Applied Catalysis A: General 505 (2015) 98–104

Contents lists available at ScienceDirect

Applied Catalysis A: General

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

Promoter effect of sodium in graphene-supported Ni and Ni–CeO_2 catalyst for the low-temperature WGS reaction

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ARTICLE INFO

Article history:
Received 27 April 2015
Received in revised form 7 July 2015
Accepted 23 July 2015
Available online 26 July 2015

Keywords:
Graphene
Ni
Na doping
Ceria
Water–gas shift

ABSTRACT

The low temperature water–gas shift (WGS) reaction has been studied over Ni–CeO_2/Graphene and Ni/Graphene. The catalysts were prepared with 5 wt.% Ni and 20 wt.% CeO_2 loadings, by deposition-precipitation employing sodium hydroxide and urea as precipitating agents. The materials were characterized by TEM, powder X-ray diffraction, Raman spectroscopy, H_2-temperature-programmed reduction and X-ray photoelectron spectroscopy (XPS). The characterization and the reaction results indicated that the interaction between the active species and the support is higher than with activated carbon, and this hinders the reducibility of ceria and thus the catalytic performance. On the other hand, the presence of residual sodium in samples prepared by precipitation with NaOH facilitated the reduction of ceria. The catalytic activity was highly improved in the presence of sodium, what can be explained on the basis of an associative reaction mechanism which is favored over Ni—O—Na entities.

1. Introduction

The water-gas shift reaction (WGS, $CO + H_2O \rightarrow CO_2 + H_2$) has gained increased attention in the last years due to its importance in the production and purification of hydrogen from fossil and renewable resources. It can be coupled at the exit of a reforming unit to obtain a high purity hydrogen stream which can be used to feed fuel cells [1]. Metal/ceria systems have been proved to offer excellent performance for the low temperature stage of WGS [2], Pt/ceria being the most promising catalyst in terms of activity and selectivity [3,4]. The ability of CeO_2 for the $Ce^{+4} + e^- \leftrightarrow Ce^{+3}$ redox process and the formation of oxygen vacancies favour the mobility of surface oxygen species [5], which are active in the reaction. Furthermore, a synergistic effect is obtained between metal and ceria. On one hand, ceria reducibility is favoured when the metal is in close contact with its surface and, on the other hand, ceria can stabilize the metal nanoparticles avoiding their agglomeration [6]. However, given the low availability of ceria, it is interesting to optimize its use, for example by spreading it onto a high surface area support. In this sense, we have reported in previous papers the promoter effect of ceria in activated carbon-supported Pt catalysts, where the interaction between the metal and the oxide is enhanced [7]. Another challenge in the developing of a WGS catalyst is the replacement of platinum by a more economical metal. In this sense, nickel has been the metal of choice for certain reforming reactions due to its competitive price, high availability and activity [8,9], and it has proved to be active and selective in the WGS reaction when it is highly dispersed [10,11].

An excellent metal dispersion and an optimal metal-ceria interaction are therefore mandatory to achieve an optimal catalytic performance. In this scenario, graphite oxide (GO) emerges as an excellent candidate to act both as substrate for the synthesis of supported nanoparticles and as precursor of the support. GO displays a rich oxygen chemistry, which allows its dispersion in aqueous solutions and the interaction with the metal and/or oxide precursors that would improve their dispersion. Several studies can be found concerning the use of GO as support [12], catalyst by its own [13,14] and as precursor of graphene (G) or reduced graphene oxide (rGO) [15]. For this latter approach, both metal/G or metal/rGO [16,17] and metal/oxide/G or metal/oxide/rGO systems [18,19,20] have also been developed. The synthesis of the metal and oxide nanoparticles can be performed before its deposition on the support, for example by colloidal methods [19], or simultaneously to the synthesis of graphene [18]. The resulting material provides good nanoparticle dispersion with homogeneous distribution [21]. In some cases, it has been suggested that additional improvement on the catalytic performances, due to a synergism between GO and the active phase, was achieved [22]. Depending on the metal, the

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http://dx.doi.org/10.1016/j.apcata.2015.07.036

synthesis of the nanoparticles can be performed under mild conditions, as is the case for Ag [19], or may require the use of stronger reducing agents [17,20].

In this work we have performed the synthesis of the binary Ni/Graphene and the ternary Ni–CeO_2/Graphene systems employing urea and sodium hydroxide as precipitating agents for depositing the active phases on the graphene support. The catalysts have been thoroughly characterized and their catalytic performance has been tested in the low temperature stage of the WGS reaction.

