



# Effect of Re addition on the WGS activity and stability of Pt/CeO<sub>2</sub>–TiO<sub>2</sub> catalyst for membrane reactor applications



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## ABSTRACT

The catalytic performance of RePt/CeO<sub>2</sub>–TiO<sub>2</sub> catalysts for the WGS reaction under conditions compatible with membrane reactor was investigated. The WGS activity and stability of the Pt/CeO<sub>2</sub>–TiO<sub>2</sub> catalyst was significantly influenced by the addition of rhenium. The intrinsic WGS activity per atom of platinum improves with the addition of Re to Pt/CeO<sub>2</sub>–TiO<sub>2</sub> catalyst. The addition of rhenium also has a beneficial effect on its stability under WGS conditions compatible with membrane reactor use. The improvement in WGS activity and stability is proposed to be associated with the improvement in the reduction behavior of the highly dispersed CeO<sub>2</sub> and ReO<sub>x</sub> species present in the bimetallic RePt catalyst respect to the monometallic Pt/CeTi counterpart and to the presence of rhenium species in close contact with Pt that could introduce an additional redox activity sites stable under WGS conditions and/or prevent the sintering of Pt crystallites under WGS conditions.

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## 1. Introduction

An innovative approach for the improvement of the water gas shift (WGS) reaction is the use of fluidized membrane reactors, combining the WGS reaction and H<sub>2</sub> separation through a selective Pd membrane [1,2]. However, the feasibility of the WGS membrane reactor requires the development of advanced WGS catalysts because the use of conventional high-temperature WGS catalysts based on Fe–Cr oxides implies high reactor size and careful control of temperature, H<sub>2</sub>O/H<sub>2</sub> and CO<sub>2</sub>/CO ratios. For such reasons the interest in the development of new water–gas shift catalysts compatible with membrane reactor has grown significantly along the last few years. In this perspective, the development of new WGS catalysts based on supported platinum has received much interest during last decades because of their high activity at temperatures compatible with Pd membranes ( $T > 400^\circ\text{C}$ ). Among the various Pt-support combinations examined in bibliography [3–16], the Pt supported on CeO<sub>2</sub> dispersed over a TiO<sub>2</sub> matrix has shown remarkable activity in the WGS reaction [14–16]. Model and theoretical

studies on CeO<sub>2</sub>–TiO<sub>2</sub> support [17–20] have suggested that the high WGS activity on this support is associated to the presence of CeO<sub>2</sub> clusters of high reducibility that improve the chemical activity of the oxide–metal interfaces at which the WGS reaction takes place. In spite of the fact that Pt/CeO<sub>2</sub>–TiO<sub>2</sub> is a promising WGS formulation, this catalyst deactivates under membrane WGS conditions by loss of Pt metal surface and irreversible over-reduction of CeO<sub>2</sub> and TiO<sub>2</sub> surface species. Recently, the use of bimetallic Re–Pt formulations offered improved stability and activity compared to monometallic Pt formulations supported on TiO<sub>2</sub> [8,21,22] and Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> [23]. The origin of the high WGS activity and stability of bimetallic Re–Pt WGS catalyst is still a matter of debate. For instance, Sato et al. [22] claimed that the higher WGS activity of bimetallic Re–Pt catalyst is derived from the formation of bimetallic clusters containing Pt and Re, while other authors [8] postulate that the high WGS activity of the Re–Pt catalyst is related with the improved Pt dispersion. Azzam et al. [21] have recently reported that addition of Re to Pt/TiO<sub>2</sub> catalysts induced two effects: (i), stability is improved by preventing Pt particles to sinter, and (ii), the activity of the Pt increases significantly due to an increase in the rate of dissociation of water. Following the improvement in activity and stability observed for bimetallic Re–Pt formulations supported on TiO<sub>2</sub> and Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub>, in this work we study if the addition of

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**Table 1**  
Labeling and nominal composition of Pt catalysts.

