PdZnAl catalysts for the reactions of water-gas-shift, methanol steam reforming, and reverse-water-gas-shift

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ABSTRACT

Pd/ZnO/Al$_2$O$_3$ catalysts were studied for water-gas-shift (WGS), methanol steam reforming, and reverse-water-gas-shift (RWGS) reactions. WGS activity was found to be dependent on the Pd:Zn ratio with a maximum activity obtained at approximately 0.50, which was comparable to that of a commercial Pt-based catalyst. The catalyst stability was demonstrated for 100 h time-on-stream at a temperature of 360 °C without evidence of metal sintering. WGS reaction rates were approximately 1st order with respect to CO concentration, and kinetic parameters were determined to be E_a = 58.3 kJ mol^{-1} and k_0 = 6.1 × 10^7 mol^{-1}. During methanol steam reforming, the CO selectivities were observed to be lower than the calculated equilibrium values over a range of temperatures and steam/carbon ratios studied while the reaction rate constants were approximately of the same magnitude for both WGS and methanol steam reforming. These results indicate that although Pd/ZnO/Al$_2$O$_3$ are active WGS catalysts, WGS is not involved in methanol steam reforming. RWGS rate constants are on the order of about 20 times lower than that of methanol steam reforming, suggesting that RWGS reaction could be one of the sources for small amount of CO formation in methanol steam reforming.

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1. Introduction

As fuel cell research and development has become a flourishing area in recent years, fuel processing, including hydrogen generation, purification, and storage, is drawing a great deal of attention. Fuel cell systems are being developed for several applications, including distributed and portable power generation and other consumer applications [1–3]. Reforming of hydrocarbons is typically conducted at high temperatures, and water-gas-shift (WGS) is normally required to reduce the CO concentration in the reformate from as high as 15% down to 1–2% [4]. WGS technology for large-scale applications is a well-established commercial process. The WGS reaction (1) is an equilibrium controlled, mildly exothermic reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H^0 = -41.1 \, kJ/mol. \quad (1)$$
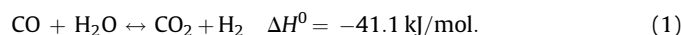
For conventional industrial applications two types of WGS catalysts are used. Fe-based high-temperature-shift (HTS) catalysts typically operate around 400–550 °C. Because these catalysts are less susceptible to poisons, it is preferable to convert the bulk of the CO at higher temperatures for many commercial applications

[5]. A more active Cu-based catalyst is typically used as a low-temperature shift (LTS) catalyst at 200–250 °C [5]. Conventional WGS catalysts are not seen as attractive options for small-to-medium scale fuel cell systems. Fe-based HTS catalysts are far too inactive and pose serious volume and weight restraints. Cu-based LTS catalysts are very active at lower temperatures, but they become unstable at higher temperatures (>280 °C) and their pyrophoric nature makes them undesirable for safe and efficient operation [6]. Interest in WGS technology has grown significantly over the last few years as a result of recent advancements in fuel cell technology and the need to develop advanced fuel processors for conversion of hydrocarbon fuels into hydrogen. Several catalyst types have been studied as potential alternatives.
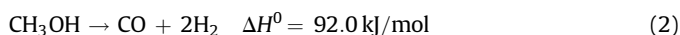
The most promising types of WGS catalysts, and those most extensively studied, have been Pt–CeO$_2$ based [6–9]. However, instability of this catalyst under fuel processing conditions has been a recurring problem [8–10]. There is much debate over what deactivation mechanisms are actually involved, and research on the Pt–CeO$_2$ based catalyst continues with a particular emphasis on increasing catalytic activity and stability.

Recently, a PdZn alloy catalyst was shown to have the activity and selectivity for methanol steam reforming comparable to that of Cu-based catalysts [11–13], while it differs significantly from that of metallic Pd [14–20]. While Pd predominantly produces CO and

H_2 (methanol decomposition, reaction (2)), the main products are CO_2 and H_2 (methanol steam reforming, reaction (3)) on the PdZn alloy catalyst. More importantly, the PdZn alloy catalyst exhibits improved thermal stability [13]. Previous studies also reported that PdZn is not only highly active for methanol reforming, but also for other reactions such as dehydrogenation/coupling of methanol to acetic acid [12] and methanol oxidation [21,22]. Tsai et al. reported that an explanation for the identical catalytic function for PdZn and Cu is due to the fact that PdZn exhibits a similar valence electron density of states as pure Cu [23]. In a separate study by Neyman et al., the valence band spectrum of the PdZn alloy was found to resemble closely the spectrum of Cu (1 1 1), in good agreement with the calculated density of states for a PdZn alloy of 1:1 stoichiometry and implying close similarities in the reactivity of PdZn and Cu [24]. Since Cu possesses excellent WGS reactivity, it has prompted us to evaluate the WGS activity of PdZn alloy catalyst which may potentially be more stable at elevated temperatures.

$$CH_3OH \rightarrow CO + 2H_2 \quad \Delta H^0 = 92.0 \, kJ/mol \quad (2)$$

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \quad \Delta H^0 = 49.5 \, kJ/mol. \quad (3)$$

This paper focuses on some recent findings that suggest the PdZnAl type catalyst which, up until now has exclusively been developed for the methanol steam reforming reaction, also appears to be active for the WGS reaction. Kinetic comparisons for the WGS, methanol steam reforming (SR), and reverse-water-gas-shift (RWGS) rates were made to identify the potential roles of WGS and RWGS in the methanol steam reforming reaction.

