

# Methanol steam reforming over Pd/ZnO catalysts: Nature of the active sites and origin of CO formation

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## Introduction

Pd/ZnO type catalysts reduced at temperatures > 300°C are highly active and selective for H<sub>2</sub> production in methanol steam reforming. Iwasa et al. proposed that the high performance is due to the presence of PdZn alloy, whereas Pd<sup>0</sup> facilitates the formation of undesired CO by methanol decomposition [1]. However, the nature of the active sites and their roles in the origin of CO formation are still not clearly understood.

The objectives of the present work were (1) to investigate the relation between the surface composition (i.e. PdZn/ Pd<sup>0</sup> ratio) and the activity and (2) to provide a better understanding of reaction pathways leading to CO formation. The fundamental understanding gained will guide the design and synthesis of highly selectivity steam reforming catalysts for hydrogen production.

## Materials and Methods

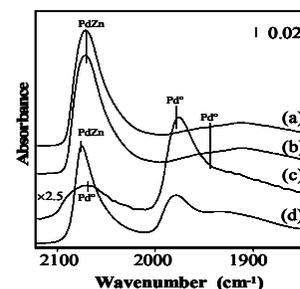
PdZn type catalysts were prepared by an incipient wetness impregnation. Pd/ZnO catalysts were prepared by impregnating ZnO support with palladium II acetate salt dissolved in acetone [2]. Pd/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts were synthesized co-impregnating Pd nitrate and Zn nitrate solutions on alumina support [3]. The catalysts were characterized using BET measurements, H<sub>2</sub> chemisorptions, XRD, and FTIR spectroscopy. Catalytic activity was studied for methanol steam reforming (MSR), the water-gas shift (WGS) and reverse-water-gas shift (RWGS) reactions.

## Results and Discussion

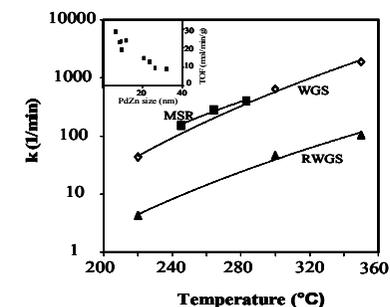
A Pd/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst was studied for MSR after reduction and oxidation treatments. After reduction, the catalyst is highly active and stable (conversion =76%, CO selectivity = 2.3%). Oxidation initially leads to a diminution of the performance, compared to after reduction treatment. However, a significant improvement of the activity was observed after 18 hours time-on-stream (conversion =72%, CO selectivity = 6%). The analysis by CO adsorption, followed by IR spectroscopy, was conducted to determine the nature of the surface species after reduction/oxidation and reaction (Figure 1). The reduction led to the formation of a PdZn alloy. Exposure to the reaction conditions did not affect IR spectra, implying the active species are PdZn alloy. After oxidation, PdZn alloy decomposed and formed the Pd<sup>0</sup> species as confirmed by CO-FTIR. Re-exposure to reaction conditions (a gas feed mixture of H<sub>2</sub>O+CH<sub>3</sub>OH) transformed the Pd<sup>0</sup> to a PdZn alloy. These IR results demonstrate that the PdZn particles are the active species under the reaction conditions.

For MSR, the formation of CO was previously attributed to the decomposition of CH<sub>3</sub>OH on Pd<sup>0</sup> [1]. However, in our studies it was found that CO could also be formed on a Pd/ZnO/Al<sub>2</sub>O<sub>3</sub>

catalyst with only PdZn alloy. To better understand the origin of CO formation, PdZn catalysts were studied for the MSR, WGS and RWGS reactions. Although the kinetic rate constants for MSR and WGS,  $k_{MSR}$  and  $k_{WGS}$ , respectively, were almost the same, WGS is not likely to be involved in MSR since CO selectivity is below the equilibrium values. On the other hand,  $k_{RWGS}$  is 20 times lower than that for MSR and WGS but of the same order of magnitude as the rate constant for CH<sub>3</sub>OH decomposition over Pd<sup>0</sup>. Hence, RWGS could be one possible reaction pathway for CO production during MSR. In MSR, CO selectivity is dependent on the PdZn particles size [4] with low CO formation on large sized PdZn alloy. To verify the involvement of RWGS in the CO production in MSR, a series of Pd/ZnO catalysts with a wide range of PdZn alloy particle size was investigated. It was found that RWGS activity is dependent on the PdZn particles size (inset Figure 2), i.e., TOF is lower on larger sized PdZn alloy for RWGS. It is likely that large sized PdZn alloy particles have less number of defect sites and defect sites may favor methanol decomposition or CO<sub>2</sub> and/or H<sub>2</sub> adsorption, leading to CO formation. These findings provide insights about the origin of active sites for MSR and guidance on the synthesis of highly active and selective MSR catalysts for hydrogen production.



**Figure 1:** IR spectra recorded (a) after reduction, (b) after (a) and exposure to H<sub>2</sub>O/MeOH, (c) after oxidation and (d) after (c) and exposure to H<sub>2</sub>O/MeOH.



**Figure 2:** Rate constant as a function of the temperature for MSR, the WGS and RWGS reactions. Inset TOF for the RWGS reaction as a function of the PdZn particles size (nm)

## Significance

Fundamental understanding of the active sites and reaction pathways to CO formation on the PdZn alloy catalysts provides insight into the structure and function relationship on bimetallic catalysts and is critical to improve catalyst design.

## References

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