Highly dispersed Pt$^{\delta+}$ on Ti$_x$Ce$_{(1-x)}$O$_2$ as an active phase in preferential oxidation of CO

S. Rico-Francés [a], E.O. Jardim [a], T.A. Wezendonk [b], F. Kapteijn [b], J. Gascon [b], A. Sepúlveda-Escribano [a], Enrique V. Ramos-Fernandez [a],[*]

[a] Laboratorio de Materiales Avanzados, Departamento de Química Inorgánica – Instituto Universitario de Materiales de Alicante. Universidad de Alicante, Apartado 99, E-03080 Alicante, Spain

[b] Catalysis Engineering, Chemical Engineering Department, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

ARTICLE INFO

ABSTRACT

Structure–activity relationships for 1 wt.% Pt catalysts were investigated for a series of Ti$_x$Ce$_{(1-x)}$O$_2$ ($x = 1$, 0.98, 0.9, 0.5, 0.2 and 0) supports prepared by the sol–gel method. The catalysts prepared by impregnation were characterized in detail by applying a wide range of techniques as N$_2$-isotherms, XRF, XRD, Raman, XPS, H$_2$-TPR, Drifts, UV–vis, etc. and tested in the preferential oxidation of CO in the presence of H$_2$. Also several reaction conditions were deeply analyzed. A strong correlation between catalyst performance and the electronic properties let us to propose, based in all the experimental results, a plausible reaction mechanism where several redox cycles are involved.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Hydrogen production and purification are two processes of great interest nowadays. On the one hand, hydrogen is used in large amounts in refineries and considered as a green energy carrier. When used as fuel in Proton Exchange Membrane Fuel Cells (PEMFC) electricity can be produced in a very efficient manner. On the other hand, hydrogen is typically produced by steam reforming of methane. After the steam reforming unit, the stream contains elevated CO amounts that need to be reduced below 10 ppm, which is the maximum tolerable level for platinum electrodes used in PEMFC. The first purification step is carried out by a two-step Water Gas Shift (WGS) process, at high and at low temperature; however, the remaining CO concentration is still above the tolerable level for PEMFC. Therefore, further purification is required. Several options compete for CO removal: membranes, methanation and preferential oxidation to CO$_2$, the latter being the most promising one [1,2].

An efficient catalyst for the PROX reaction should convert CO to CO$_2$ and should not promote the competing oxidation of H$_2$. Indeed, such an ideal catalyst should convert CO molecules in the presence of an excess of H$_2$, together with other components that can negatively affect the activity, like H$_2$O or CO$_2$.

Cerium oxide has been proven as an efficient catalyst support to be used for this reaction. Mechanistic studies have shown that the oxygen lattice plays an important role in the reaction, since it follows a Mars van Krevelen mechanism [3]. It means that CO is chemisorbed on the Pt nanoparticles and oxygen is supplied by the support, generating reduced Ce(III) cations that are oxidized back with oxygen from the feed. In this way, the support plays a vital role in the reaction. It is well known that the incorporation of a second metal in the CeO$_2$ lattice can enhance ceria reducibility. ZrO$_2$ oxide is the most studied dopant by far, as it can increase the oxide reducibility over an order of magnitude [4,5]. However, ZrO$_2$ is very inert and cannot be reduced even at high temperatures in the presence of H$_2$. It means that part of the mixed metal support (ZrO$_2$–CeO$_2$) is not reducible. Based on our knowledge about doped ceria, in this work we present the use of TiO$_2$–CeO$_2$ solid solutions as supports; a mixture of reducible oxides (Ti^{4+} and Ce^{4+}) will eventually improve the performance. If both oxides synergistically participate in the Mars van Krevelen mechanism, an improve of catalytic performance might be produced.

* Corresponding author. Tel.: +34 96 590 9350; fax: +34 965909820.
E-mail address: Enrique.ramos@ua.es (E.V. Ramos-Fernandez).

Table 1
Chemical composition of the Pt/Ti$_x$Ce$_{(1-x)}$O$_2$ catalysts, with x = 1, 0.98, 0.9, 0.5, 0.2 and 0.

	Ti content, (at.%)	Ce content, (at.%)	Pt dispersion[a] (%)	TOF (60 °C) s^{-1}
Pt/TiO$_2$	100	0	12.6	0.0259
Pt/Ti$_{0.98}$Ce$_{0.02}$O$_2$	97	3	58.2	0.0393
Pt/Ti$_{0.9}$Ce$_{0.1}$O$_2$	84	16	78.1	0.0546
Pt/Ti$_{0.5}$Ce$_{0.5}$O$_2$	55	45	85.3	0.0661
Pt/Ti$_{0.2}$Ce$_{0.8}$O$_2$	20	80	75.7	0.0242
Pt/CeO$_2$	0	100	58.9	0.0058

[a] Calculated by CO chemisorption, assuming 1CO:1Pt stoichiometry.

2. Experimental

2.1. Synthesis of supports and catalysts

Ti$_x$Ce$_{(1-x)}$O$_2$ supports with different molar compositions (x = 1, 0.98, 0.9, 0.5, 0.2 and 0), were synthesized using the sol–gel method [6]. The proper amount of cerium nitrate (Ce(NO$_3$)$_3$·6H$_2$O, 99.00% Aldrich) was dissolved in an aqueous HNO$_3$ solution (0.02 M) contained in a round bottom flask. Then, titanium iso-propoxide (Ti[OCH(CH$_3$)$_2$]$_4$, 97.00% Aldrich) was added drop-wise under continuous stirring. A white precipitate appeared. The suspension was heated for 30 min at 80 °C under stirring. In this step, a fraction of the alcohol formed after alkoxide hydrolysis was evaporated. In order to obtain a complete gelification, the suspension was refluxed at 80 °C for two hours. The gel obtained was dried in an oven at 40 °C for 8 days. Pure TiO$_2$ was prepared following the same procedure, using only titanium precursor. Furthermore, pure CeO$_2$ support was prepared by homogeneous precipitation with the same cerium precursor and urea (Fluka, 98%) dissolved in ultrapure water. The mixture was heated at 90 °C with constant stirring during 11 h. At the end, ammonia solution was added drop-wise to complete precipitation. The solid was separated by filtration and washed with ultrapure water. Finally, the solids prepared were calcined at 500 °C for 5 h, with a heating rate of 2 °C min^{-1}.

