Applied Catalysis A: General 492 (2015) 201–211

Contents lists available at ScienceDirect

Applied Catalysis A: General

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

Preferential oxidation of CO in excess of H_2 on $Pt/CeO_2–Nb_2O_5$ catalysts

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ARTICLE INFO

Article history:
Received 26 June 2014
Received in revised form
26 November 2014
Accepted 15 December 2014
Available online 23 December 2014

Keywords:
Platinum
Niobia
Ceria
DRIFT
PROX

ABSTRACT

A series of $CeO_2–Nb_2O_5$ mixed oxides with different Nb content, as well as the pure oxides, have been synthesized by co-precipitation with excess urea. These materials have been used as supports for platinum catalysts, with $[Pt(NH_3)_4](NO_3)_2$ as precursor. Both supports and catalysts have been characterized by several techniques: N_2 physisorption at 77 K, X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy, UV–vis spectroscopy, scanning electron microscopy, transmission electron microscopy, temperature-programmed reduction and temperature-programmed desorption (CO and H_2), and their catalytic behaviour has been determined in the PROX reaction, both with an ideal gas mixture (CO, O_2 and H_2) and in simulated reformate gas containing CO_2 and H_2O. Raman spectroscopy analysis has shown the likely substitution of some Ce^{4+} cations by Nb^{5+} to some extent in supports with low niobium contents. Moreover, the presence of Nb in the supports hinders their ability to adsorb CO and to oxidize it to CO_2. However, an improvement of the catalytic activity for CO oxidation is obtained by adding Nb to the support, although the Pt/Nb_2O_5 catalyst shows very low activity. The best results are found with the $Pt/0.7CeO_2–0.3Nb_2O_5$ catalyst, which shows a high CO conversion (85%) and a high yield (around 0.6) after a reduction treatment at 523 K. The effect of the presence of CO_2 and H_2O in the feed has also been determined.

1. Introduction

One of the most interesting aspects of ceria-based catalysts is that their properties strongly depend on the pre-treatment conditions used and on the exact composition of the oxide. In this sense, it is known that the oxygen storage capacity (OSC) of pure ceria is inhibited when it is used in high temperature applications, *e.g.* automotive applications. However, it can be thermally stabilized, for example, by incorporation of a second cation such as Zr [1]. The large number of applications of ceria-based catalysts lie on properties such as (i) the crystal size, that can be tailored by modifying the synthesis conditions [2]; (ii) its reducibility, that can be altered by incorporation of other metals (*e.g.*, Ce–Zr) due to the formation of a solid solution [1]; (iii) the present of defect sites, which modifies this reducibility [3], and (iv) the ability of cerium to easily change between the Ce^{3+} and Ce^{4+} states. It is also known that the ionic conductivity of ceria is enhanced by doping with other rare-earth cations. Moreover, these effects depend on the ionic radius of the doping cation [4], and its ability to distort the ceria lattice structure [5]. O'Connell et al. [6] suggested that the anion vacancies produced by the introduction of M^{3+} ions into the ceria lattice may enhance its catalytic behaviour. It is known that doping with other ions could enhance the activity for different reasons. For example, in the case of M^{5+} ions as niobium, the introduction of extra oxygen anions that would be more easily removed is expected [7].

Niobium-based materials are effective catalysts in several applications, such as pollution abatement [8], selective oxidation [9], epoxidation [10], hydrocarbon conversion reactions [7], hydrogenation and dehydrogenation [11], photochemistry and electrochemistry [12] among others. The number of references in the literature concerning niobium catalysts has been steadily increasing over the last two decades, which reflects the growing interest in this area of research. A major application of niobium-based catalysts has been in the area of oxidation reactions, due to the redox properties of niobium oxide catalysts. Niobia-doped ceria materials have shown a good tolerance to carbon deposition

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http://dx.doi.org/10.1016/j.apcata.2014.12.032
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[9] and excellent properties as solid oxide fuel cell (SOFC) anodes [12]. However, more research is necessary in order to extent the improved performance of these systems for other applications [12]. For example the excellent electrical properties of niobia-doped ceria were already reported by Naik and Tien [13] and De Guire et al. [14]. Some authors have also studied niobia-based catalysts for the CO oxidation reaction. Guerrero et al. [15] studied the promoting effect of alumina-supported niobia in the PROX reaction. The results showed that at low niobia loading, the catalysts exhibited an increase in the CO oxidation activity and selectivity. On the contrary, Marques et al. [16] showed a low selectivity for Pt–Sn/Nb_2O_5 or Pt/Nb_2O_5 catalysts in the CO oxidation reaction in the presence of H_2, which could be explained in terms of platinum modification by niobia (strong metal–support interaction effect – SMSI) and thepresence tin (bimetallic effect).

The aim of this work has been to study the catalytic activity of platinum supported on ceria–niobia mixed oxides of different composition in the preferential CO oxidation in the presence of H_2 (PROX). The physico-chemical properties of supports and catalysts have been evaluated by a number of techniques, in an attempt to correlate them with the observed catalytic behaviour.

