



Gold catalysts for low temperature water-gas shift reaction: Effect of ZrO₂ addition to CeO₂ support

Floriana Vindigni^a, Maela Manzoli^a, Tatyana Tabakova^b, Vasko Idakiev^b,
Flora Boccuzzi^a, Anna Chiorino^{a,*}

^a Department of Chemistry and NIS Centre of Excellence, University of Torino, via P. Giuria 7, 10125 Torino, Italy

^b Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., bl. 11, 1113 Sofia, Bulgaria

ARTICLE INFO

Article history:

Received 14 March 2012
Received in revised form 18 May 2012
Accepted 24 May 2012
Available online 1 June 2012

Keywords:

WGSR
Highly dispersed gold
Ceria
Zirconia
CeO₂-ZrO₂ mixed phase
Acid/base properties
FTIR

ABSTRACT

New gold catalysts supported on ceria modified by addition of ZrO₂ have been synthesized and tested in the water-gas shift reaction (WGSR) at low temperature, where they displayed better catalytic activity than gold supported on pure ceria, following the trend: AuCe50Zr50 > AuCe80Zr20 > AuCe. Morphologic, textural, structural and spectroscopic characterisation showed that the addition of zirconia to ceria leads to the formation of mixture of tetragonal ceria-zirconia phases. Moreover, depending on the zirconia amount, a different Au dispersion is observed. Au agglomerates (10–20 nm) and nanoparticles (about 2.5 nm) have been detected by HRTEM on AuCe80Zr20, while only nanoparticles have been found on AuCe50Zr50. FTIR spectroscopy of CO adsorbed at 120 K showed also the presence of Au clusters, more abundant on AuCe50Zr50 than on AuCe80Zr20. However, at low temperature the best catalytic activity of AuCe50Zr50 is correlated not only to the abundance of gold clusters and nanoparticles, but also to the effect of ZrO₂ addition that influences the acid/base surface properties of ceria, as successfully demonstrated by adsorption and surface reaction of acetone vapor at room temperature. FTIR measurements performed before and after reaction showed that the carbonate-like species have the lowest stability on the AuCe50Zr50 surface. This feature, along with the presence of a high gold dispersion, makes AuCe50Zr50 the best catalyst in terms of activity and stability.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Traditionally hydrocarbons (oil or natural gas) have been the hydrogen source, although in the future the exploitation of some renewable materials, such as biomass, or waste recycling is expected. In technological terms the main challenges arise during the initial conversion of the source material into a “synthesis gas” mixture comprising carbon monoxide, carbon dioxide, hydrogen and water. The high concentration of carbon monoxide, as well of the desired high purity hydrogen, makes an additional purification of the synthesis gas essential when it is intended for feeding the PEMFC: as carbon monoxide poisons the electrodes in the PEMFC, it is necessary to obtain residual carbon monoxide levels typically below 50 ppm. The WGSR is usually involved in the preliminary CO abatement from the “synthesis gas”, hopefully carried out at low temperature. In the past 10 years it has been discovered that oxide-supported gold catalysts can have a remarkably high activity for the WGS reaction at low temperature providing that the materials are prepared in proper ways. There has been much debate

in the literature with regard to the activity and stability of supported gold catalysts variously prepared or activated. The method of preparation and pre-treatment [1] of the gold catalysts is critical and activity changes of several orders of magnitude can be observed depending on the methods chosen. It has been shown that an intimate contact between gold and the oxide support is important and any preparative procedure that does not generate such an interaction, or any subsequent treatment that can destroy such an interaction, may result in catalysts with low activity. It is generally accepted that the nature of the support plays a decisive role on the dispersion and shape of gold particles, that is reflected directly on the catalytic activity. The effect of support on the reactivity of gold-based catalysts has been commented recently by Chen and Goodman [2].

Many evidences have been found that Au supported on different metal oxides shows significant WGS activity [3–17]. Moreover, systems based on ceria have been considered with attention, as also Au/CeO₂ [18–30] has been found to perform very well in the WGSR.

