

The Effects of PdZn Crystallite Size on Methanol Steam Reforming

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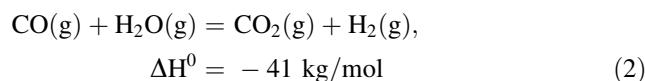
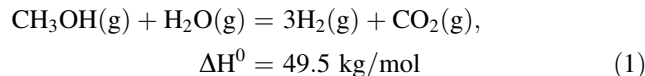
Abstract Exceptional activity and selectivity of Pd/ZnO catalysts for methanol steam reforming have been attributed to the formation of PdZn alloy. In this paper, we evaluated the crystallite size effects of PdZn alloy on methanol steam reforming. An organic preparation method was used to avoid the complexity from the alteration of ZnO morphology typically associated with the conventional aqueous preparation method. Both Pd loading and reduction temperature ($>350\text{ }^{\circ}\text{C}$) were used to vary the crystallite size of PdZn alloy. Experimental activity studies and transmission electron microscope (TEM) characterizations indicated that formation of large sized PdZn crystallites exhibit high reactivity and low CO selectivity during methanol steam reforming.

Keywords PdZn alloy · Pd/ZnO catalysts · PdZn crystallites · Methanol steam reforming · Hydrogen production

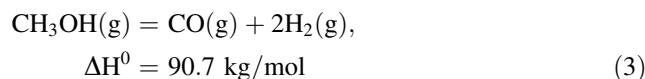
1 Introduction

Among hydrocarbon fuels, methanol has been widely studied as a source of hydrogen production for the fuel cell due to its high hydrogen/carbon ratio, low sulfur content, and relatively low reforming temperature ($250\text{--}350\text{ }^{\circ}\text{C}$). Due to the high energy density of methanol ($\sim 5.6\text{ kWh/kg}$ compared to $\sim 0.12\text{ kWh/kg}$ for lithium ion batteries), even a very inefficient chemical to electrical device could be a significant improvement over the available secondary

battery technology [1]. The methanol steam reforming reaction, as shown in Eq. 1, produces three moles of hydrogen for every mole of methanol reacted. However, if significant amount of CO is formed, the water–gas-shift (WGS) reaction, shown in Eq. 2 is required to not only maximize hydrogen production but also minimize the CO poisoning of the fuel cell. CO produced by steam reformation must be reduced to ppm levels before introducing the reformat to the PEM fuel cell.



Most research has focused on Cu-based catalysts which exhibit a high reactivity and selectivity to CO_2 and H_2 [2]. However, the Cu-based catalysts have significant disadvantages, including their pyrophoric nature and the tendency to deactivate at high temperature ($> \sim 280\text{ }^{\circ}\text{C}$) [1, 2]. In addition, stability under certain oxidizing environments is a concern [3]. On the other hand, group VIII metals exhibit different performance than copper based catalysts. Over Group VIII metal catalysts, methanol readily decomposes to CO and H_2 (Eq. 3), and require a separate WGS conversion unit.



Iwasa et al. was the first to report that Pd supported on ZnO and reduced at $>300\text{ }^{\circ}\text{C}$ exhibits exceptional high selectivities to CO_2 and H_2 [4]. Combined TPR, XRD, XPS, and TEM methods revealed the formation of PdZn

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alloy under reduction conditions at temperatures higher than 300 °C [5–7]. It was shown that the reactions proceeded selectively towards methanol steam reforming over the catalysts having the PdZn alloy phase, whereas the catalysts having metallic Pd phase exhibited poor selectivities to CO₂. Upon PdZn alloy formation, Iwasa's group proposed a reaction mechanism markedly different than decomposition Eq. 3, as with Group VIII metals alone, followed by the water–gas-shift reaction Eq. 2. It has been argued that since this reaction does not include the decomposition of methanol to CO, and does not contain CO as an intermediate in the formation of CO₂, less-than-equilibrium amounts of CO can be produced during steam reforming of methanol [8].

