Catalysis Today 212 (2013) 225–231

Contents lists available at SciVerse ScienceDirect

Catalysis Today

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

Ag nanowires as precursors to synthesize novel Ag-CeO_2 nanotubes for H_2 production by methanol reforming

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ARTICLE INFO

Article history:
Received 16 February 2012
Received in revised form
13 September 2012
Accepted 26 September 2012
Available online 15 November 2012

Keywords:
H_2 production
Ag-nanowires
Ag-CeO_2 nanotubes
OSRM
SRM

ABSTRACT

Novel Ag-CeO_2 nanotubes were synthesized by the precipitation method based on preformed Ag NW added as active phase precursors. This nanotubular material was used as catalysts to evaluate the methanol reforming reaction for H_2 production. Nanotubular structures with an external diameter from 120 to 280 nm and internal diameter from 40 to 80 nm were identified by electron microscopy techniques. These nanostructures were mainly composed of CeO_2 nanoparticles (~11 nm). The X-ray powder diffraction patterns of the Ag-CeO_2 nanotubes showed diffraction peaks characteristic of the cubic structure of the CeO_2 and metallic Ag. No diffraction peaks corresponding to those of the Ce–Ag alloys or other impurities were found in these samples. The catalytic activity was improved as the nanotubes concentration was increased in the catalysts. However, the H_2 production was diminished, so, an increase in the Ag particle size promotes the methanol combustion, decreasing hydrogen production and increasing the water formation as well as the CO_2 production. It seems that the Ag is the phase mainly responsible of hydrogen production although the large particles reduce the CO formation.

1. Introduction

The synthesis of metal nanoparticles (NPs) today is one of the most intensively developing fields of preparative chemistry [1–3]. Due to their small sizes and large specific surface areas, NPs exhibit, in fact, novel properties which may significantly differ from those of the bulk material [4,5]. A number of important applications of NPs have been reported in the literature due to their diverse properties among which the most prominent is in the field of catalysis. There are several articles and reviews which have described the use of NPs as catalysts for a variety of reactions [6–9]. The development of synthetic routes to obtain NPs with a very well controlled size is important from a practical point of view [10], since most physicochemical properties depend on their shape and size, including also their catalytic activity, which correlates with the crystal phase and surface structure. It is known that the supported noble metal catalysts represent the largest group of heterogeneous catalysts, being of major economic importance, especially in refinery technology [11]. The preparation of these catalysts is a fundamental step in order to achieve the desired activity, selectivity and life time [12].

CeO_2 has been widely used in purifying vehicle exhausts, becoming the most important rare oxide for controlling NO_x. CeO_2 increases the dispersion of active components and thermal stability of the support and it also enhances the migration and exchange of oxygen species in the reactions by storing and releasing oxygen of CeO_2 so as to improve CO, hydrocarbon (HC) oxidation and NO_x reduction [13–15]. Among the various functions of ceria, the oxygen storage capacity is one of its most important. This function inevitably affects the oxidation state of the elements which are combined with ceria by providing oxygen to or withdrawing it from them; hence, ceria modifies their catalytic performance. For example, Pt supported on ceria is present in an oxidized state through the Pt—O—Ce bond formation even in a reducing atmosphere, and this oxidized state of Pt has a very high activity in decomposing methanol [16].

Hydrogen is considered to be the future of clean energy [17], becoming more and more important with the development of fuel cells and with the rising energy demand [18]. Methanol is regarded as a good fuel candidate for H_2 production because of its easy handling, low cost, high energy density as well as being commercialized as an important chemical feedstock [19]. This makes the methanol steam reforming a feasible process that opens up an opportunity to the use of a renewable energy source for hydrogen production. Hydrogen can be obtained directly from methanol according to the three different processes: steam reforming (SRM)

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http://dx.doi.org/10.1016/j.cattod.2012.09.021

[20–23] (1), partial oxidation (POM) [24–28] (2) and oxidative steam reforming (OSRM) [29–34] (3).

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2, \quad \Delta H^\circ_{298} = 49.4\,kJ\,mol^{-1} \quad (1)$$

$$CH_3OH + 1/2O_2 \rightarrow 2H_2 + CO_2, \quad \Delta H^\circ_{298} = -192.2\,kJ\,mol^{-1} \quad (2)$$

$$CH_3OH \rightarrow 2H_2 + CO, \quad \Delta H^\circ_{298} = 22.4\,kJ\,mol^{-1} \quad (3)$$

In this context, the search for a highly effective catalytic system for the selective steam-reforming process is of great research interest. Copper-based catalysts are mainly used for its excellent selectivity in the formation of CO_2 and H_2 [31–36]. When compared to other metals, Ag has been less used as an active phase in the catalysts. Nevertheless, Mo et al. [37–38] reported that the selectivity of hydrogen (SH_2) and carbon monoxide (SCO) varied with the kind of metal and support. They obtained good SH_2 (>90%) from modified CeO_2 (Ag/Ce_2OZn catalyst) and concluded that CeO_2 and ZnO oxides synergistically promoted a high selectivity toward H_2 from POM over Ag/Ce_xZn using Ag crystallites (Ag < 5 nm). In the case of bimetallic Ni-Ag catalysts it was reported that the sintering of Ni particles can be partially inhibited by using additional metals such as Ag, thus the deactivation of the catalyst by the sintering of Ni particles can be suppressed [39].