The success of ceria in several catalytic applications is mainly due to its characteristic feature, the ability to shift easily between oxidized and reduced state (Ce⁴⁺ ↔ Ce³⁺) [31], giving its unique oxygen storage capacity (OSC). This OSC, strictly connected to

* Corresponding author.

E-mail address: anna.chiorino@unito.it (A. Chiorino).

high oxygen defectivity, makes CeO_2 an appropriate support for precious metals, promoting noble metal activity and dispersion [32]. In fact, oxygen vacancies, that are the most relevant surface defects, play a crucial role for binding catalytically active species: when Au nanoparticles are supported on ceria, the system exhibits a high activity for the WGS reaction over a wide temperature range [33]. Despite that, pure cerium dioxide is poorly thermostable as it undergoes sintering at high temperature, thereby losing its crucial oxygen storage and release ability [34,35]. In addition, all known WGS catalysts based on ceria show similar problems related to the deactivation with time-on-stream and/or shut-down restart operation. For example, Kim and Thompson [36] reported fast deactivation of their Au–ceria catalyst, which was attributed to the blockage of the active sites by carbonates and/or formates formed during the WGS reaction. They reported that the oxygen deficiency is an important factor with regard to the formation of carbonate and formate species on oxide surface. It was also found that the initial activities for the Au/ CeO_2 catalysts could be fully recovered by calcination of the deactivated catalysts in flowing air at elevated temperatures. Since the deposition of carbonates and/or formates was facilitated by oxygen-deficient sites on the catalyst surface, they proposed that deactivation could be influenced by the addition of constituents, as ZrO_2 , to control oxygen deficiency and decrease the formation of carbonates species [37]. It was previously reported that the incorporation of ZrO_2 into a solid solution with CeO_2 has a significant effect on both OSC and stability of this defective oxide [33,38]. In particular, the Zr presence, unlike on pure ceria, allows the storage and release of oxygen also from the bulk lattice structure and not just from surface layers. However, ZrO_2 addition gives rise to a modification of support surface and, as a consequence, could also affect the gold dispersion. Tibiletti et al. in a DFT and in situ EXAFS study on Au/ CeZrO_4 catalyst evidenced that the presence of zirconium in the oxide support stabilizes the oxygen defects surrounding the gold particles [39]. These defects are critical in the reaction mechanism and promote the WGS activity. Later, some of the same authors reported that the catalysts deactivation was due to the detachment of the gold particles from the CeZrO_4 support in the presence of water [40]. This is due to the hydrolysis of the interface between the gold and the oxide that decreases the metal support interaction by a breakage of the Au-support link at the metal-oxide interface.

In this paper the catalytic activity in the WGS reaction of new gold catalysts supported on ceria, modified with the addition of ZrO_2 is presented. In particular, we will focus on the results obtained at low temperature. Morphologic, textural and spectroscopic analysis has been undertaken in order to examine the impact of zirconia addition to CeO_2 and to explain the catalytic trend displayed below 500 K. In particular, HRTEM and BET measurements were performed to investigate the effect of the Zr presence on both ceria texture and Au dispersion. In order to have information on the surface sites distribution, FTIR studies have been done at 120 K on the catalyst before and after the water-gas shift reaction, using CO as probe molecule. The results have been presented together with a careful comparison with Au supported on bare CeO_2 to understand if the addition of ZrO_2 can improve the catalytic activity and decrease the deactivation. Finally, to evaluate the surface acid/base properties of the samples, FTIR spectra of adsorbed acetone on oxidized supports have been undertaken and analyzed.

2. Experimental

2.1. Catalyst preparation

The syntheses of the supports and of the gold catalysts were carried out in a “Contalab” laboratory reactor enabling complete

control of the reaction parameters (pH, temperature, stirrer speed, reactant feed flow, etc.) and high reproducibility.