In addition, it was found that a high Pd content in Pd/ZnO catalysts favors methanol reforming activity and suppresses CO selectivity [7]. Although the importance of a high Pd content for selective methanol steam reforming has been firmly established [7], the roles of higher Pd loadings have not been clearly understood. It may be intuitive to think that the formation of large sized PdZn alloy crystallites would be more prevalent with the higher Pd loadings, which may contribute to higher methanol steam reforming activity and lower selectivity to CO. Such a dependence on the size of PdZn alloy crystallites has recently been suggested by Karim et al. [9] based on their methanol steam reforming studies on PdZnO supported on alumina with two different PdZn crystallite sizes (~1.5 nm vs. ~2 nm). The roles of a high Pd content in Pd/ZnO are difficult to elucidate especially on the catalysts prepared using the conventional aqueous impregnation method since ZnO is partially dissolved during impregnation and the extent of ZnO dissolution depends on the Pd loading [10]. In this paper, a series of Pd/ZnO catalysts with Pd loadings of 0.5, 2.5, and 10% were prepared using an organic preparation method to avoid the dissolution of ZnO or the alteration of ZnO morphology. A combination of reduction temperature (higher than that required for PdZn alloy formation) and Pd loading was used to vary the PdZn alloy size so that its effect on CO selectivity can be studied.

2 Experimental

A series of Pd/ZnO catalysts were prepared via incipient wetness technique by impregnating ZnO powder (Aldrich, 99%) with palladium II acetate salt (Aldrich, 99.9%) dissolved in acetone. Nominal Pd loadings in the Pd/ZnO catalysts are 0.5, 2.5, and 10 wt%. The impregnated samples were dried under vacuum at 110 °C for at least 8 h prior to calcining in air. Calcination was conducted at a ramping rate of 2 °C/min followed by holding isothermally at 350 °C for 3 h.

Transmission electron microscopy imaging was conducted on a JEOL 2010 high-resolution analytical electron microscope operating at 200 kV with a LaB₆ filament. Powder samples were collected on copper grids with Formvar/carbon support film. High-resolution images were collected and analyzed by Gatan DigitalMicrograph[®] 3 software. X-ray diffraction (XRD) patterns were collected on a Philips X'Pert MPD (Model PW3040/00) diffractometer using Cu K α radiation. The diffraction patterns were analyzed using Jade 5 (Materials Data Inc., Livermore, CA) and the Powder Diffraction File database (International Centre for Diffraction Data, Newtown Square, PA.).

Activity tests were carried out in a 4 mm I.D. quartz tube reactor. Approximately 0.200 g of catalyst was loaded between two layers of quartz wool inside the reactor. A thermocouple was placed in the middle of the catalyst bed. A pre-mixture feed of water/methanol (molar ratio of 1.8/1) was introduced into the reactor using a syringe pump. The feed was fully vaporized through a vaporizer, operating at 200 °C, and then introduced to the reactor. Prior to activity tests, the catalysts were reduced in-situ under a 10% H₂/N₂ at 350 °C unless otherwise indicated. A glass condenser at 0 °C was used to separate liquid products from gaseous products. The product gases, CO, CO₂, and H₂, were separated using MS-5A and PPQ columns, and analyzed on-line by means of a MTI Quad Micro GC (Model Q30L) equipped with a TCD.

3 Results and Discussions

We have previously found that the impregnation of Pd using the highly acidic Pd nitrate aqueous precursor alters the textural properties such as porosities and crystalline structures of ZnO due to ZnO dissolution [10]. In this study, a series of catalysts of 0.5, 2.5, and 10 wt% Pd on ZnO were prepared using the organic preparation method to avoid the complexities of this phenomenon. In our previous studies, we reported that temperatures higher than 250 °C are required for PdZn alloy formation [7]. In this study, catalysts were reduced at 425 °C prior to activity testing, thus facilitating the PdZn alloy formation. XRD spectra of these three catalysts reduced at 425 °C are shown in Fig. 1. No metallic Pd diffraction peaks at 2θ of about 40 and 43.3° are observed. Also as expected, 10% Pd/ZnO has more defined PdZn alloy crystalline phase or larger PdZn alloy crystallite size than that of 2.5% Pd/ZnO. PdZn alloy crystalline phase was not detectable on 0.5% Pd/ZnO catalyst, likely due to the fact that the PdZn crystallites are less than the detection limit of XRD (<2 nm).