The goal of the present work was to study the use of the Ag nanowires as templates to generate a Ag/CeO_2 nanotubes-based catalysts and study the effects of the Ag/Ce composition for Steam and Oxidative steam Reforming of Methanol (OSRM) to produce H_2-rich gas. These catalysts were prepared by precipitation method and characterized by several different techniques including BET (N_2 adsorption–desorption), SEM (Scanning Electron Microscopy), EDX (Energy Dispersive X-ray Spectroscopy), XRD (X-ray Diffraction), (S)TEM (Scanning/Transmission Electron Microscopy) and TPR (Temperature Programmed Reduction). Thus the morphology and structure were characterized using electron microscopy techniques. The purity of phases in the catalyst was studied using XRD. The surface area was measured using BET and the catalytic activity using TPR.

2. Experimental

The Ag nanowires were synthesized through a PVP (polyvinylpyrrolidone) assisted reaction in ethylene glycol [10,40]. H_2PtCl_6 was reduced in ethylene glycol at 160 °C to synthesize platinum nanoparticles as nucleation seeds; the reaction was carried out 160 °C. Then silver nitrate and PVP40 were dissolved in ethylene glycol and added to this mixture under constant stirring. After 1 h, the silver nanowires were precipitated from the reaction mixture with acetone.

The Ag nanowires-CeO_2 catalyst was prepared by the precipitation method [41]. An aqueous solution of $Ce(NO_3)_3{\cdot}6H_2O$ and the Ag nanowires were mixed under constant stirring, the Ag concentrations were 1 and 5 wt% related to the nominal weight of CeO_2. NH_4OH (Baker) was added drop wise to complete the precipitation. The precipitated mixture was aged for 24 h and the residual liquid was removed by decanting. Then the mixture was heated at 50 °C for 24 h and at 100 °C for another 24 h. The resulting material was then calcined at 500 °C, at a rate of 5 °C/min for 5 h under an air stream, and finally cooled down slowly to room temperature (R.T.). All the samples were reduced at 450 °C using a H_2 (40 mL/min) stream for 1 h before characterization except for TPR analysis. The labeling of different catalysts will be referred as xAg/CeO_2, where x = 1 and 5 wt% of metal on the catalysts respectively. The actual Ag content determined by EDS technique was 0.97 and 4.93 for 1Ag-CeO_2 and 5Ag-CeO_2 nanotube catalysts respectively.

2.1. Characterization

X-ray diffraction (XRD) powder patterns were recorded in a Siemens D-5000 diffratometer, using Cu Kα (λ = 0.15406 nm). The morphology of the Ag/CeO_2 catalysts was analyzed by scanning electron microscopy (SEM) using a Jeol JSM-6610LV, at an acceleration voltage of 20 kV, the images were obtained with the backscattered electron signal (BSE). HRTEM and local chemical analysis of the bimetallic nanoparticles were carried out in a microscope JEOL-JEM 2010 with a resolution of 0.19 nm, fitted with an energy dispersive X-ray Spectrometer (NORAN). For the aberration (Cs) corrected characterization, the samples were analyzed using scanning transmission electron microscopy (STEM) with a JEOL ARM (200F) 200 kV FEG-STEM/TEM, equipped with a hexapole corrector (CEOS GmbH) for the electron probe. The probe size used for acquiring the HAADF as well as the BF-STEM images was 9 C (23.2 pA) and the CL aperture size was 40 μm. High angle annular dark-field (HAADF) STEM images were acquired with a camera length of 8 cm/6 cm and the collection angle of 68–280 mrad/90–270 mrad was used. This scattering semi-angle easily fulfilled the requirement for the detector to eliminate contributions from unscattered or low-angle scattered beams. The BF-STEM images were obtained using a 3 mm/1 mm aperture and a collection angle of 17 mrad/5.6 mrad was used (camera length in this case was 8 cm). The HAADF as well as the BF images were acquired using a digiscan camera [42]. For the electron microscopy analysis, the sample was dispersed in ethanol and a drop of this suspension was deposited onto a holey carbon grid. Surface area (BET) and temperature-programmed reduction (TPR) were carried out on an automatic multitask unit RIG-100 from ISR INC equipped with a thermal conductivity detector (TCD) with output to a computer [22,31–34,43]. For the TPR analysis, the oxidized catalyst (0.1 g) was placed in the reactor and purged with UHP Ar at room temperature and then the TPR measurement was performed using 5% H_2/Ar gas mixture (40 ml/min). The temperature was increased at a rate of 10 °C/min from room temperature to 500 °C. The effluent gas was passed through silica gel to remove water before measuring the amount of hydrogen consumed during the reduction by the TC detector. The signal was calibrated by 0.5 ml pulses of 5% H_2/Ar at the end of the experiment. After testing the catalytic activity reaction, the surface of these catalysts was cleaned by a He stream (30 ml/min) for 30 min at 450 °C and cooled at room temperature, then the sample was purged with UHP Ar flow and the TPR was performed.

2.2. Catalytic activity

Catalytic activity measurements were carried out in a conventional fixed-bed flow reactor (8 mm i.d.) using a commercial flow system RIG-100-ISRI which has been described in detail elsewhere [22,31–34,43]. Briefly, the catalytic test was evaluated in a temperature range from 200 to 450 °C with less than 4% error in the curves. 0.1 g of the catalyst was activated in a stream of H_2, from room temperature to 450 °C for 1 h. The catalyst was brought up to the reaction temperature in He and the reaction mixture was introduced. For the SRM reaction, He was used and the total flow rate was kept at 40 mL/min (GHSV = 24,000 h^{-1} based on the total flow). For the OSRM reaction, 30 mL of O_2(5%)/He mixture was passed through stainless steel saturator containing methanol, 30 mL of He was passed through stainless steel saturator containing water. These gases were added by means of a mass flow controller (RIG-100) and bubbled through a tank containing the water and methanol respectively. The effluent gas of the reactor was analyzed by gas-chromatography (Gow-Mac 580 instrument) equipped with a two columns system (molecular sieve 5 Å and Porapack Q columns), double injector controlled by Clarity software