

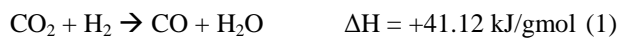
Reverse water gas shift reaction over Pt nanoparticles supported on oxygen ion conductive ceramics

Elena A. Baranova, Maxime Lortie, Spyridon Ntais, Rima J. Isaifan

Department of Chemical and Biological Engineering, Centre for Catalysis Research and Innovation, University of Ottawa 161 Louis-Pasteur Ottawa ON K1N 6N5 Canada

Yttria-stabilized zirconia (YSZ) and doped ceria (Sm-CeO<sub>2</sub> or Gd-CeO<sub>2</sub>) conductive ceramics are widely used in the solid oxide fuel cell and sensor technologies as well as in electrochemical promotion of catalysis (EPOC) [1]. Recently, these materials in the form of powders have attracted considerable attention as a support for the metal or metal oxide catalyst particles in heterogeneous catalysis for oxidation of volatile organic compounds (VOCs) [2, 3]. The presence of mobile O<sup>2-</sup> species can strongly alter the catalytic activity of the nanoparticle catalysts via *in-situ* modification of the catalyst work function due to the thermal migration of the O<sup>2-</sup> species from the support onto the surface of the nano-catalyst. In addition an electrochemical exchange at the triple phase boundary between nanoparticles and conductive ceramics could take place contributing to the overall catalytic activity increase [3].

The reaction of carbon dioxide hydrogenation has gained growing attention in the carbon capture technologies for the production of industrially viable chemicals, such as long chain hydrocarbons, methanol, formic acid and carbon monoxide [4]. When co-feeding CO<sub>2</sub> and H<sub>2</sub> over a hydrogenation catalyst, there are two main processes that can take place, i.e.:



The former is the reverse water-gas shift reaction (RWGS), which is a redox reaction, the latter is a synthesis reaction leading to the formation of hydrocarbons or/and alcohols. Thus, for  $x = 1$ ,  $y = 4$  and  $z = 0$ , one has the methanation reaction, and for  $x = 1$ ,  $y = 4$  and  $z = 1$ , one has the methanol synthesis reaction.

When CO is selectively formed (eq.1) and combined with H<sub>2</sub>, the resulting syngas can be used as a feed-stock for the Fischer Tropsch process [4]. The major drawback for this process is that CO<sub>2</sub> is a thermodynamically stable molecule, therefore high temperatures are required to overcome the activation energy of this reaction. Development of efficient catalysts would minimize the activation energy, resulting in lower temperatures and ultimately, lower costs.

In the present work Pt nanoparticles (3.8 ± 0.2 nm) interfaced with O<sup>2-</sup> conductive YSZ and non-ionically conductive carbon and gamma-alumina (γ-Al<sub>2</sub>O<sub>3</sub>) supports are investigated for RWGS reaction in the temperature range of 300 – 800 °C. Detailed investigation of the effect of metal-support interaction on RWGS reaction and CO production is presented.

The experimental procedure consisted of placing 50 mg of the catalyst (1 wt% of Pt on the support) in a quartz, 35 mL reactor. Gases mixture of H<sub>2</sub> (1007 ppm certified balance He, Linde), CO<sub>2</sub> (1004 ppm certified balance He, Linde) are passed through the reactor. The effluent is dehumidified and sent to a mass spectrometer (Ametek Proline) for gas analysis.

Pt nanoparticles are synthesized using the

modified polyol method in ethylene glycol [5] and deposited on 8 mol% Y<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub> (Tosoh, specific surface area (a<sub>s</sub>) ~13 m<sup>2</sup>·g<sup>-1</sup>), SDC (Fuel Cell Materials, a<sub>s</sub> = 35 m<sup>2</sup>·g<sup>-1</sup>) carbon black (Vulcan XC-72R, Cabot Corp, a<sub>s</sub> = 254 m<sup>2</sup>·g<sup>-1</sup>) and γ-Al<sub>2</sub>O<sub>3</sub> (Alfa - Aesar, a<sub>s</sub> = 120 m<sup>2</sup>·g<sup>-1</sup>), resulting in ≤ 1wt % of metal on the support. Catalytic activity measurements were carried out for 3 cycles in order to examine catalytic stability and reproducibility.

The lowest catalytic activity observed were that of Pt on non-conductive supports (γ-Al<sub>2</sub>O<sub>3</sub> and C). An increase of 12% in CO<sub>2</sub> conversion is observed when YSZ is used as a support. For all catalysts, the selectivity towards CO production was found to be close to 100%. In addition, γ-Al<sub>2</sub>O<sub>3</sub> was the only catalyst that exhibited catalytic deactivation while all other catalyst showed consistent, reproducible results. A deactivation of 8 % in conversion was observed with the γ-Al<sub>2</sub>O<sub>3</sub> supported catalyst from the first cycle to the last. The highest observed CO<sub>2</sub> conversion was 32% at 750°C using Pt/YSZ. Both Pt/C and Pt/γ-Al<sub>2</sub>O<sub>3</sub> had a maximum conversion of 21% at 750°C.

The significant increase in CO<sub>2</sub> conversion observed with YSZ could be attributed to the strong metal support interaction (SMSI). This phenomenon as well as the self-induced electrochemical promotion of RWGS over Pt/ionically conductive supports will be discussed.

#### References:

1. C.G. Vayenas, S. Bebelis, C. Pliangos, S. Brosda, D. Tsiplakides, New York, 2001.
2. P. Vernoux, M. Guth, X. Li, *Electrochem. Solid-St. Lett.* 12 (2009) E9.
3. R.J. Isaifan, E.A. Baranova, *Electrochem. Commun.* 27 (2013) 164.
4. W. Wang, S. Wang, X. Ma, J. Gong, *Chem.Soc. Rev.* 40 (2011).
5. E. Baranova, C. Bock, D. Ilin, D. Wang, and B. MacDougall, *Surf. Sci.* 600 (2006) 3502.