The methanol conversion and CO selectivity as a function of temperature over 0.5, 2.5, and 10 wt% Pd/ZnO

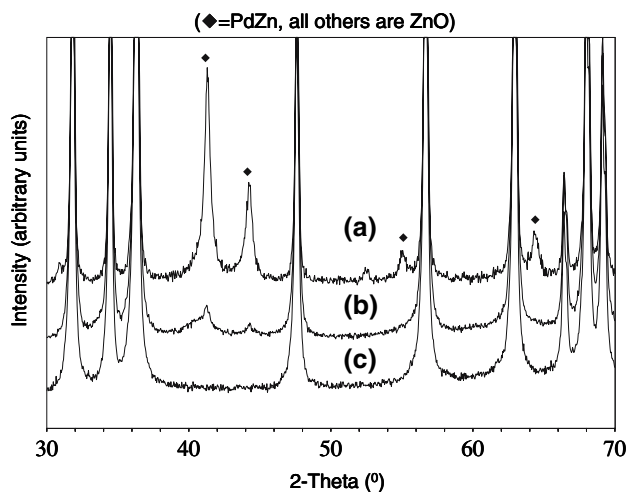


Fig. 1 XRD spectra for (a) 10% Pd/ZnO (b) 2.5% Pd/ZnO and (c) 0.5% Pd/ZnO catalysts, reduced at 425 °C

catalysts are shown in Fig. 2a, b, respectively. As shown in Fig. 2a, methanol conversion increases with Pd loadings. Increasing the Pd loadings not only increases the methanol conversion, but also suppresses the CO formation during

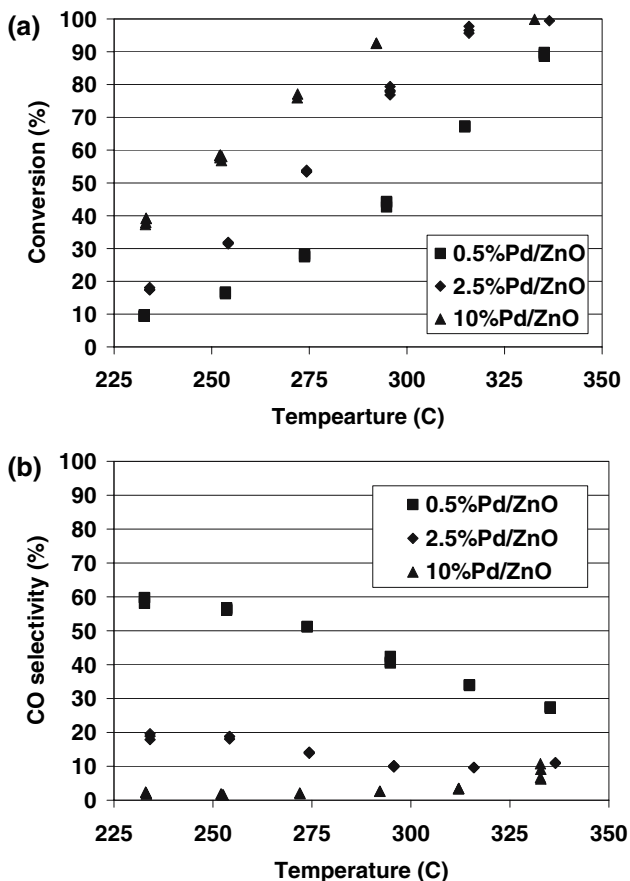


Fig. 2 (a) Conversion and (b) CO selectivity as a function of reaction temperature for Pd/ZnO catalysts (GHSV = 14,400 h⁻¹, 1 atm, H₂O/C = 1.8 (molar), P_{N₂} = 0.25 atm)

reforming. The CO selectivity decreases as the Pd loading increases, as illustrated in Fig. 2b. These results are consistent with our previous report on Pd/ZnO catalysts prepared using an acidic and aqueous preparation method [7]. Significantly decreased CO selectivity on Pd/ZnO catalysts with higher Pd loadings (2.5 and 10%) could be attributed to the formation of larger PdZn alloy particles prevalent in these two catalysts as confirmed by XRD measurements (Fig. 1). Interestingly, CO selectivity on 0.5% and 2.5% Pd/ZnO catalysts decreases with temperature while CO selectivity on 10% Pd/ZnO catalyst slightly increases with temperature (Fig. 2a). The decrease in CO selectivity with reaction temperature on 0.5% and 2.5% Pd/ZnO catalysts (Fig. 2a) could imply continuous sintering of PdZn alloy in these two samples. On the other hand, 10% Pd/ZnO has a higher Pd loading and relatively larger PdZn alloy crystallites. The further sintering of PdZn in the 10% Pd/ZnO catalyst is less likely to occur compared with the 0.5 and 2.5% Pd/ZnO catalysts. Therefore, on 10% Pd/ZnO catalyst, thermodynamically favored CO formation at higher temperatures has a more dominant role than sintering of PdZn alloy in determining CO selectivity, and it is not surprising to see CO selectivity slightly increases with temperature on 10% Pd/ZnO as we previously observed on Pd/ZnO catalysts with >5 wt% Pd [7].

