

Influence of the ZnO surface structure on the reactivity of Pd/ZnO catalysts for methanol steam reforming

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Introduction

Since the pioneering work of Iwasa et al [1], Pd/ZnO catalysts have attracted much attention. These catalysts have exceptionally high activity and selectivity to H₂ and CO₂ (i.e. low CO selectivity), for methanol steam reforming, when reduced at elevated temperatures (> 300°C). Fundamental understanding of the catalyst surface structure and function is needed to design a highly selective catalyst with minimum CO formation since CO is a poison for the PEMFC. A recent study on model catalysts [2] showed that the ZnO surface structure affects the formation of PdZn alloy and its surface interaction with CO which may ultimately affect the CO selectivity. The objective of the present work was to elucidate the effect of surface structure of high surface-area nanostructured ZnO supports on the reactivity of Pd/ZnO catalysts for methanol steam reforming.

Materials and Methods

Two Pd/ZnO catalysts (denoted ZnO-A and ZnO-B) were prepared using an incipient wetness method on two types of ZnO supports with distinguished morphologies, i.e., nano rods and nano plates respectively. Pd acetate solution was prepared by dissolving Pd II acetate in acetone. The Pd loadings are 3.5 and 5 wt % for Pd/ZnO-A and Pd/ZnO-B catalysts, respectively. The texture and structure of the catalysts were investigated by BET measurements, X-ray diffraction (XRD), FTIR spectroscopy and Transmission electronic microscopy (TEM). The catalytic activity was tested for the steam reforming of methanol.

Results and Discussion

The characterization by TEM indicated a considerable difference between the two ZnO powders in term of morphology and surface structures (Figure 1). The ZnO-A, consists of nano-rods with (-120) exposed facet whereas the ZnO-B has a more plate-like morphology and (-122) exposed facet. XRD and TEM analysis showed that the PdZn particles size is similar for both Pd/ZnO catalysts (Table 1). Here, it is essential to compare catalysts with a similar PdZn particle size since the CO selectivity dependent on the PdZn particle size [3]. The absence of metallic Pd, responsible for the high CO production [4], was confirmed by XRD and FTIR spectroscopy. The effect of the ZnO surface structure on the activity was thus unambiguously studied. As shown in Table 1, under the conditions where a similar methanol conversion is reached, CO selectivity is drastically different on these two catalysts. CO selectivity on the Pd/ZnO-A catalyst is significantly lower than that of the Pd/ZnO-B catalyst. Since the methanol conversions were similar and the metal surfaces area of the Pd/ZnO-A catalyst is lower than that of Pd/ZnO-B, the turnover frequency is higher for the Pd/ZnO-A sample.

Hence, the results clearly show that the surface structure of the ZnO support plays a noteworthy role in the overall activity and selectivity of Pd/ZnO catalysts. It is likely that ZnO-A exhibits dominant surface structure for facile PdZn alloy formation as discovered on the model catalyst studies [2].

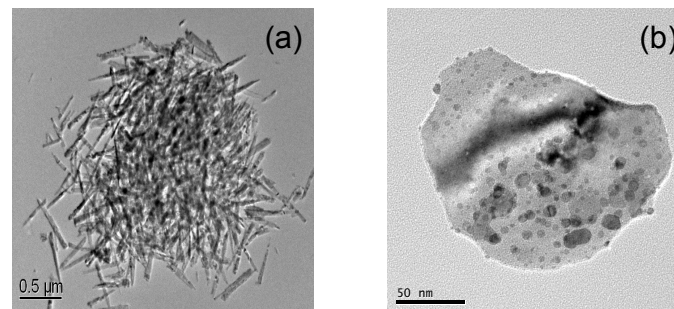


Figure 1. TEM pictures for the Pd/ZnO-A (a) and Pd/ZnO-B (b) catalysts

Table 1. Characterization data and reactivity measurements

Catalyst	BET surface (m ² /g)	PdZn Particle size (nm)		CH ₃ OH conversion* (%)	CO selectivity* (%)
		XRD	TEM		
Pd/ZnO-A	41.5	11.5	6.5	8.0	3.6
Pd/ZnO-B	42.0	10.4	6	8.2	14.3

* Reaction temperature = 250°C, contact time = 70 ms (i.e. GHSV = 51 430 h⁻¹)

Significance

Nano structured ZnO supports with controlled morphologies provide a great potential in bridging the gap between model and practical high surface area catalysts. Fundamental understanding of the effect of the ZnO surface structure on the formation of PdZn alloy and subsequent activity and selectivity is essential to design a highly active and selective catalyst for hydrogen production for PEMFC applications.

References

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