For catalysts preparation, the supports were impregnated with an aqueous solution of the platinum precursor (H$_2$PtCl$_6$·6H$_2$O, Alfa Aesar 99.90%, 10 ml g^{-1} support) of the adequate concentration to load 1 wt.% Pt. The slurry was stirred for 12 h at room temperature in a rotary evaporator, and then the solvent was removed under vacuum at 70 °C. After drying, the solids were calcined at 500 °C for 2 h, with a heating rate of 3 °C min^{-1}.

2.2. Characterization of supports and catalysts

The composition of the supports was determined by X-Ray fluorescence (XRF). An X-Ray sequential spectrometer (PHILIPS MAGIX PRO) equipped with a rhodium X-ray tube and beryllium window was used. The textural properties of the supports were characterized by N$_2$ adsorption–desorption measurements at −196 °C. Gas adsorption experiments were performed in homemade fully automated manometric equipment. Prior to the adsorption experiments, samples were out-gassed at 250 °C for 4 h under vacuum (10^{-4} Pa). The "apparent" surface area was estimated after application of the BET equation.

X-Ray powder diffraction patterns were recorded on a Bruker D8-Advance system with a Göebel mirror and a Kristalloflex K 760-80 F X-Ray generator, fitted with a Cu cathode and a Ni filter. Diffractograms were registered between 20 and 80° (2θ) with a step of 0.1° and a time per step of 3 s.

X-ray photoelectron spectroscopy (XPS, K-ALPHA, Thermo Scientific) was used to analyze the catalysts surface. All spectra were collected using Al–K radiation (1486.6 eV), monochromatized by a twin crystal monochromator, yielding a focused X-ray spot with a diameter of 400 µm, at 3 mA × 12 kV. The alpha hemispherical analyzer was operated in the constant energy mode with survey scan pass energies of 200 eV to measure the whole energy band and 50 eV in a narrow scan to selectively measure the particular elements. Thus, XPS was used to assess the chemical bonding state as well as the elemental composition of the sample surface. Charge compensation was achieved with the system flood gun that provides low energy electrons and low energy argon ions from a single source. The intensities were estimated by calculating the integral of each peak, after subtraction of the S-shaped background and by fitting the experimental curve to a combination of a Lorentzian (30%) and Gaussian (70%) lines [7]. All binding energies (BE) were referenced to the C 1s line at 284.6 eV, which provided binding energy values with an accuracy of ±0.2 eV. The surface atomic ratios were estimated from the integrated intensities corrected by the atomic sensitivity factors.

Temperature-programmed reduction with H$_2$ (H$_2$-TPR) experiments were carried out in a U-shaped quartz cell reactor using a 5% H$_2$/He gas flow of 50 cm^3 min^{-1}, with a heating rate of 10 °C min^{-1}. Previous to the TPR run, the samples (100 mg) were treated with flowing 50 cm^3 min^{-1} of He at 150 °C for 2 h. Hydrogen consumption was followed by on-line mass spectrometry calibrated by carrying out the reduction of CuO and assuming complete reduction to metallic copper.

Raman spectra were recorded on a LabRam spectrometer (Jobin-Yvon Horiba) coupled to an Olympus microscope with a lens of 50×/0.5LMPlanFI. He/Ne laser excitation source (633 nm) was used, and the spectrometer resolution in these conditions was 3 cm^{-1}. The wavelength was calibrated using Si signal at 520 cm^{-1}.

The UV–vis spectroscopy analysis was carried out in a Jasco V-650, a double-beam spectrophotometer with a photomultiplier tube detector. The high sensitivity of the photomultiplier tube detector enables accurate measurements of low concentration samples. The accessory used for measure the solid samples is an integrating sphere ISV-722 UV–vis. Spectra were taken in the wavelength range of 200–800 nm (scan speed 400 nm min^{-1} and data interval of 1 nm).

Nicolet 6700 FT-IR (Thermo Scientific) spectrometer equipped with MCT-A detector and high-temperature DRIFTS cell (spectral resolution 4 cm^{-1}) was used to study CO adsorption on the catalyst, obtaining information about Pt coordination and electronic structure. Spectra were recorded at room temperature after calcinations in air at 500 °C followed by a reduction with H$_2$ flow at 250 °C and CO adsorption (0.5% and 1% CO flow until saturation) at 25 °C. After flushing with He (50 cm^3 min^{-1}), temperature was increased and spectra were taken every 50 °C until achieving 500 °C. Each reported spectrum is an average of 280 scans.

CO chemisorption studies were carried out in the Micromeritics ASAP 2020C system. The purity of all gases used was greater than 99.999%. In a typical analysis, 0.3–0.4 g of sample was pretreated in flowing He at 120 °C for 2 h, followed by evacuation at 120 °C. Afterwards, the sample was reduced in-situ by flowing H$_2$ at 250 °C for 1 h. This temperature was maintained during evacuation at 5 Pa for 2 h. The sample was subsequently cooled down to the analysis temperature of 35 °C. The ramp rate for heating and cooling was fixed at 5 °C min^{-1}. Adsorption measurements were carried out at partial CO pressures from 80 to 600 Torr. First, the total CO adsorption