

# Study of the water gas shift reaction over Pt/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts

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## Introduction

Pt-based catalysts have been widely investigated in WGS reaction ( $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$ ) because the CO conversion turnover rate is higher on Pt in comparison to other noble metals. In particular, Pt/CeO<sub>2</sub> has been reported as a promising WGS catalyst due to its high activity but deactivates on stream. Several researchers have studied the WGS reaction on Pt/ZrO<sub>2</sub> catalysts due to ZrO<sub>2</sub> high hardness, good mechanical resistance and thermal stability. The WGS reaction has been also studied on Pt supported on binary Ce-Zr mixed oxides, but conclusions regarding catalysts activity and stability are not conclusive. In this work, we study the WGS reaction on Pt/CeO<sub>2</sub>, Pt/ZrO<sub>2</sub> and Pt/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> catalysts.

## Experimental

CeO<sub>2</sub>-ZrO<sub>2</sub> mixed oxides of different compositions (Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub>, Ce<sub>0.50</sub>Zr<sub>0.50</sub>O<sub>2</sub> and Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub>) and pure ZrO<sub>2</sub> were prepared by sol-gel method. Ceria was obtained by precipitation method [1]. Pt-supported catalysts (0.4%) were prepared by incipient-wetness impregnation of the supports with an aqueous solution of [Pt(NH<sub>3</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub>. Samples were characterized by BET surface area, XRD, H<sub>2</sub> chemisorption and TPR. The activity of the catalysts were studied using conversion vs. time tests at 250°C. The reaction was also followed by DRIFTS.

## Results/Discussion

The specific surface areas ( $S_g$ ) and H<sub>2</sub> consumptions determined in TPR experiments of Pt-based catalysts are shown in Table 1. According to these results, introduction of zirconia into ceria lattice increases both the surface area and the reducibility of ceria. By considering that H<sub>2</sub> was totally consumed for reducing Ce<sup>4+</sup> to Ce<sup>3+</sup> species, the values presented in Table 1 imply that on Pt/CeO<sub>2</sub> about 11% of the ceria support was reduced, while on Pt/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub>, Pt/Ce<sub>0.50</sub>Zr<sub>0.50</sub>O<sub>2</sub> and Pt/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> the amounts of reduced ceria were 26, 28 and 31%, respectively. In addition, catalyst activities for the WGS reaction were determined at 250°C. Turnover frequencies followed the order: Pt/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> > Pt/Ce<sub>0.50</sub>Zr<sub>0.50</sub>O<sub>2</sub> > Pt/CeO<sub>2</sub> >

Pt/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> > Pt/ZrO<sub>2</sub> (Table 1). WGS activity on Pt/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> catalysts depends on the chemical composition of support. On Pt/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> samples with  $x \geq 0.5$ , the WGS turnover rate is higher than on Pt/CeO<sub>2</sub>. The increase in ceria reducibility as a result of zirconia incorporation into ceria lattice increases also the concentration of surface OH groups that are formed on Ce<sup>3+</sup> reduced sites.

Table 1. Characterization and catalytic activity of Pt-supported catalysts

Catalyst	$S_g$ (m <sup>2</sup> g <sup>-1</sup> )	D <sub>Pt</sub> (%)	H <sub>2</sub> consumption (μmol H <sub>2</sub> g <sub>cat</sub> <sup>-1</sup> )	r <sub>CO</sub> <sup>0</sup> (mol CO g <sub>Pt</sub> <sup>-1</sup> h <sup>-1</sup> )	TOF (h <sup>-1</sup> )
Pt/CeO <sub>2</sub>	41	37	316	2.440	1304
Pt/Ce <sub>0.75</sub> Zr <sub>0.25</sub> O <sub>2</sub>	84	40	576	3.165	1544
Pt/Ce <sub>0.50</sub> Zr <sub>0.50</sub> O <sub>2</sub>	73	48	410	3.315	1347
Pt/Ce <sub>0.25</sub> Zr <sub>0.75</sub> O <sub>2</sub>	62	46	229	2.585	1096
Pt/ZrO <sub>2</sub>	45	73	131	1.207	323

The WGS associative mechanism on Pt supported on ceria-based solids would occur via the formation of formate species that is promoted by the presence of terminal OH groups on partially reduced ceria. Thus, the superior WGS activity exhibited by Ce-rich Pt/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> samples may be explained by considering that a higher concentration of surface OH groups is formed on these samples during the sample reduction step. In contrast, the WGS activity on Pt/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> is lower than on Pt/CeO<sub>2</sub> probably because the formate species stability increases on Zr-rich Pt/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> samples. As a matter of fact, we purged catalytic systems with Ar at 250°C after WGS reaction and collected DRIFTS spectra (Figure 1) which confirmed the presence of adsorbed formate species on Zr-rich Pt/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> samples. These results suggest that the formate decomposition rate could be rate-limiting in the WGS associative mechanism on Zr-rich Pt/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> samples as proposed in [2].

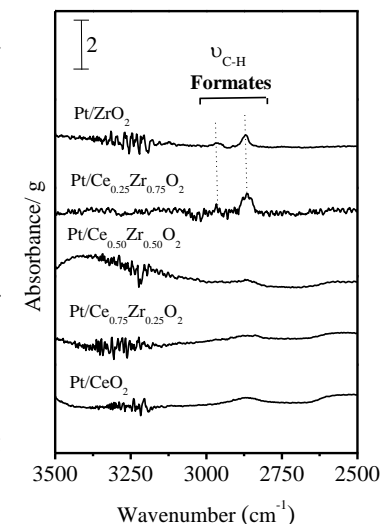


Figure 1. DRIFTS spectra in the formate  $\nu_{\text{C-H}}$  region after Ar treatment at 250°C.

## References

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2. C.I. Vignatti, M.S. Avila, C.R. Apesteguía, T.F. Garetto, *Catal. Today* (2011), doi:10.1016/j.cattod.2010.12.041