To further study the effects of sintering or crystallite size of PdZn alloy on methanol steam reforming activity and selectivity, 0.5, 2.5, and 10% Pd/ZnO catalysts were reduced over a range of temperatures from 350 to 650 °C and then tested for methanol reforming activity at 275 °C. The methanol conversion and CO selectivity over these catalysts are shown in Fig. 3a, b, respectively. In Fig. 3a, it can be seen that methanol conversion slightly decreases with increasing reduction temperature. Reduction temperature has a more dramatic effect on CO selectivity than methanol conversion, particularly on the 0.5% Pd/ZnO catalyst as shown in Fig. 2b. On 0.5% Pd/ZnO catalyst, increasing the reduction temperature from 350 to 650 °C decreases the CO selectivity from 49% to 18%. CO selectivity also decreases with increasing reduction temperature on 2.5% Pd/ZnO catalyst, although at a much less extent than that on 0.5% Pd/ZnO catalyst. On 10% Pd/ZnO, reduction temperature has no noticeable effect on CO selectivity (Fig. 3b). Since higher reduction temperatures are expected to result in more severe sintering of PdZn alloy particularly on the Pd/ZnO catalysts with lower Pd content such as 0.5 and 2.5% Pd/ZnO catalysts, the suppressed CO selectivity at high reduction temperatures on these two catalysts can be attributed to the presence of large PdZn alloy crystallites resulting from sintering of PdZn alloy. If the turnover frequency of methanol steam reforming is independent of PdZn alloy size, methanol conversion should decrease significantly with reduction

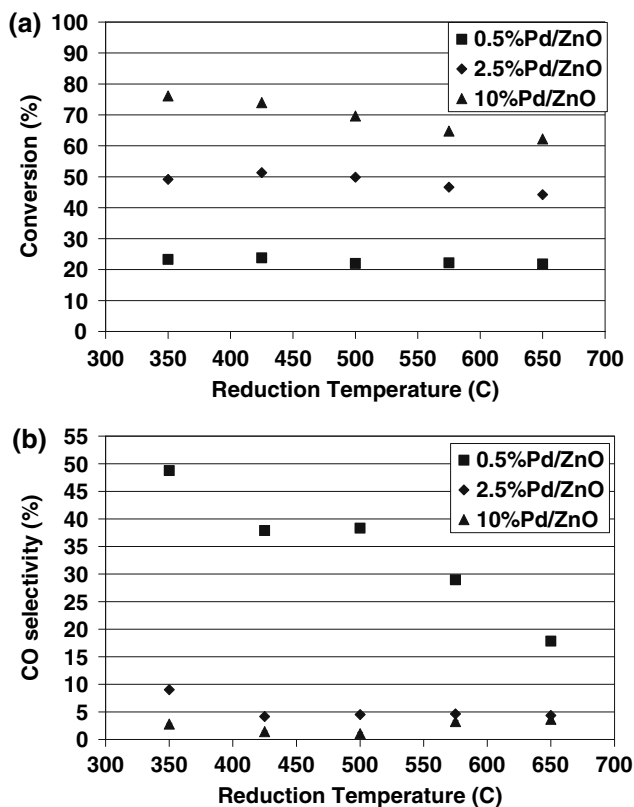


Fig. 3 (a) Conversion and (b) CO selectivity as a function of reduction temperature for Pd/ZnO catalysts (GHSV = 14,400 h⁻¹, 275 °C, 1 atm, H₂O/C = 1.8 (molar), P_{N₂} = 0.25 atm)

temperature particularly on Pd/ZnO catalysts with a low Pd content such as 0.5% Pd/ZnO. The fact that the overall methanol conversion only slightly decreases with reduction temperature (Fig. 3a) suggests that large PdZn alloy particle may exhibit high turnover frequency as proposed by Karim et al. [9].