Pure ceria and zirconia supports were prepared by precipitation of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ or ZrCl_4 with K_2CO_3 at pH 9.0 and at 333 and 353 K, respectively; the precipitates were dried and calcined in air at 673 K for pure ceria, at 773 K for pure zirconia.

The mixed CeO_2 – ZrO_2 supports (80:20 and 50:50 ratios as wt.%) were obtained by coprecipitation method (CP). Mixed aqueous solutions of $\text{Ce}(\text{NO}_3)_3$, ZrCl_4 and precipitant K_2CO_3 reacted under vigorous stirring at constant pH 9.0 and temperature 353 K. The resulting precipitates were aged at the same temperature for 2 h (h), then filtered and washed until removal of NO_3^- and Cl^- ions. After washing the precipitates were dried in vacuum at 353 K and calcined under air at 673 K for 2 h.

All catalysts were prepared by the deposition–precipitation method (DP) of gold on mixed supports suspended in water, via interaction of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and K_2CO_3 at a constant pH 7.0 and at a temperature of 333 K. After aging for 1 h, the precipitates were washed, dried in vacuum at 353 K, and calcined under air at 673 K for 2 h. The gold loading for each catalyst was 3 wt%. The catalysts were referred to AuCe, when pure ceria was used as support and to AuCe80Zr20 and AuCe50Zr50 in the case of Ce–Zr mixed supports with CeO_2 : ZrO_2 ratio 80:20 and 50:50, respectively. An Au/ ZrO_2 (AuZr) sample prepared in the same way was used as comparison for structural characterisation.

2.2. Characterisation techniques

Specific surface areas of the powders were determined by N_2 adsorption at 77 K (BET method) with a Micromeritics ASAP 2100 apparatus on the oxides outgassed at 423 K.

X-ray powder diffraction (XRPD) patterns were collected with a PW3050/60 X'Pert PRO MPD diffractometer from PANalytical working in Bragg–Brentano geometry, using as a source the high-powered ceramic tube PW3373/10 LFF with a Cu anode ($\lambda = 0.541 \text{ \AA}$) equipped with a Ni filter to attenuate K_β . Scattered photons have been collected by a real time multiple strip (RTMS) X'celerator detector. A suspension of the powdered samples has been deposited onto a silicon plate mounted on a rotating goniometer head. Data were collected in the $10 \leq 2\theta \leq 100^\circ$ angular range, with 0.02° 2θ steps. The samples were examined in their as-received form.

High-resolution transmission electron microscopic (HRTEM) analysis has been performed by means of a JEOL JEM 3010-UHR microscope operating at 300 kV, equipped with a ($2k \times 2k$)-pixel Gatan US1000 CCD camera and with an OXFORD INCA EDS instrument for atomic recognition via energy dispersive spectroscopy (EDS). The powdered samples were deposited on a copper grid covered with a lacey carbon film.

FTIR spectra were taken on a PerkinElmer 1760 spectrometer (equipped with a MCT detector) with the samples in self supporting pellets introduced in cells allowing thermal treatments in controlled atmospheres and spectrum scanning at room temperature (r.t.) or at controlled temperatures (from 120 to 300 K) in vacuum or in reduced pressure of probe gases. From each spectrum, the spectrum of the sample before the inlet of the probe was subtracted. The spectra were normalized respect to the gold content of each sample. Band integration was carried out by “Curvefit”, in Spectra Calc (Galactic Industries Co.) by means of Lorentzian curves. FTIR analysis were undertaken on the catalysts previously submitted to a thermal treatment in O_2 at 473 K to clean the surface of the catalysts, which is covered of water and carbonate-like species because of the air exposure. After oxidation, the samples were heated from r.t. to 373 K in H_2 , to mimic the same pretreatment to which the catalysts underwent before the WGS catalytic tests. These pre-activated catalysts will be denoted as “fresh” catalysts.

Download English Version:

<https://daneshyari.com/en/article/46105>

Download Persian Version:

<https://daneshyari.com/article/46105>

[Daneshyari.com](https://daneshyari.com)