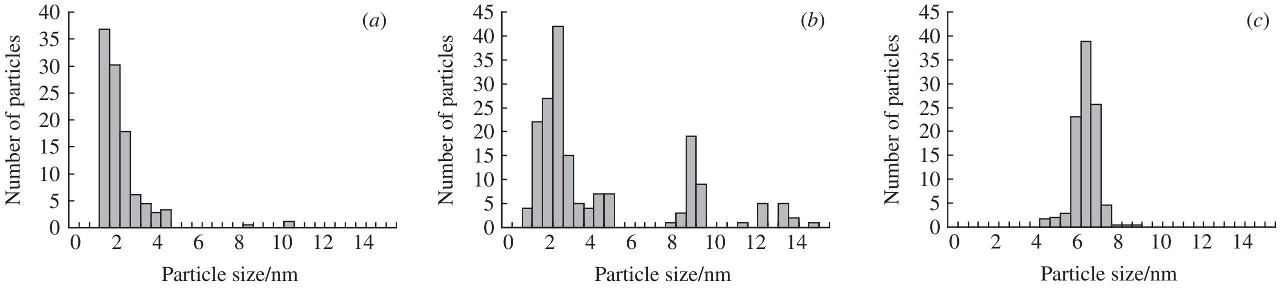

Figure 2 Pd particle size distribution determined from the microscopic images of (*a*) Pd/C, (*b*) Pd–Zn/C prepared using $Pd(OAc)_2$ and $Zn(OAc)_2OH_2$ complexes and (*c*) Pd–Zn/C prepared using complex **1**.

Figure 1 compares the activity and selectivity of the Pd–Zn/C catalysts in acetylene hydrogenation. Activities of all samples are comparable, though one can observe an activity decrease in the sequence [Figure 1(*a*)], as evidenced by this shift of the acetylene conversion profile toward higher temperature for Pd–Zn/C *via* **1**: Pd/C ~ Pd–Zn/$C_{\text{coimpregnated}}$ > Pd–Zn/C *via* **1**.

The selectivity trend is opposite. The ethylene selectivity is low for the 0.9% Pd/C sample prepared *via* a $Pd(AcO)_2$ precursor (Figure 1, curve *1*). The introduction of Zn to the Pd/C significantly improved the selectivity. Note that the Pd–Zn/C catalyst prepared using complex **1** showed notably higher selectivity compared to the catalyst prepared by co-impregnation *via* individual $Pd(OAc)_2$ and $Zn(OAc)_2{\cdot}2H_2O$ complexes (Figure 1, curves *2* and *3*).

We performed a comparative microscopic study of the catalysts in order to characterize the selectivity of the catalyst prepared *via* the heterobimetallic lantern complex $PdZn(OAc)_4(OH_2)$. Figure 2 displays the particle size distribution (PSD) determined from corresponding TEM images. For the monometallic 0.9% Pd/C catalyst, the majority of Pd particles fell within a range of 1–2 nm [Figure 2(*a*)]. For the bimetallic Pd–Zn/C sample prepared by co-impregnation from $Pd(OAc)_2$ and $Zn(OAc)_2{\cdot}2H_2O$ complexes, TEM revealed a bimodal PSD with Pd metal particle size varying from 2 to 15 nm [Figure 2(*b*)]. The bimetallic Pd–Zn/C prepared using the bimetallic complex $PdZn(OAc)_4(OH_2)$ has a relatively narrow PSD centered at 6–7 nm [Figure 2(*c*)].

Figure 3(*a*) shows a representative SEM image of 0.9% Pd–0.59% Zn/C catalyst prepared by co-impregnation. In accordance with EDS analysis, the Pd and Zn co-impregnation procedure results in a catalyst with both bimetallic [Figure 3(*b*)] and monometallic Pd [Figure 3(*c*)] or Zn [Figure 3(*d*)] particles and agglomerates with prevalence of the monometallic particles.

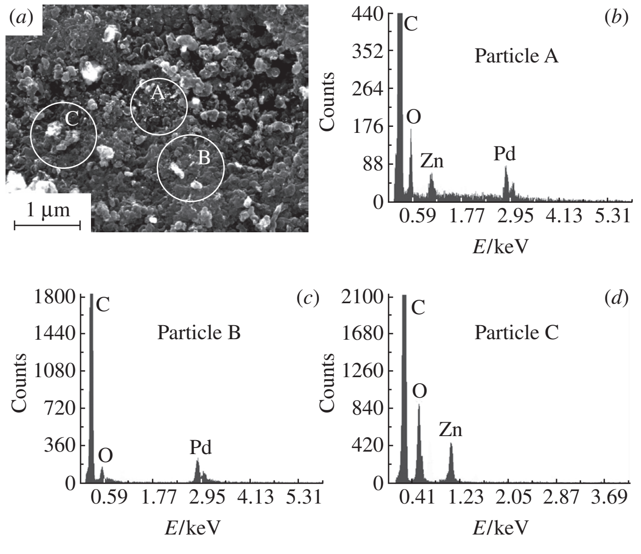

Figure 3 (*a*) SEM image of the Pd–Zn/C catalyst [from $Pd(OAc)_2$ and $Zn(OAc)_2OH_2$ complexes] and (*b*), (*c*), (*d*) the corresponding EDS spectra.

