

WO₃/CeO₂/YSZ nanocomposite as a potential catalyst for methanol reforming

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Accepted 28 January 2005
Available online 13 June 2005

Abstract

A WO₃/CeO₂/YSZ nanocomposite material [W/Zr nominal atomic ratio = 0.025, Ce/Zr nominal atomic ratio = 0.020] was prepared by wet impregnation and characterized by means of X-ray photoelectron and diffuse reflectance infrared Fourier transform spectroscopic techniques, X-ray diffraction and thermal analysis.

Both tungsten and cerium oxides are significantly reduced at the interface with YSZ: Ce(III), in particular, seems to be the prevailing species.

The interaction of the WO₃/CeO₂/YSZ nanopowder with pyridine and CO₂ allowed to investigate the acidic/basic sites. Weak contributions at 1602, 1625 and 1647 cm⁻¹ suggest the presence of Lewis and Brønsted acidic sites, whereas basic sites are not evidenced by the interaction with carbon dioxide. The presence of tungsten oxide causes the decrement of the acidic/basic sites, as indicated by the comparison with the results obtained on the CeO₂/YSZ support. Consistently, the interaction with methanol is mainly molecular.

The oxidation of methanol was investigated both in the absence and in the presence of water. In the last case carbon dioxide starts forming from room temperature.

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Keywords: Nanocomposite oxide-based catalyst; Methanol; Tungsten oxide; Cerium oxide; Yttria-stabilized zirconia

1. Introduction

In recent years, the interest in clean and efficient energy sources is growing significantly. The two-folds objective of promoting economic competitiveness and environmental sustainability guides the research in the development of advanced and clean energy technologies. Among the various recently developed devices, fuel cells (FCs) are the most promising thanks to their high efficiencies [1,2].

Solid oxide fuel cells (SOFCs), in particular, show a great deal of advantages such as fuel flexibility and higher stability; moreover, SOFCs do not encounter problems with slow oxygen reduction kinetics [3].

In this paper we focus our attention on nanocomposite oxide-based systems to be used as active materials in anodes. Nanocomposite materials offer great possibilities. An appropriate

preparation procedure allows to deposit nanodimensioned oxide particles taking thus advantage of the reactivity of nanoclusters [4]. Moreover, an active oxide can be used as a support.

A WO₃/CeO₂/YSZ sample was prepared depositing (by means of wet impregnation) CeO₂ and WO₃ nanoclusters on a commercial YSZ (this material is commonly used in SOFC). The obtained powder was characterized by means of X-ray diffraction (XRD), thermal analysis (TGA) as well as X-ray photoelectron (XPS) and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopic techniques.

Both cerium and tungsten oxides can play an important role in oxidation reactions. Cerium oxide is a mixed conductor exhibiting both ionic and electronic conductivity (n-type); the accessibility of (IV) and (III) oxidation states enhances its catalytic activity [5]. Tungsten oxide is known to be an active catalyst for olefin oxidation [6–8], however, the substoichiometric tungsten oxides (such as WO_{2.95}, WO_{2.90} and WO_{2.75}) show more selectivity than WO₃. This behav-

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ior is discussed in terms of a mechanism involving the W(V) and/or W(IV) ions as well as the different crystalline structure of the substoichiometric oxides with respect to WO_3 and the presence of crystallographic shear planes [6,7].

The active sites distributed on the sample surfaces were investigated by means of probe molecules (pyridine and carbon dioxide) and compared with those observed on WO_3 [9] and CeO_2/YSZ [10].

IR spectroscopy can readily distinguish pyridine coordinated with Lewis acidic sites from pyridinium ions originated by the interaction between pyridine and the Brønsted acidic sites [11–14]. Pyridine H-bound to the surface can also be distinguished. Different species can derive from the interaction of carbon dioxide with the acidic/basic surface sites. The adsorption on hydroxyl groups gives rise to bicarbonate species, whereas the interaction with Lewis acidic sites causes the formation of carbonyl (because of the presence of an oxygen vacancy) or carboxyl groups. The adsorption on basic sites (coordinatively unsaturated oxygen anions) originates unidentate carbonates, whereas the interaction with an acidic metal ion and its neighboring basic oxygen originates bidentate carbonates [15–18].

