

## Efficient Bi-functional Catalyst for Single Stage Water Gas Shift Conversion for Fuel Cell Applications

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### Introduction

Currently, there is growing interest in the development of single stage water-gas-shift (WGS),  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ , conversion catalysts due to its key role to generate  $\text{H}_2$  for fuel cells. The two stage WGS, used presently at industrial scale is not an appropriate choice for small-scale applications (fuel cell cars) because of its technical complexity [1]. Supported noble metal catalysts (Pt, Ru, and Rh) are promising “single stage” WGS catalysts because they are robust, stable during start-up – shutdown cycles [1]. Due to availability and cost of noble metals, Pt is often the metal chosen. Since Pt is not able to activate water [2], bi-functional, hydrophilic oxide supported catalysts are needed [3, 4], where platinum activates CO and support activates  $\text{H}_2\text{O}$ . Two pathways for water activation on the support are proposed in literature [3, 4]. Water can either help re-oxidise the support in a red-ox cycle or form hydroxyl groups which complete the WGS reaction. In this communication, we report on the nature of the support and its influence on the WGS reaction with an aim to develop active and stable catalysts for single stage commercial application in fuel cells.

### Materials and methods

A series of Pt (0.5wt%) based catalysts were prepared by wet impregnation of oxide supports ( $\text{ZrO}_2$ ,  $\text{CeO}_2$ ,  $\text{Ti}_{0.5}\text{Ce}_{0.5}\text{O}_2$  and  $\text{TiO}_2$ ) with aqueous solutions of  $\text{H}_2\text{PtCl}_6$ . The surface areas were measured by the BET method using ASAP 2400 (Micromeritics). Platinum loading was determined using a Philips X-ray fluorescence spectrometer (PW 1480). The mean Pt particle sizes were measured by  $\text{H}_2$  or CO chemisorption using the Chemisorb 2750 (Micromeritics) and transmission electron microscopy (TEM) (Philips CM30).

### Results and Discussion

The mean Pt particle size was comparable in all catalysts ( $1.75 \pm 0.15$  nm, hydrogen chemisorption). The catalysts were tested for WGS reaction under differential conditions at  $300^\circ\text{C}$  (Fig. 1). All the catalysts were selective to hydrogen; methane formation was below detection limits. The most active catalyst is Pt/TiO<sub>2</sub>. Indeed support has a significant influence on the intrinsic activity of the catalyst; the TOF ( $\text{s}^{-1}$ ) for CO conversion changed from 2 for Pt/ZrO<sub>2</sub> to 10 for Pt/TiO<sub>2</sub>. In order to understand the influence of the support on catalyst activity, pulse transient and *in situ* FTIR measurements were carried out under WGS conditions (using CO,  $\text{H}_2\text{O}$  at  $300^\circ\text{C}$ ).

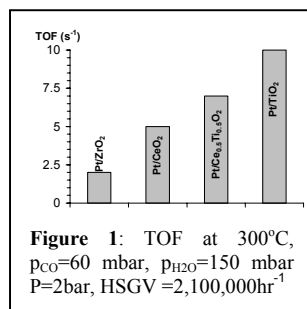


Figure 1: TOF at  $300^\circ\text{C}$ ,  $p_{\text{CO}}=60$  mbar,  $p_{\text{H}_2\text{O}}=150$  mbar,  $P=2$ bar,  $\text{HSGV}=2,100,000\text{hr}^{-1}$

Figure 2 shows that for Pt/CeO<sub>2</sub> catalyst, CO<sub>2</sub> is generated during CO pulses and both CO<sub>2</sub> and H<sub>2</sub> is generated in contacting with H<sub>2</sub>O. Carbon balance and *in situ* FTIR results indicate that 30% of the CO consumed was retained on the catalyst surface as formate and/or carbonate. In case of Pt/TiO<sub>2</sub>, the product compositions were different. CO<sub>2</sub> and H<sub>2</sub> were generated during CO pulses, but only H<sub>2</sub> was produced in contacting with H<sub>2</sub>O. No carbonaceous species were retained on TiO<sub>2</sub> surface. The results of CO/H<sub>2</sub>O pulses and *in situ* FTIR studies over Pt/CeO<sub>2</sub>, Pt/TiO<sub>2</sub>, Pt/ZrO<sub>2</sub> and Pt/Ti<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>2</sub> show that the nature of the support has a crucial role in determining WGS reaction sequences. The support not only determines formation and stability of intermediates but also affects the activation of  $\text{H}_2\text{O}$  (either by formation of surface hydroxyls or oxidation of reduced support forming H<sub>2</sub>).

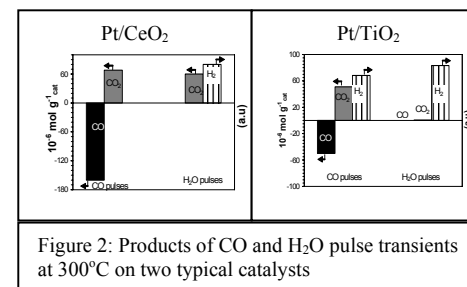


Figure 2: Products of CO and H<sub>2</sub>O pulse transients at  $300^\circ\text{C}$  on two typical catalysts

Even though, Pt/TiO<sub>2</sub> catalyst is very promising (Fig 1) in terms of activity, it lost about 30 -35 % of initial activity after 20 hours on stream. Detailed, kinetic, *in situ* spectroscopic and catalyst characterization studies indicate that sintering of Pt and loss of dispersion is the main reason for deactivation. In order to improve the stability of the catalyst, a new promising catalytic composition containing Pt and Re on TiO<sub>2</sub> support (bi-metallic catalyst) has been developed. This catalyst possesses higher activity than Pt/TiO<sub>2</sub> and is very stable during long-term tests up to  $400^\circ\text{C}$ , (Fig. 3). Our results show that Re anchors the Pt particles and provides extra sites for  $\text{H}_2\text{O}$  activation (rate determining step). This catalyst has high activity and meets the requirements ( $8 \cdot 10^{-5} \text{ mol H}_2 \text{ g}^{-1} \text{ cat} \text{ s}^{-1}$ ) of 50kW fuel cell car using only 1kg catalyst. Kinetic and mechanistic details of WGS reaction, over the studied catalysts, will be discussed.

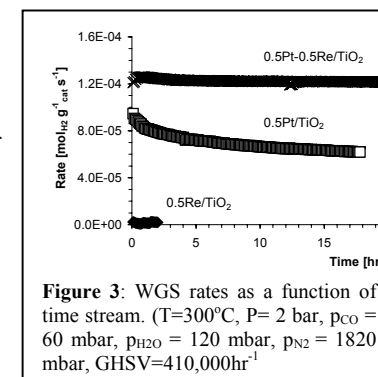


Figure 3: WGS rates as a function of time stream. ( $T=300^\circ\text{C}$ ,  $P=2$  bar,  $p_{\text{CO}}=60$  mbar,  $p_{\text{H}_2\text{O}}=120$  mbar,  $p_{\text{N}_2}=1820$  mbar,  $\text{GHSV}=410,000\text{hr}^{-1}$ )

### References

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