2. Experimental

Al_2O_3 supported Pd–ZnO catalysts were prepared using a one-step co-impregnation method. Specifically, a concentrated palladium nitrate solution (20.19 wt% Pd, Engelhard Corp.) was mixed with $Zn(NO_3)_2 \cdot 6H_2O$ (99.5%, Aldrich) at 60 °C. A neutral γ-Al_2O_3 support (Engelhard Corp.) with a BET surface area of 230 $m^2 \, g^{-1}$ was pre-calcined at 500 °C for 2 h and kept at 110 °C prior to the incipient-wetness impregnation step. The support was impregnated at 60 °C with an appropriate amount of the pre-mixed Pd and Zn nitrate solution to obtain the final products with various Pd loadings (7.3–13.2 wt%) and Pd/Zn molar ratios (0.25–0.76) while keeping the total weight percentage of Pd and Zn constant (25 wt%). The wet sample was kept at 60 °C for 1 h before drying in air at 110 °C overnight. The dried sample was then calcined at 350 °C for 3 h. For comparison purposes, a commercial LTS CuZnAl catalyst and Pt-metal-based WGS catalyst were also studied.

WGS activity tests were conducted in a 7-mm i.d. fixed-bed quartz tube reactor at ambient pressure. Two K-type thermocouples were installed in the reactor for the measurement of inlet and catalyst bed temperatures. Catalyst (0.100 g) was mixed with 0.500 g SiC (inert diluent) to maintain isothermal conditions, and placed in the reactor. The catalyst was reduced using 10% H_2/Ar gas mixture at 400 °C for 2 h prior to the test. Feed to the test bed was a gas blend intended to simulate effluent from a propane wet partial oxidation reactor. A pre-mixed gas containing 14.5% CO, 3.6% CO_2, 35.8% H_2, and 46.1% N_2 (Matheson) was introduced into the system using a mass flow controller (Brooks 5850E series). The dry premixture was mixed with water in a vaporizer at 200 °C before being introduced to the reactor. Water was fed using a syringe pump (Cole Parmer 74900 series). Unless otherwise reported, the resulting wet feed mixture contained 31.6% H_2, 12.6% CO, 3.2% CO_2, 12.6% H_2O, and 40.0% N_2. A condenser and a desiccant bed were used to dry the product stream before analysis. The gaseous effluent was analyzed using a micro-GC (MTI) equipped with MS-5A and PPQ columns and a thermal conductivity detector.

Table 1
Catalyst composition details for the series of PdZnAl catalysts with varied Pd:Zn ratios (as determined by calculation)

| Sample i.d.	Pd:Zn (mol:mol)	Pd (wt%)
PdZnAl-0.25	0.25	7.3
PdZnAl-0.38	0.38	8.9
PdZnAl-0.50	0.50	11.1
PdZnAl-0.76	0.76	13.2

Methanol steam reforming and kinetic rate tests were conducted using the same experimental setup. Using a syringe pump, pre-mixed H_2O/CH_3OH solutions were introduced into the vaporizer and reactor for reforming tests. WGS kinetic rate measurements were conducted by feeding an equimolar mixture of CO and H_2O. A syringe pump was used for the water introduction. RWGS kinetic rate measurements were conducted by feeding an equimolar mixture of CO_2 and H_2.

A JEOL 2010 high-resolution transmission electron microscope (TEM) was used to obtain the microstructures of samples. Small amounts of powder catalysts were first embedded in a hard grade LR white resin and cured at 60 °C for 6 h. The hardened polymer bars were sectioned into 50 nm thick slices and collected onto copper grids with Formvar/carbon support film.

3. Results and discussion

3.1. The effects of Pd loading and Pd/Zn ratio on the WGS reaction

Similar to a previously conducted study of methanol steam reforming catalyst [11], a series of catalysts with various Pd loadings and Pd:Zn ratios were prepared on a high surface area Al_2O_3 support. Catalyst composition information is shown in Table 1. For each sample, the total amount of Pd and Zn on the Al_2O_3 support was kept constant at 25 wt% while the ratio of Pd:Zn was varied. Catalytic activity comparisons were made using a feed blend representing typical effluent from that of a propane wet partial oxidation reaction. This resulting WGS feed composition as stated above was used at a GHSV of 40,000 h^{-1}. These conditions simulate a relatively fast throughput and demanding shift requirements, which include a low H_2O:CO ratio ($\sim$1.0) and high CO:CO_2 ratio ($\sim$4.0). Fig. 1 shows the CO conversion as a function of Pd:Zn molar ratio at a reaction temperature of 325 °C. While CO conversion slightly increases with the Pd:Zn ratio from 0.28 to 0.50, a sharp decrease in CO conversion from 47 to 24% was observed when Pd:Zn ratio increases from 0.50 to 0.76. However,
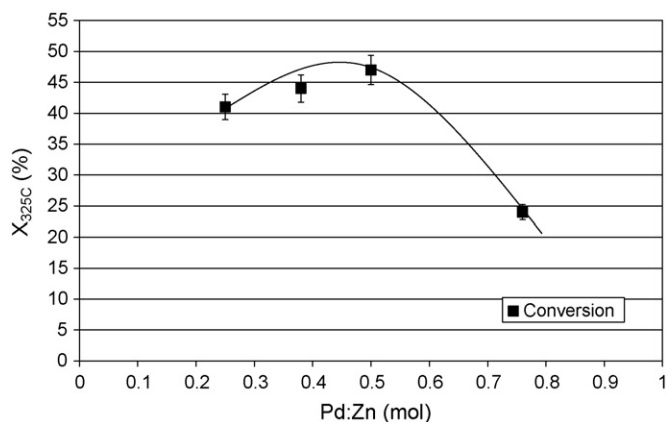
Fig. 1. Effect of Pd:Zn molar ratio on CO conversion under WGS conditions at 325 °C (feed composition: H_2 = 31.6%, CO = 12.6%, CO_2 = 3.2%, H_2O = 12.6%, N_2 = 40.0%, GHSV = 40,000 h^{-1}).