ARTICLE IN PRESS

Catalysis Today xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

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

The impact of synthesis method of CNT supported $CeZrO_2$ and Ni-$CeZrO_2$ on catalytic activity in WGS reaction

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ARTICLE INFO

Keywords:
CNTs
Ceria-zirconia
Nickel
WGS

ABSTRACT

Carbon nanotube (CNT) supported catalysts containing ceria-zirconia mixed oxide ($CeZrO_2$) and nickel were synthesized and tested in water gas shift (WGS) reaction. Physicochemical characterization including N_2 adsorption, X-ray diffraction (XRD), scanning and transmission microscopy (SEM/TEM), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA) and temperature programmed reduction with H_2 (H_2-TPR), as well as catalytic tests of WGS reaction showed that the synthesis method had significant impact on composition, morphology, structural properties and catalytic performance of obtained hybrid materials. The catalysts obtained by co-precipitation of metal oxides (NiO and/or $CeZrO_2$) on CNT walls demonstrated better dispersion of active phase and smaller particle size than catalyst obtained by depositing of powder $CeZrO_2$ or Ni-$CeZrO_2$. Moreover, the catalyst obtained by co-precipitation revealed better performance in WGS reaction; however, some CH_4 formation was noticed over Ni-$CeZrO_2$/CNT system. The role of $CeZrO_2$ in catalysts performance in WGS as well as the importance of good metal-oxide contact were confirmed.

1. Introduction

Considering the request of sustainability, there is a need to switch from fossils to renewable sources and waste raw materials. From environmental point of view, hydrogen is an ideal energy carrier and can be obtained e.g. via steam reforming of biofuels. However, hydrogen utilization in fuel cells requires its purification and removal of CO to the levels of less than 50 ppm since it poisons the Pt catalyst in the polymer electrolyte membrane. The removal of CO from the feed gas can be carried out via water gas shift reaction (WGS) (Eq. (1)), generating at the same time the additional H_2.

$$CO + H_2O \leftrightarrows CO_2 + H_2 \quad (1)$$

The conventional WGS catalyst is Fe_2O_3–Cr_2O_3 mixed oxide, which is a high temperature shift catalyst and works at 320–450 °C. The Cu/ZnO/Al_2O_3, that is a low temperature shift catalyst, works at 200–250 °C. In the last decades much attention has been paid to such metals as Ru, Pd, Pt, Au and Cu [1–6]; however, the Ni-based catalysts could be also used in WGS reaction [7–9].

The performance of a certain metal in WGS reaction depends on various factors, such as for example particle size and its dispersion over an oxide support, usually Al_2O_3, TiO_2, SiO_2 Fe_2O_3 or CeO_2 [10–12]. High interest in CeO_2 as a promising material for catalytic processes arises from its unique properties. Cerium oxide is well known from promoting the dispersion of noble metals and increasing thermal stability of the most popular support, which is Al_2O_3. It is also known for storing or releasing oxygen in lean or rich conditions, respectively. The addition of ZrO_2 to ceria promotes bulk reduction of ceria-zirconia system. The redox ageing often leads to improved TPR behavior at moderate temperatures, which implies high thermal stability and oxygen storage capacity in the $CeZrO_2$. Moreover, the presence of Zr^{4+} shifts the temperature of Ce^{4+} reduction into lower values. Nevertheless, during the reduction of $CeZrO_2$, only cerium is reduced from 4+ to 3+, while zirconium ions stay on +4 oxidation state [13]. It has been found that thermodynamic properties of ceria-zirconia solid solutions differ dramatically from those of pure ceria [14] and catalysts supported on $CeZrO_2$ are more resistant to thermal ageing than those containing only CeO_2.

