

## Vanadium-modified ceria-based catalysts for water gas shift reaction

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### Introduction

The efficiency of fuel processors for fuel cell applications depends on effective CO removal. In this context, water gas shift reaction (WGS) has been widely studied as it fits well to this process making a primary CO clean up along with a secondary hydrogen production. It can ensure a reduction of CO content in the outlet stream up to 1 vol.%. This stream must be treated by a second purification step that may be CO preferential oxidation (PROX) or PSA device. The whole process must reach a 50 ppm CO concentration to avoid the poisoning of the cell electrode. WGS reaction at relatively low temperature is limited by kinetics, and this is therefore where the current demand for advanced catalysts is the greatest. Noble metal/reducible oxide systems have advantages not shown by the traditional Cu-based catalysts as they can combine high activity and stability. Several metal/support associations have been studied [1,2] and amongst those systems, Pt/CeO<sub>2</sub> catalyst seems to be the most promising, exhibiting good performance. This contribution addresses the effects brought about by adding vanadium to CeO<sub>2</sub>-supported catalysts on catalytic activity, attempting to correlate the systems reactivity properties to the vanadium oxide species.

### Materials and Methods

CeO<sub>2</sub> used as support was synthesized following the procedure described elsewhere [3]. Several modified supports, with different vanadium content, were prepared by impregnation with an aqueous solution of NH<sub>4</sub>VO<sub>3</sub>. Finally, Pt catalysts were prepared by incipient wetness impregnation with a H<sub>2</sub>PtCl<sub>6</sub> solution. The catalysts were characterized concerning their chemical (XRF), textural (N<sub>2</sub> adsorption), structural (XRD, FTIR, Raman) and surface (XPS) properties. Catalytic performance was evaluated on WGS reaction at atmospheric pressure in a fixed bed tubular reactor attached to a gas chromatograph. Samples were submitted to “in situ” reduction step at 350°C under pure hydrogen before reaction at 300°C. The reactant mixture was composed by CO, H<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub> simulating an actual reformat composition.

### Results and Discussion

The catalysts chemical composition, textural and structural data are collected in Table 1. It was seen that the introduction of vanadium on ceria led to a gradual drop in the support oxide surface and it was associated with the incursion of V<sub>2</sub>O<sub>5</sub> into the pore of the support as well as the formation of CeVO<sub>4</sub> on the samples with high vanadium content. The presence of such phases was indeed confirmed by XRD, FTIR and Raman results. As a matter of fact, the results indicated that the vanadium loading and calcination temperature are the leading factors for determining the species to be formed. V-O-V stretching vibrations from polymeric surface vanadate species were detected by Raman for the low vanadium-loading samples. Accordingly, the FTIR spectra presented only one large band at 980 cm<sup>-1</sup> attributed to

the stretching vibrations of the (V=O)<sup>3+</sup> bond of monolayered V(V) species (VO<sub>x</sub>) [4]. Sample 8V-CeO<sub>2</sub> presented two broad bands at 820 and 980 cm<sup>-1</sup> related to vanadium monolayer species and V<sub>2</sub>O<sub>5</sub>/CeVO<sub>4</sub> crystallites, respectively. As for the higher V content, the results revealed that it is marked by a band corresponding only to V<sub>2</sub>O<sub>5</sub>/CeVO<sub>4</sub>. XPS results showed that the majority of vanadium cation population is in V<sup>5+</sup> form and Ce<sup>3+</sup> content increased along with the total vanadium concentration. Indeed, higher Ce<sup>3+</sup> concentration is a consequence of the development of V<sup>3+</sup>-O-Ce<sup>3+</sup> bonds, which has been related to the ability of surface vanadia to remove the most easily reducible surface oxygen of ceria [5]. For loadings below 8% (Table 1) the presence of a narrower distribution of oxidation states, mainly V<sup>5+</sup>, agrees with the formation of monolayer species VO<sub>x</sub> which contains (V=O)<sup>3+</sup> units as also suggested by other spectroscopic techniques.

**Table 1. Chemical composition, surface area, structural analysis and reaction results.**

| Catalyst                | %Pt  | %V    | S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> ) | d <sub>CeO<sub>2</sub></sub> (nm) | r (μmol/g.s) |
|-------------------------|------|-------|--|-----------------------------------|--------------|
| Pt/CeO <sub>2</sub>     | 1.18 | -     | 93   | 8.17                              | 1.9          |
| Pt/0.8VCeO <sub>2</sub> | 1.13 | 0.78  | 68   | 8.10                              | 3.6          |
| Pt/3VCeO <sub>2</sub>   | 1.15 | 3.32  | 65   | 8.13                              | 3.8          |
| Pt/8VCeO <sub>2</sub>   | 1.09 | 8.05  | 50   | 8.36                              | 3.3          |
| Pt/10VCeO <sub>2</sub>  | 1.08 | 10.72 | 35   | 8.65                              | 2.0          |

Catalytic performance was evaluated by calculating the reaction rates (r) at differential conditions and the data are also presented in Table 1. The results showed that the catalysts containing vanadium surface species are more active and a reasonable decrease in CO content could be accomplished over such samples at a wide range of temperature (200 – 350 °C). In conclusion, it may be stated that the presence of submonolayer vanadium content caused an improvement in the redox properties of ceria, creating additional reaction sites. An excess of vanadium amount hindered cerium redox cycle due to the stabilization of 3+ oxidation state mostly as CeVO<sub>4</sub>.

### Significance

This contribution reports on the enhancement in water gas shift reaction activity accomplished over a vanadium-modified Pt/CeO<sub>2</sub> used in a fuel processor system for hydrogen production.

### References

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