Applied Catalysis B: Environmental 113–114 (2012) 72–78

Contents lists available at SciVerse ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Superior performance of multi-wall carbon nanotubes as support of Pt-based catalysts for the preferential CO oxidation: Effect of ceria addition

E.O. Jardim, M. Gonçalves, S. Rico-Francés, A. Sepúlveda-Escribano, J. Silvestre-Albero*

Laboratorio de Materiales Avanzados, Departamento de Química Inorgánica-Instituto Universitario de Materiales, Apartado 99, E-03080 Alicante, Spain

ARTICLE INFO

Article history:
Received 27 August 2011
Received in revised form 7 November 2011
Accepted 8 November 2011
Available online 20 November 2011

Keywords:
CO oxidation
PROX
CNT
CeO_2
Platinum

ABSTRACT

Preferential oxidation of CO in excess hydrogen (PROX) was studied over Pt catalysts supported on multi-wall carbon nanotubes in the temperature range between room temperature and the temperature of the water–gas shift unit (~473 K). Experimental results show that the Pt/CNT catalyst exhibit a superior performance in terms of catalytic activity and selectivity towards CO_2 formation compared to a Pt/AC catalyst prepared under similar conditions. Apparently, preferential CO oxidation in excess hydrogen over Pt nanoparticles supported on carbon materials is a *particle size* dependent reaction, i.e. larger particles exhibit higher activity and selectivity. In any case, the incorporation of oxygen functionalities to the carbon support becomes detrimental for the CO oxidation reaction independently of the carbon support used. Finally, CeO_2 addition to the Pt/CNT catalyst further improves both catalytic activity and selectivity at low temperatures (CO conversion rate of 46% at 313 K), the catalytic performance being superior to that exhibited by a traditional PROX catalyst such as Pt/CeO_2.

1. Introduction

Operational conditions in polymer electrolyte membrane fuel-cell technology (PEMFC) require the presence of "pure" hydrogen fuels, i.e. hydrogen streams without any significant pollutant. Nowadays, hydrogen is produced through the steam reforming of hydrocarbons or alcohols, followed by the water–gas shift reaction (WGS), with the subsequent formation of trace amount of carbon monoxide (0.5–1 vol.%) [1–3]. Taking into account that CO is a poison for the Pt-based anodes used in fuel cell technology at the operation temperature (~353 K), CO must be selectively removed without modifying the hydrogen stream obtained after the WGS reaction. Among the different methods investigated, low temperature preferential CO oxidation in hydrogen-rich streams (PROX) is presently considered as the most promising and economic approach to decrease the CO concentration in WGS streams to the few ppm levels necessary for the efficient operation of fuel cells.

Reported catalysts for this reaction are based on noble metal nanoparticles (Pd, Pt, Rh and Ru) supported on oxide supports, mainly alumina [4–6]. In general, a suitable catalyst for the PROX reaction must adsorb and oxidize CO to CO_2 avoiding the competing adsorption and oxidation of H_2 to H_2O. Particle size and shape, oxidation state of the metal and the nature of the support have been suggested as crucial factors defining both the catalytic activity and selectivity on this reaction. Among the different oxide supports analyzed, CeO_2 has been proposed as an excellent promoter for the CO oxidation reaction at low temperature due to its ability to supply active oxygen under oxygen lean environments [7–9]. Concerning non-oxide supports, Snytnikov et al. [10] reported a moderate activity and selectivity at low temperature for noble metal nanoparticles (Pd, Pt and Ru) supported on a special carbonaceous material. Further analysis using activated carbon as a support showed that the catalytic activity and selectivity could be slightly modified using two approaches, either by the incorporation of a second metal (e.g. PtSn/carbon) or by the addition of a partially reducible oxide (e.g. Pt/CeO_2/carbon) [11–13]. In any case, the reported results when using carbon as a support are still far away from the observed behaviour for the well-established Pt/CeO_2 catalyst, due to the absence of an additional oxygen supply at the metal–support interface. Recent studies by Tanaka et al. [14] have anticipated a promoting effect of carbon nanotubes when used as a support of Pt catalysts for the CO oxidation reaction. Although the carbon nanotubes used had low purity, catalytic measurements showed a large improvement in the CO conversion rate for high metal loadings (15 wt.% Pt).

Taking into account these premises, this manuscript compares the catalytic behaviour of Pt nanoparticles supported on high purity carbon nanotubes (CNT), with that of similar Pt nanoparticles supported on a conventional high surface area activated carbon. The effect of the Pt particle size, the surface chemistry of the carbon support and the effect of CeO_2 addition in both systems

---

* Corresponding author. Tel.: +34 96590 9350; fax: +34 96590 3454.
E-mail address: joaquin.silvestre@ua.es (J. Silvestre-Albero).

0926-3373/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcatb.2011.11.018

will be discussed for the preferential CO oxidation reaction under hydrogen-rich conditions. These catalysts will be evaluated in the temperature range from room temperature to the normal operation temperature of the low temperature WGS unit (~473 K), with special interest in obtaining catalysts with a high catalytic activity and selectivity towards CO_2 formation (H_2 oxidation to H_2O must be avoided) at the normal operational temperature of PEMFC (~353 K) in on-board fuel processors.