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http://dx.doi.org/10.1016/j.cattod.2017.03.035
Received 9 December 2016; Received in revised form 6 March 2017; Accepted 20 March 2017
0920-5861/

Cerium oxide (either alone or in $CeZrO_2$) promotes many reactions, including NOx reduction, Fischer-Tropsch synthesis, water gas shift or partial oxidation and steam reforming of hydrocarbons [9,15–18]. It has been shown that CO can react with lattice oxygen of CeO_2 when it adsorbs on a metal active site being in contact with the ceria support [19]. Moreover, reduced ceria can be re-oxidized by water [20].

Another type of catalyst support are carbon nanotubes (CNTs). Owing to their unique features, such as high specific surface area, high thermal and electrical conductivity, high mechanical strength, and superb performance for adsorption and spillover of hydrogen, CNTs have been found promising alternative support for metal or metal oxide catalysts [21–24].

CeO_2 or ceria promoted metals (Pt, Pd, Ni) supported on CNTs have been already studied in different reactions including those allowing CO oxidation, e.g. WGS [25,26] and PROX [21]. However, deposition on CNT ceria-zirconia mixed oxide ($CeZrO_2$), which reveals better catalytic properties than CeO_2, has not been reported yet.

High activity of Ni supported on commercial, nanosize $CeZrO_2$ (Ni-$CeZrO_2$) in steam reforming reaction [27] as well as the ability of this catalyst to dissociate H_2O [20] have been already proven. Hence, we have decided to attach the commercial nanosize $CeZrO_2$ and Ni-$CeZrO_2$ catalyst to CNTs and test such a hybrid material in WGS reaction. Beside placing $CeZrO_2$ and Ni-$CeZrO_2$ on CNTs we had also synthesized both catalysts directly on CNT walls using co-precipitation method. In this work we show the impact of synthesis method on physicochemical properties of CNT supported $CeZrO_2$ and Ni-$CeZrO_2$ catalysts, and their performance in WGS reaction.

2. Experimental

2.1. Catalysts synthesis

The CNT supported $CeZrO_2$ (CZ) and Ni-$CeZrO_2$ (NiCZ) catalysts were obtained using two methods: deposition (denoted “D”) and co-precipitation (denoted “C”). Prior to the attachment of active phase to multi-wall CNTs (Sigma Aldrich, outer diameter of 6–13 nm; inner diameter of 2–6 nm; length of 2.5–20 μm), the carbon support was functionalized in concentrated HNO_3 at 70 °C for 5 h. After functionalization CNTs were washed with distilled water until pH = 7 and dried at 120 °C overnight.

2.1.1. The deposition method

In order to obtain the CNT supported commercial $CeZrO_2$, denoted CZ/CNT(D), of a nominal $CeZrO_2$ loading of 20 wt.%, the below described procedure was applied. The commercial nanosize $CeZrO_2$ (Actalys, Rhodia, Ce/Zr molar ratio = 0.7/0.3) suspended in acetone was instilled into the acetone suspension of functionalized CNTs. Both suspensions were obtained using the ultrasonic bath. The mixture was then alternately stirred for 5 min and sonicated for 3 min. It has been found that longer sonication leads to agglomeration of $CeZrO_2$ nanoparticles, which is undesirable. Stirring/sonication steps were repeated 4 times. Next, the CNT supported $CeZrO_2$ was filtered under vacuum. The residual liquid was free from $CeZrO_2$, indicating that the oxide was completely deposited over CNTs. Next, the CNT supported catalyst was dried at 120 °C overnight and calcined at 700 °C under flowing Ar (15 ml/min).

The CNT supported Ni-$CeZrO_2$ catalyst, denoted NiCZ/CNT(D), was obtained analogically to CZ/CNT(D). The Ni-$CeZrO_2$ catalyst of a nominal Ni loading of 10 wt.% was obtained by the wetness incipient impregnation of commercial $CeZrO_2$ as has been reported elsewhere [18]. Prior to deposition on CNTs the catalyst was calcined at 700 °C for 2 h in air.