Sample	Pt (wt%)	Re (wt%)	Re/Pt at
Pt/CeO <sub>2</sub> -TiO <sub>2</sub>	0.5	–	–
RePt/CeO <sub>2</sub> -TiO <sub>2</sub>	0.34	0.16	0.50

rhenium has the same effect on the activity/stability of Pt catalysts supported on CeO<sub>2</sub>-TiO<sub>2</sub>. For that purpose we studied the influence of the Re addition on the structural and chemical properties of Pt/CeO<sub>2</sub>-TiO<sub>2</sub> catalysts and their role on the activity for the WGS reaction under conditions compatible with Pd membrane reactors. Careful characterization of Pt-Re/CeO<sub>2</sub>-TiO<sub>2</sub> catalysts was done in an attempt to better understand the role played by Re on Pt particles when supported on CeO<sub>2</sub>-TiO<sub>2</sub>. In fluidized Pd membrane reactors, catalyst particles suffer strong mechanical stress due to fluidization. Therefore the mechanical stability of the RePt/CeO<sub>2</sub>-TiO<sub>2</sub> catalyst particles has also been investigated under fluidizing conditions. Finally, in order to predict the performance of the bimetallic RePt/CeO<sub>2</sub>-TiO<sub>2</sub> catalyst at different inlet gas compositions, the effect of variation in the concentration of CO, H<sub>2</sub>O, H<sub>2</sub> and CO<sub>2</sub> on the WGS reaction rate was also investigated.

## 2. Materials and methods

### 2.1. Catalysts preparation

The ceria-titania support (CeO<sub>2</sub>-TiO<sub>2</sub>, 6 wt% Ce) consisting of CeO<sub>2</sub> nanoentities dispersed on TiO<sub>2</sub> were prepared by wet impregnation of TiO<sub>2</sub> (titanium (IV) oxide, anatase, Alfa Aesar) with aqueous solution of cerium nitrate (Alfa Aesar, Reacton 99.5%). After cerium impregnation, the solid was dried under air at 110 °C and subsequently calcined in air at 600 °C for 8 h. The supported Pt catalyst (Pt/CeO<sub>2</sub>-TiO<sub>2</sub>) was prepared by impregnation of the CeO<sub>2</sub>-TiO<sub>2</sub> support using appropriate quantities of aqueous solution of Pt precursor (H<sub>2</sub>PtCl<sub>6</sub> Johnson-Matthey) to achieve a 0.5 wt% metal loading. After Pt-loading, the sample was dried at 80 °C overnight and subsequently it was calcined in air at 500 °C for 4 h. The supported Re-Pt catalyst (RePt/CeO<sub>2</sub>-TiO<sub>2</sub>) was prepared by sequential impregnation of Pt/CeO<sub>2</sub>-TiO<sub>2</sub> (0.34 wt% Pt) using aqueous solution of rhenium precursor (NH<sub>4</sub>ReO<sub>4</sub> Alfa Aesar). After Re-loading, the sample was dried at 80 °C overnight and calcined in air at 500 °C for 4 h. The Pt:Re atomic ratio was 1:0.5. Table 1 summarizes the labeling and nominal composition of prepared catalysts.

### 2.2. Catalysts characterization

Chemical analyses of the catalysts were carried out on an ICP-AES Perkin-Elmer Optima 3300 DV spectrometer. Textural properties of the catalyst were obtained from the nitrogen adsorption isotherms measured at -196 °C using a Micromeritics ASAP 2100 instrument. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. Prior to the measurements, the samples were degassed under vacuum at 200 °C for 12 h. XRD patterns of both powdered fresh and used catalysts were recorded at room temperature on a Seifert XRD 3000P diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). XRD patterns were collected in the range of  $2\theta$  from 4°–90° (0.02°/step, integration time of 50 s/step). Identification of the phases was achieved by reference to the JCPDS diffraction data file.

Metallic dispersion was evaluated by CO pulse chemisorption in a Micromeritics TPD/TPR 2900 instrument. Firstly, the samples, ca. 0.5 g were reduced in H<sub>2</sub>/Ar flow (50 mL min<sup>-1</sup>) at 300 °C during 1 h. Afterwards, the hydrogen retained by catalyst was removed by purging the cell under inert flow (Ar) during 15 min and then

the samples were passivated with oxygen and subsequently saturated with CO<sub>2</sub> at atmospheric pressure. After that, passivated catalyst was treated with hydrogen at 300 K to further reduce the passivated Pt particles. Pulses (0.1 mL each) of CO were injected at 1 min intervals until no further gas uptake by the catalyst was observed as indicated by constant peak areas of the last injections. The total amount of adsorbed gas was calculated by adding the gas uptake observed in the series of gas injections until saturation was reached. In order to calculate the metal dispersion an adsorption stoichiometry of Pt/CO = 1 was assumed.