2. Experimental

2.1. Catalysts preparation

A series of niobia–ceria supports were prepared by the urea precipitation method. The appropriate amounts of $Ce(NO_3)_3{\cdot}9H_2O$ (Aldrich, 99%) and ammonium niobate (V) oxalate hydrate (Aldrich, 99.99%) to obtain different $xCeO_2$–$(1-x)Nb_2O_5$ supports with $x = 1$, 0.9, 0.7, 0.4 and 0, together with excess urea (Fluka, 98%), were dissolved in 400 ml of ultra-pure water. The solutions were heated at 363 K to induce urea hydrolysis, with constant stirring for 11 h. Finally, ammonia solution was added drop-wise to ensure complete precipitation. The solids were separated by filtration, washed with ultra-pure water, and dried overnight at 383 K. Finally, they were calcined in air at 773 K for 4 h, with a heating rate of 3 K min^{-1}. Pt/$xCeO_2$–$(1-x)Nb_2O_5$ catalysts were prepared by incipient wetness impregnation method. The supports were impregnated with an aqueous solution of $[Pt(NH_3)_4](NO_3)_2$ (Aldrich, 99.9%), in the appropriate amount to achieve a 1 wt.% Pt loading. Finally, the catalysts were dried at 383 K overnight, and calcined in air at 773 K for 2 h, with a heating rate of 3 K min^{-1}.

2.2. Catalysts characterization

The textural properties of the supports were characterized by N_2 adsorption measurements at 77 K. Gas adsorption experiments were performed in a home-developed fully automated manometric apparatus. Prior to the adsorption experiments, samples were out-gassed under vacuum (10^{-4} Pa) at 523 K for 4 h. The "*apparent*" surface area was estimated after application of the BET equation.

The actual metal loading of the different catalysts was determined by ICP in a Perkin-Elmer device (Optimal 3000). To this end, the metal was extracted from the catalysts by refluxing them in aqua regia for 8 h.

X-ray fluorescence (XRF) analyses were obtained on a X-ray sequential spectrometer PHILIPS MAGIX PRO equipped with a rhodium X-ray tube and a beryllium window.

X-ray powder diffraction patterns were recorded on a Bruker D8-Advance system with Göebel mirror and a Kristalloflex K 760-80F X-ray generation, fitted with a Cu cathode and a Ni filter. Spectra were registered between 20 and 80° (2θ) with a step of 0.05° and a time per step of 3 s.

TEM images were obtained on a JEOL electron microscope (model JEM-2010) working at 200 kV. It was 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.

SEM micrographs were obtained on a scanning electron microscope Hitachi S3000N, which is equipped with a Bruker XFlash 3001 X-ray detector for microanalysis (EDS) and mapping.

Raman spectra were recorded on a FT-Raman Bruker RFS/100 spectrometer with coupled microscope. Spectra were recorded at room temperature (274 K, 85% relative humidity) between 4000 and 400 cm^{-1} with a spectral resolution of 4 cm^{-1}. Raman spectra were obtained using different conditions depending on the type of sample used. In the case of samples with a very intense Raman effect, a laser power of 100 mW and 32 scans was used, whereas for other samples (for example, those with a larger amount of niobium) 200 mW were used and between 128 and 256 scans collected. Calibration was carried out with a silicon single crystal at $520.7 \pm 2\ cm^{-1}$.

Temperature-programmed reduction (TPR) with H_2 measurements were carried out on calcined catalysts in a U-shaped quartz cell using a 5% H_2/He gas flow of 50 mL min^{-1}, with a heating rate of 10 K min^{-1}. Samples were treated with flowing He at 423 K for 1 h before the TPR run. Hydrogen consumption was followed by on-line mass spectrometry.

Temperature-programmed CO desorption experiments on supports and reduced catalysts were carried out in a U-shaped quartz cell using 10%CO/He at 50 mL min^{-1}. Samples were first reduced with flowing H_2 at 523 K (5 K min^{-1}) for 1 h and then cooled to room temperature in He flow (50 mL min^{-1}) to remove hydrogen from the catalyst's surface. Then, the samples were exposed to the CO/He flow for 1 h. Physisorbed CO was removed by purging with He at room temperature. CO desorption was performed in He flow up to 773 K, with a heating rate of 10 K min^{-1}, and monitored by on-line mass spectrometry.

Temperature-programmed desorption of H_2 was carried out on supports and catalysts in a U-shaped quartz cell using a 10% H_2/He gas stream (50 mL min^{-1}). Samples were reduced with flowing H_2 at 523 K (5 K min^{-1}) for 1 h and then cooled to room temperature in flowing He (50 mL min^{-1}). Then, samples were exposed to the H_2/He flow for 1 h. Weakly adsorbed H_2 was removed by purging with He, and then H_2 desorption was performed in flowing He by heating at 10 K min^{-1} up to 773 K. Hydrogen evolution was monitored by on-line mass spectroscopy.

X-ray photoelectron spectroscopy (XPS) analyses were performed with a VG-Microtech Multilab 3000 spectrometer equipped with a hemispherical electron analyzer and a Mg Kα ($h = 1253.6$ eV; 1 eV = 1.6302×10^{-19} J) 300-W X-ray source. The powder samples were pressed into small Inox cylinders, mounted on a sample rod placed in a pre-treatment chamber, and reduced in flowing H_2 for 1 h at 523 or 773 K before being transferred to the analysis chamber. Before recording the spectra, the samples were maintained in the analysis chamber until a residual pressure of *ca.* 5×10^{-7} N m^{-2} was reached. The spectra were collected at pass energy of 50 eV. The intensities were estimated by calculating the integral of each peak, after subtracting the S-shaped background, and by fitting the experimental curve to a combination of Lorentzian (30%) and Gaussian (70%) lines. All binding energies were referenced to the C 1s line at 284.6 eV, which provided binding energy values with an accuracy of ±0.2 eV.

2.3. Catalytic behaviour

The activity of the catalysts in the PROX reaction was determined in the temperature range 313–473 K at atmospheric pressure, with a reaction mixture (50 mL min^{-1}) containing