

Methanol Steam Reforming on Pd/ZnO Catalyst

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Introduction

In recent years fuel cell energy systems have attracted much attention due to their high energy efficiencies and power densities¹. Reforming of methanol to provide the hydrogen necessary for polymer electrolyte membrane fuel cells (PEMFCs) has become an attractive fuel supply option. Copper based catalysts are active and selective for the methanol steam reforming reaction. However, sintering of the copper metal at temperatures > 280°C and its pyrophoric nature when exposed to air is problematic². Precious metals and other Group VIII metals are active for the conversion of methanol, however, are unselective to the reforming reaction. Another option is the use of bimetallic alloy compositions, not containing copper, with Pd/ZnO being the most active and selective for the methanol steam reforming reaction².

Iwasa et. al was among the first to report that Pd supported on ZnO and reduced at >300°C has exceptional high activity and selectivity to CO₂ and H₂³. Work at the Pacific Northwest National Laboratory confirmed the formation of a PdZn alloy resulting in a highly selective methanol reforming catalyst⁴. Preparation studies indicated the use of highly acidic Pd nitrate aqueous precursors alter the textural properties such as porosity and crystalline structure, where dissolution is evident⁵. The use of an organic precursor in the preparation method can minimize these effects^{5,6}. Pd loading and Pd/ZnO ratio optimization studies were done on Al₂O₃ supported catalysts⁷. On a Pd/ZnO/Al₂O₃ catalyst similar activities and selectivities were reported as that on a conventional Cu-based catalyst at 220°C⁷, although due to higher stability of the Pd alloy much higher operating temperatures can be used and the exploitation of increased kinetics can be utilized⁸. Kinetic studies using a Pd/ZnO based catalyst in a microreactor resulted in a reported power law expression suitable for the design of a miniature fuel processor⁹.

This paper presents recent results pertaining to several unique characteristics of the Pd/ZnO type catalyst for the methanol steam reforming reaction. Discussion will include structure-sensitivity of the PdZn crystallite and catalytic performance of Pd/ZnO for the water-gas-shift (WGS) reaction.

Materials and Methods

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 acetone⁶. Al₂O₃ supported Pd/ZnO catalysts were prepared using a one-step co-impregnation method⁷. Activity tests were carried out in a 4 mm I.D. quartz tube reactor. The product gases, CO, CO₂, and H₂, were analyzed on-line by means of a MTI Quad Micro GC (Model Q30L) equipped with a TCD. Transmission electron microscopy imaging was conducted on a JEOL 2010 high-resolution analytical electron microscope operating at 200 kV with a LaB₆ filament.

Results and Discussion

Evaluation of the PdZn crystallite size on methanol steam reforming was made. Both Pd loading and reduction temperature (>350°C) were used to vary the PdZn alloy size. Experimental activity studies and transmission electron microscope (TEM) characterizations indicated that large sized PdZn crystallites significantly suppress CO selectivity and exhibit high activities during methanol steam reforming. These results are shown in Figure 1 below.

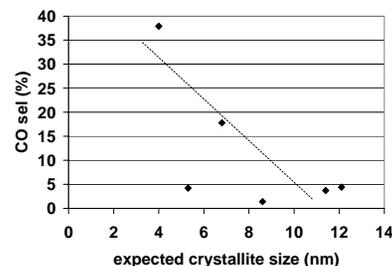


Figure 1. PdZn crystallite size measured from TEM as a function of CO selectivity (GHSV=14,400 hr⁻¹, 275°C, 1 atm, H₂O/C=1.8 (molar), P_{N₂}=0.25atm).

Significance

The Pd/ZnO type catalyst offers high activity and selectivity for the methanol steam reforming reaction. This catalyst is a prime candidate for use in fuel processing systems. Several characteristics unique to the Pd/ZnO catalyst have been studied offering insight into improving catalyst design.

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