Figure 4(*a*) exhibits typical SEM image of the 0.9% Pd–0.59% Zn/C sample prepared *via* bimetallic complex **1**. EDS analysis detected only Pd–Zn bimetallic particles [Figure 4(*b*)] Calculations of the EDS spectra gives a 4:1 Pd:Zn atomic ratio in average for the metallic particles. Note that according to ICP elemental analysis, the catalyst has a Pd:Zn atomic ratio of 1:1 [calc. (%): Pd, 0.93; Zn, 0.593]. A possible explanation of the higher Pd:Zn elemental ratio could be the fact that the Zn sublimates under exposure to an electron beam during EDS analysis.[12] This suggestion is supported by the fact that we observed a continuous decrease in the Zn intensity upon electron beam irradiation. The bimetallic particles changed their shape after exposure to the electron beam. The second EDS analysis of the same particles led to their noticeable agglomeration because of the beam damage of the catalyst.

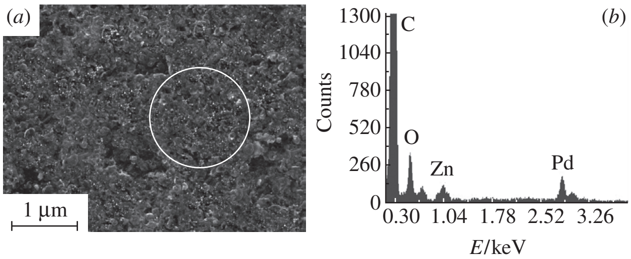

Figure 4 (*a*) SEM image of the Pd–Zn/C catalyst (from complex **1**) and (*b*) the corresponding EDS spectrum.

To further examine Pd–Zn particles in the catalyst prepared *via* bimetallic complex **1**, we calculated the lattice fringers using HRTEM images and the Digital Micrograph software.[11] The particles with a 2.06 Å lattice spacing were identified (Figure 5), which suggests that a Pd:Zn atomic ratio of 1:1 in complex **1** provides the formation of a β_1-tetragonal Pd–Zn phase[9(*a*),13] with contracted lattice spacing, as compared to monometallic Pd (2.25 Å). Note that, for PdO, Zn or ZnO particles, the next

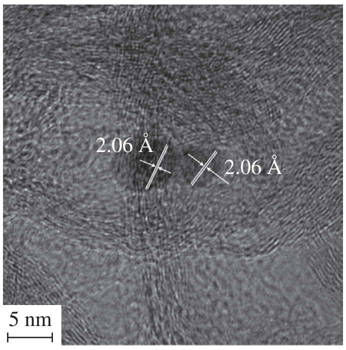

Figure 5 TEM image of the Pd–Zn/C catalyst prepared *via* complex **1**.

nearest d-lines of the sample would be 2.82, 1.33 or 2.53 Å, respectively.[14–16] These data are in a good agreement with our previous findings obtained by EXAFS and XRD.[8(*a*)]

The characterization data provide the following explanation of the favorable selectivity of the Pd–Zn/C sample prepared using complex **1**. In accordance with published data, selectivity changes can be attributed to either the particle size effect or Pd–Zn alloy formation. The particle size effect is related to the formation of a β-PdH hydride phase.[1,17] The probability of palladium β-hydride formation decreases with decreasing Pd particle size. Therefore, highly dispersed Pd catalysts show better selectivity in alkene formation in the course of triple C–C bond hydrogenation.[18,19] However, this explanation should be omitted since TEM and SEM analysis revealed a lower dispersion of metallic particles in the Pd–Zn/C sample prepared using complex **1**, as compared to the monometallic Pd/C.

Thus, the most plausible explanation for the favorable selectivity of the catalyst prepared *via* complex **1** is the formation of homogeneous bimetallic Pd–Zn alloy nanoparticles revealed by TEM and SEM. This explanation is in line with the results of density functional calculations of acetylene hydrogenation pathway reported by Studt *et al*. for various Pd alloys.[20] The addition of metals such as Ag, Zn, Ga or Pb primarily changes the stability of adsorbed acetylene and ethylene rather than the activation energies. The addition of these metals affects the electronic structure of Pd and decreases the heat of adsorption of acetylene and ethylene. However, acetylene adsorption remains sufficiently exothermic, and its hydrogenation is facile, though some decrease in the activity can be expected, as it was observed for Pd–Zn/C prepared *via* **1** [Figure 1(*a*)]. On the other hand, the decrease in ethylene adsorption heat facilitates its desorption since the activation barrier for ethylene desorption becomes lower than the activation barrier for its hydrogenation. As a result, the selectivity of Pd–Zn catalyst in ethylene formation is significantly enhanced, as compared to monometallic, though at the expense of some activity loss.

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