H<sub>2</sub>-temperature-programmed reduction of the catalysts was carried out using a Micromeritics TPR/TPD 2900 instrument in a U-shaped quartz reactor. The fresh and used catalysts were reduced with 50 mL (STP) min<sup>-1</sup> of 10 vol% H<sub>2</sub>/Ar reducing mixture. The temperature was progressively increased from room temperature (RT) up to 800 °C at a linearly programmed rate of 10 °C min<sup>-1</sup>.

Analysis of the morphology and particle size was determined by TEM micrographs obtained in a field emission scanning electron microscopy (FE-SEM) using a JEOL 2100F (200 kV) Microscope. Samples were dispersed on carbon grids after sonicating the samples in ethanol for 0.5 h.

DRIFT spectra of chemisorbed CO were performed with a JASCO FTIR 6300 spectrometer equipped with a liquid-nitrogen-cooled MCT detector and a KBr beam splitter. Experiments were performed using a DRIFT chamber (Spectra Tech) with ZnSe windows directly connected to a flow system equipped with mass flow controllers that allowed selection of feed gas composition. The catalysts were calcined *in situ* under air flow from room temperature to 450 °C, and reduced in H<sub>2</sub>/He 10 vol% flow from room temperature to 300 °C at a heating rate of 5 °C min<sup>-1</sup> and finally flushing under He flow (20 mL min<sup>-1</sup>). For DRIFTS experiments CO was introduced into the DRIFT chamber at room temperature by flowing He/CO (5 vol% CO) (25 mL min<sup>-1</sup>) by 0.5 h. The spectra were recorded at room temperature after flushing under He flow for 0.5 h.

Mechanical stability of the catalyst particles (15 g) was tested under bubbling fluidizing regime with N<sub>2</sub> flow for 48 h. Fluidizing tests were performed at ambient temperature and 450 °C to simulate the WGS reaction temperature. The size distribution of the particles was determined before and after each fluidizing experiments *via* laser diffraction with a Fritsch Analysette 22 in wet conditions.

### 2.3. WGS catalytic activity

Water Gas Shift experiments were carried out in a continuous tubular fixed-bed quartz reactor (9 mm internal diameter) at atmospheric pressure using 0.1 g of catalyst sieved between 212 and 425  $\mu\text{m}$  particle size. The samples were calcined at 450 °C and activated by reduction *in situ* at 220 °C for the supported-Pt catalyst or 300 °C for the supported-RePt catalyst, with a 10 vol% H<sub>2</sub>/N<sub>2</sub> mixture flow for 1 h before reaction. Subsequently, the reduced catalysts were tested at atmospheric pressure with a mixture of H<sub>2</sub>/CO<sub>2</sub>/CO/H<sub>2</sub>O/CH<sub>4</sub>/N<sub>2</sub> simulating biogas syngas (0.21/0.16/0.23/0.36/0.02/0.02 mol) and SV = 23,230 L h<sup>-1</sup> kg<sub>cat</sub><sup>-1</sup>. Activity tests were performed at 400 °C (compatible with Pd membranes) maintaining the reaction for 20 h. The reaction products were analyzed on-line by GC with TCD (Agilent) equipped with Porapak Q (CO<sub>2</sub>) and molecular sieve 5A (H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO, H<sub>2</sub>O, CH<sub>4</sub>) packed columns connected in series, using He as carrier gas. Activity data were reported as carbon monoxide conversion:

$$\text{CO}(\%) = ([\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}})/[\text{CO}]_{\text{in}}$$

Accurate kinetic rate expression for the WGS reaction on the PtRe/CeO<sub>2</sub>-TiO<sub>2</sub> catalyst was derived from kinetic studies performed using a small amount of the catalyst (0.5 g, size

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