2. Experimental

2.1. Preparation of the Pt catalysts

High purity multi-wall carbon nanotubes (i.d. 2–6 nm) were supplied by Bayer Materials Science (BAYTUBES C150 HP). As-received carbon nanotubes were submitted to an oxidation treatment with concentrated HNO_3 for 24 h at 403 K. After the oxidation treatment, carbon nanotubes were washed with distilled water until pH ~7 and dried at 333 K overnight (CNTox). Pt/CNT and Pt/CNTox catalysts were prepared by wet impregnation using a basic (ammonium hydroxide) aqueous solution (pH 9) containing the appropriate concentration of Pt precursor ($Pt(NH_3)_4[NO_3]_2$) to achieve a Pt loading of 1 wt.%. For the sake of comparison, two conventional Pt/AC and Pt/ACox catalysts were prepared by wet impregnation of a commercial activated carbon (RGC-30) from Westvaco Corp., using the same experimental conditions both for the oxidation of the support and for the preparation of the catalysts. Activated carbon RGC-30 is a commercial sample characterized by a well-developed porous structure together with a very low ash content, i.e. absence of concomitant inorganic species, which could alter the catalytic process. After preparation, all catalysts were submitted to a thermal decomposition treatment at 673 K under a He flow (50 ml/min) for 1 h.

Two different CeO_2-promoted catalysts were prepared by wet impregnation of the as-received CNT and AC supports using an aqueous solution of $Ce(NO_3)_3{\cdot}H_2O$. The final ceria loading was 20 wt.% in both cases. After the impregnation, both solids were submitted to a calcination treatment at 673 K under a He flow for 2 h. In a subsequent step, Pt/CeO_2/CNT and Pt/CeO_2/AC samples were prepared by wet-impregnation using an aqueous solution of $Pt(NH_3)_4(NO_3)_2$ with the appropriate concentration to achieve a 1 wt.% Pt loading. After Pt incorporation, both catalysts were submitted to a thermal treatment at 673 K, as described above, for 1 h.

2.2. Catalyst characterization

The textural properties of the different supports have been characterized using nitrogen adsorption measurements at 77 K. Gas adsorption experiments were performed in a home-made fully automated volumetric equipment. Prior to the adsorption experiment, samples were degassed under vacuum (10^{-4} Pa) at 523 K for 4 h. The "apparent" surface area was estimated after application of the BET equation.

The chemical characterization of the as-received and acid modified carbon supports was performed using temperature-programmed decomposition measurements (TPD). TPD experiments were performed in a U-shape quartz reactor using a He flow (50 ml/min) up to 1273 K (heating rate 10 K/min). The amount of CO and CO_2 evolved was monitored by on-line mass spectrometry.

TEM micrographs were obtained on a JEOL model JEM-2010 electron microscope working at 200 kV, equipped with an INCA Energy TEM 100 analytical system and a SIS Megaview II camera. Samples for analysis were suspended in ethanol and placed on copper grids with a holey-carbon film support.

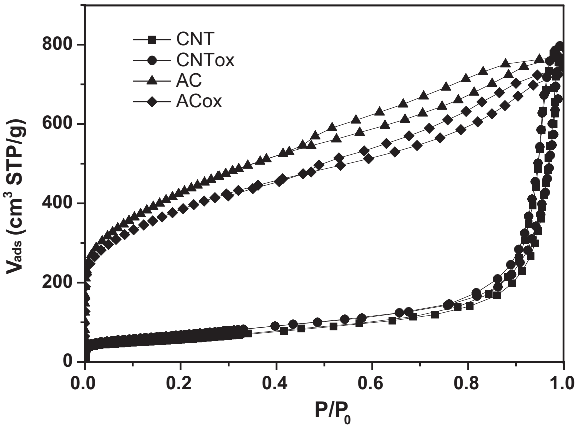

Fig. 1. Nitrogen adsorption/desorption isotherms for the CNT and AC materials before and after the oxidation treatment with HNO_3.

2.3. Catalytic behaviour

For the determination of the catalytic behaviour, the catalysts (100 mg) were placed in a U-shape quartz reactor. Before any catalytic measurement, the catalysts were in situ reduced under a hydrogen flow (50 ml/min) at 523 K for 1 h (heating rate, 5 K/min). The selective oxidation of CO in the presence of hydrogen (PROX) was studied in the temperature range 303–473 K and atmospheric pressure. The reaction mixture was 20% H_2, 2% CO, 2% O_2 and He as a balance (total flow: 50 ml/min and GHSV: 17,000 h^{-1}). Reaction products were analyzed by on-line gas chromatography (TCD), using a Plot/Q and a Molesieve capillary columns to separate the reactants and the products. The CO and O_2 conversion, as well as the selectivity towards CO_2, were calculated using the following equations:

$$X_{CO}(\%) = \frac{[CO]_{in} - [CO]_{out}}{[CO]_{in}} \times 100$$

$$X_{O_2}(\%) = \frac{[O_2]_{in} - [O_2]_{out}}{[O_2]_{in}} \times 100$$

$$S_{CO_2}(\%) = \frac{0.5x[CO_2]_{out}}{[O_2]_{in} - [O_2]_{out}} \times 100$$

3. Results and discussion

3.1. Characterization of the selected carbon supports

Fig. 1 shows the nitrogen adsorption/desorption isotherms at 77 K for the multi-wall carbon nanotubes and the commercial activated carbon RGC-30, both as-received and after an oxidation treatment with HNO_3. The adsorption behaviour of the selected carbon materials differs considerable. Multi-wall carbon nanotubes exhibit a type II isotherm, according to the IUPAC classification, characteristic of nonporous carbon materials. Above a relative pressure of 0.8–0.9 a sudden increase in the amount adsorbed can be observed together with a well-defined hysteresis loop, traditionally attributed to the presence of mesoporosity. The "apparent" surface area estimated after application of the BET equation is 200 m^2/g. On the contrary, activated carbon RGC-30 exhibits a combination of type I and type IV isotherms, characteristic of a carbon material combining both a well-developed micro and mesoporosity. The "apparent" surface area estimated for the commercial activated carbon RGC-30 achieves a value of 1520 m^2/g. In both cases, a subsequent oxidation treatment with nitric acid produces only slight