2.1.2. The co-precipitation method

Synthesis of CNT supported $CeZrO_2$, denoted CZ/CNT(C), and Ni-$CeZrO_2$, denoted NiCZ/CNT(C), was conducted by co-precipitation of $CeZrO_2$ or Ni-$CeZrO_2$ on the surface of functionalized CNTs. In order to obtain CZ/CNT(C) of a nominal $CeZrO_2$ loading of 20 wt.%, the water/acetone (1:1) solutions of $Ce(NO_3)_3{\cdot}6H_2O$ and $N_2O_7Zr{\cdot}xH_2O$ were instilled into CNT suspension in acetone. The amounts of both nitrates were calculated for synthesizing the $CeZrO_2$ of Ce/Zr molar ratio equal to 0.7/0.3–the same as in the case of commercial $CeZrO_2$. The instilling of cerium and zirconium precursors was carried out under atmosphere of Ar (15 ml/min flow through the CNT suspension). The mixture was placed in an ultrasound bath for 35 min. Next, the NaOH (1 M) was being added until pH = 10 and under continuous stirring. The mixture was then heated to 70 °C and remained at this temperature for 4 h. Afterwards, it was cooled down to room temperature and left overnight under continuous stirring. Then the material was filtrated, washed with distilled water until pH = 7, dried at 120 °C overnight and calcined at 700 °C for 2 h under flowing Ar.

The CNTs supported Ni-$CeZrO_2$ catalyst was obtained using the same procedure but in addition the $Ni(NO_3)_2{\cdot}6H_2O$ was instilled to acetone suspension of CNTs together with Ce and Zr precursors. The nominal $CeZrO_2$ and Ni loadings in NiCZ/CNT(C) were 20 and 2 wt.%, respectively. Therefore, the Ni loading in relation to $CeZrO_2$ was 10 wt.%, like in the case of NiCZ/CNT(D) catalyst.

The Ni/CNT catalyst containing 5 wt.% of Ni was obtained similarly to the CZ/CNT(C) and NiCZ/CNT(C) and for the sake of comparison was partly subjected to characterization and WGS tests.

2.2. Catalyst characterization

The CNT supported $CeZrO_2$ and Ni-$CeZrO_2$ catalyst were characterized in order to determine their textural properties, structure, morphology and composition.

The specific surface area (SSA) of catalysts was determined using the BET method and was carried out on the Autosorb (Quantachrome Instruments ver. 3.01). The N_2 adsorption- desorption curves were acquired at the temperature of liquid nitrogen. Prior to N_2 adsorption the samples were degassed at 150 °C at 6.58e–05 1/Torr for 12 h.

The X-ray diffraction was performed using TUR-M62 diffractometer with copper anticathode (λ = 1.54 Å), 34 kV voltage and 25 mA current. The XRD patterns were acquired for 2Θ angles ranging from 20 to 80°, with 0.03° steps. The XRD measurements were also conducted in temperature programmed mode in flowing Ar. For this purpose, Bruker D8 Advance diffractometer equipped with temperature programmed chamber was used. The XRD patterns were collected at temperatures ranging from 30 to 900 °C.

The thermogravimetric analysis (TGA) of the catalyst was performed using Metter-Toledo apparatus. The change of sample mass was registered both in flowing N_2 and air at temperature increasing from 25 to 900 °C with a rate of 10 °C/min.

The X-ray photoelectron spectroscopy (XPS) of the catalyst was performed using a Thermo-Scientific K-ALPHA spectrometer equipped in 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 when charge compensation was achieved with the system flood gun that provides low energy electrons and low energy argon ions from a single source. 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. An estimation of the intensities was done after a calculation of each peak integral, S-shaped background subtraction and fitting the experimental curve to a combination of a Lorentzian (30%) and Gaussian (70%) lines. Binding energies, referenced to the C1 s line at 284.6 eV, have an accuracy of ± 0.1 eV.

The morphology of CNT supported catalysts was determined using S/TEM Titan 80–300 FEI microscope equipped with EDAX EDS (energy dispersive X-ray spectroscopy) detector. For measurement a 300 kV electron beam with a convergence semi-angle of 27 and 17 mrad was used.