To elucidate the relationship between the size of PdZn crystallites and CO selectivity, further studies were conducted on 0.5, 2.5, and 10% Pd/ZnO catalysts reduced at

425 and 650 °C. Since the crystallite sizes of PdZn alloy in catalysts such as 0.5% Pd/ZnO are below the XRD detection limits, TEM was used to quantify crystallite sizes. Histograms of the crystallite size counts were done for the 0.5, 2.5, and 10% Pd/ZnO catalysts reduced at both 425 and 650 °C. The number averages of these histograms were used to determine an average crystallite size. The combination of three Pd content (0.5, 2.5, and 10%) and two reduction temperatures (425 and 650 °C) result in catalysts with a wide range of PdZn crystallite sizes (from ~4 to 12 nm). Figure 4a, b show two examples of TEM micrographs for 2.5% Pd/ZnO reduced at 425 °C with an average crystallite size of ~5.3 nm and 10% Pd/ZnO reduced at 650 °C with an average crystallite size of ~11.4 nm, respectively. The other TEM pictures for this series are not shown. CO selectivity as a function of measured PdZn crystallite size is shown in Fig. 5. Apparently, CO selectivity decreases as the PdZn crystallite size increases. These results are consistent with recent theoretical studies on PdZn alloy by Lim et al. [11] who suggest that CO formation is favored at defect sites of PdZn alloy. Since

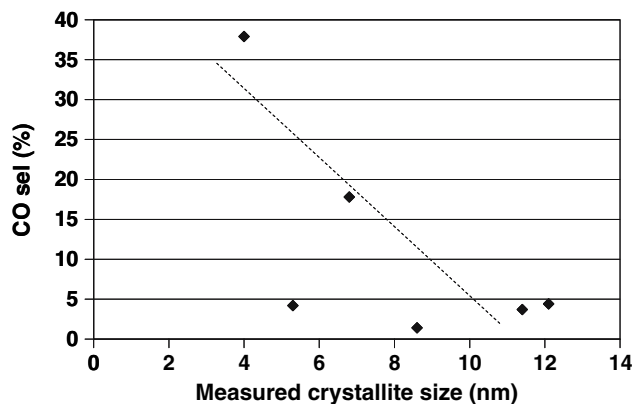
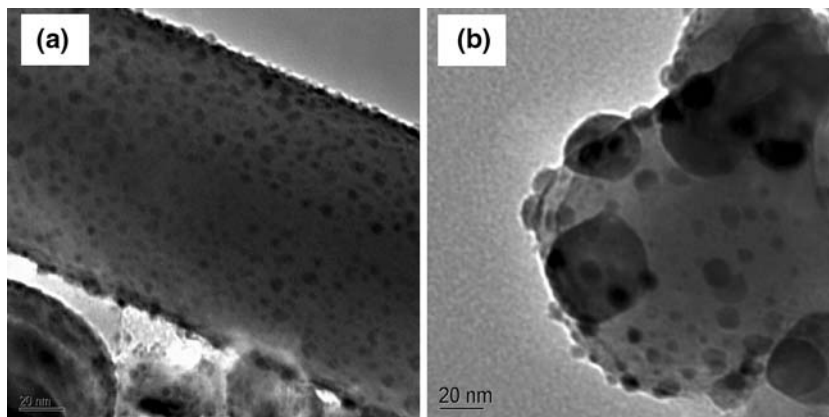


Fig. 5 Correlation of CO selectivity (%) with PdZn alloy crystallite size determined from TEM (GHSV = 14,400 h⁻¹, 275 °C, 1 atm, H₂O/C = 1.8 (molar), P_{N₂} = 0.25 atm)

Fig. 4 TEM micrographs of (a) 2.5% Pd/ZnO reduced at 425 °C with an average crystallite size of ~5.3 nm; and (b) 10% Pd/ZnO reduced at 650 °C with an average crystallite size of ~11.4 nm



large PdZn crystallites are expected to possess less defect sites (steps, edges, etc), they should not favor CO formation as shown in Fig. 5. Because CO is an undesired product for PEM fuel cell, it is important to synthesize Pd/ZnO catalysts with large PdZn crystallites to suppress CO formation for methanol steam reforming.

4 Conclusions

In agreement with previous works, Pd/ZnO catalysts prepared using an organic preparation method have been demonstrated as being selective and active for hydrogen production from methanol steam reforming. Organically prepared Pd/ZnO catalysts allow evaluation of the effects of PdZn alloy crystallite size without the complication of ZnO morphology change typically occurred using a conventional aqueous impregnation method. It was found that the size of PdZn alloy crystallites plays an important role in determining the CO selectivity. Large sized PdZn crystallites dramatically suppress CO selectivity while exhibiting high activity for methanol steam reforming.

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