The information concerning active sites was used to better understanding the interaction between methanol and the $\text{WO}_3/\text{CeO}_2/\text{YSZ}$ surface. Methanol is an important probe molecule as well as an interesting combustible for fuel cells [2]. In this paper we investigated the reactivity of the nanocomposite with respect to methanol oxidation both in the absence and in the presence of water to take into consideration the steam reforming reaction. The interaction of methanol with the support (CeO_2/YSZ) and the pure oxides (WO_3 , CeO_2 , YSZ) was already investigated and will be considered for comparison [10,19].

2. Experimental

2.1. Catalyst preparation

The CeO_2/YSZ support was prepared by impregnating commercial yttria (8 mol%) stabilized zirconia (TOSOH, TZ-8Y) with an aqueous solution of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Strem Chemicals, 99.9%) as indicated elsewhere [10]. The supporting powder was investigated by means of XP, DRIFT spectroscopic techniques and thermal analysis before the deposition procedure.

The $\text{WO}_3/\text{CeO}_2/\text{YSZ}$ nanocomposite was obtained by wet impregnation of the described CeO_2/YSZ support with an aqueous solution of ammonium metatungstate, $(\text{NH}_4)_6(\text{W}_{12}\text{O}_{39}) \cdot \text{H}_2\text{O}$ (Aldrich) [W/Zr nominal atomic ratio = 0.025, Ce/Zr nominal atomic ratio = 0.020] [20]. The obtained suspension was maintained under stirring for 2 days and then kept in rest for 1 day. Water was evaporated (in air) at 350 K and the obtained solid was treated at 773 K for 5 h (in air).

2.2. Reaction conditions and DRIFT measurements

The IR spectra were collected in a Bruker IFS 66 spectrometer (accumulating 128 scans) and displayed in the Kubelka–Munk units [21,22]. The resolution of the spectra was 4 cm^{-1} . The temperature of the powder has been checked by means of a thermocouple inserted into the sample holder directly in contact with the powder.

Prior to each experiment, ca. 50 mg of the sample were loaded in the sample cup of a low temperature reaction chamber (CHC) installed in the Praying Mantis™ accessory for diffuse reflection spectroscopy (Harrick Scientific Corporation) and fitted with ZnSe windows; the powder was kept in nitrogen flow to eliminate residual water until a stable IR spectrum was obtained (ca. 2 h). Then, the sample was exposed to the reactive species at a flow rate of $100\text{--}150 \text{ cm}^3 \text{ min}^{-1}$ before measurement. The spectrum of the clean surface was used as background.

The CHC chamber was filled with the pyridine or the alcohol vapors flowing nitrogen through a bubbler containing the liquid. In the case of exposure to a methanol + water mixture the liquid was a solution (1:1) of water (distilled) and methanol. The exposure to CO_2 (Air Liquide, 99.998%) was carried out connecting the gas outlet directly to the reaction chamber. Pyridine and methanol used for the chemisorption were taken from a commercial source (Sigma–Aldrich, spectroscopic grade) and used without further purification.

2.3. XPS measurements

XP spectra were recorded using a Perkin-Elmer PHI 5600 ci spectrometer with a standard Al $K\alpha$ source (1486.6 eV) working at 350 W. The working pressure was less than $1 \times 10^{-8} \text{ Pa}$. The spectrometer was calibrated by assuming the binding energy (BE) of the Au $4f_{7/2}$ line to lie at 84.0 eV with respect to the Fermi level. Extended spectra (surveys) were collected in the range 0–1350 eV (187.85 eV pass energy, 0.4 eV step, 0.05 s step⁻¹). Detailed spectra were recorded for the following regions: C 1s, O 1s, Zr 3d, Y 3d, Ce 3d and W 4f (11.75 eV pass energy, 0.1 eV step, 0.1 s step⁻¹). The standard deviation in the BE values of the XPS line is 0.10 eV. The atomic percentage, after a Shirley type background subtraction [23], was evaluated using the PHI sensitivity factors [24]. To take into consideration charging problems the C 1s peak at 285.0 eV was considered and the peaks BE differences were evaluated.

The sample for the XPS analysis was processed as a pellet by pressing the catalyst powder at ca. $7 \times 10^6 \text{ Pa}$ for 10 min; the pellet was then evacuated for 12 h at ca. $1 \times 10^3 \text{ Pa}$.

2.4. Thermal analysis and XRD

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out in a controlled atmosphere using the simultaneous differential techniques (SDTs) 2960 of TA Instruments. Thermograms were recorded at

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