2. Experimental section

2.1. Synthesis of graphite oxide

Graphite oxide (GO) was prepared from natural flake graphite according to a modified Hummers method [23]. Briefly, 3 g of natural graphite powder was added to a reaction flask containing concentrated H_2SO_4 (25 mL g^{-1} of support) and 1.5 g of sodium nitrate, which was previously cooled to 273 K in an ice bath. Then, potassium permanganate (9 g) was slowly added and kept under stirring at 298 K for 30 min. Then, 138 mL of deionized (DI) water was slowly added and the suspension was maintained at 373 K for 15 min. Finally, 420 mL of deionized water was added, followed by the slow addition of 30 mL of hydrogen peroxide. The suspension was filtered off and washed extensively with deionized H_2O, HCl (30%) and ethanol, and finally dried in vacuum at 333 K for 24 h to obtain the graphite oxide (GO) powder, which was kept in a desiccator until use.

2.2. Catalyst synthesis

For the synthesis of the catalysts, GO was dispersed in deionized water (1 mg mL^{-1}) and sonicated for 30 min. The required amount of $Ce(NO_3)_3 \cdot 6H_2O$ (99.99%, Sigma–Aldrich) to obtain a 20 wt.% CeO_2 was dissolved in 10 mL of DI water and added dropwise to the GO dispersion with stirring. The resulting slurry was stirred for 2.5 h. Then, the necessary amount of $Ni(NO_3)_2 \cdot 6H_2O$ (99.9%, Sigma–Aldrich) to obtain a 5 wt.% Ni loading was dissolved in 10 mL of DI water, added dropwise to the mixture and stirred for 2 h. Aqueous 0.5 M solutions of NaOH or urea were used as precipitating agents. The addition of the NaOH solution was carried out dropwise, with stirring. When urea was used, the solution was mixed with the GO suspension containing the nickel and the ceria precursors, and the resulting slurry was heated at 363 K, with stirring, to reach a pH of around 11. In both cases, the formed slurries were stirred for 2 h and, after cooling to room temperature, the solid was filtered off, washed extensively with water and ethanol, and finally dried at 313 K under vacuum for 24 h. The same procedure was applied for the catalyst with no ceria, using only a solution with the nickel precursor. Finally, the solids were heat-treated during 5 h at 623 K under flowing He (50 mL min-1), with a heating rate of 1 K min^{-1}. The resulting materials were labelled as Ni–CeO_2/G-Na and Ni/G-Na for the catalysts prepared with NaOH, and Ni–CeO_2/G and Ni/G when the precipitating agent used was urea. For the sake of comparison, a Ni/CeO_2 catalyst was also prepared with 5 wt.%. Ni loading. The ceria support was prepared by homogeneous precipitation from an aqueous solution of $Ce(NO_3)_3 \cdot 6H_2O$ (99.99%, Sigma–Aldrich) containing an excess of urea. The solution was heated at 353 K and kept at this temperature, with slow stirring, during 12 h. The solid formed was filtered and calcined at 623 K for 4 h. The CeO_2 support prepared in this way was impregnated with a solution of the nickel precursor in acetone. The excess of solvent was removed by vacuum treatment in a rotary evaporator.

2.3. Characterization

Conventional TEM analysis was carried out with a JOEL model JEM-210 electron microscope working at 200 kV and equipped with an INCA Energy TEM 100 analytical system and a SIS MegaView II camera. Samples for analysis were suspended in methanol and placed on copper grids with a holey-carbon film support.

X-ray powder diffraction patterns were recorded on a JSO Debye-flex 2002 system, from Seifert, fitted with a Cu cathode and a Ni filter, using a 2° min^{-1} scanning rate.

Raman spectra were carried out at room temperature using a DXR Raman microscope with 532 nm excitation source from an Ar^+ laser.

Temperature-programmed reduction (TPR) with H_2 measurements were carried out with the heat-treated 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 (Pfeiffer, OmniStar GSD 301).

Infrared spectra were collected by using a Nicolet Nexus spectrometer and recorded by a DTGS detector from 128 scans and with a resolution of 4 cm^{-1}. The samples were mixed with predried potassium bromide to a final concentration of approximately 1 wt.%.

X-Ray photoelectron spectroscopy (XPS) analyses were performed with a VG-Microtech Multilab 3000 spectrometer equipped with a hemispherical electron analyser 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. The catalysts were reduced *ex-situ* (H_2, 623 K, 1 h) and then introduced in octane under inert atmosphere. Suspensions were evaporated in the XPS system under vacuum conditions. 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. The binding energy (BE) of the C1s peak of the support at 284.6 eV was taken as an internal standard. The accuracy of the BE values is ±0.2 eV.

2.4. Water-gas shift reaction

The catalytic behaviour of the prepared samples in the low temperature water–gas shift reaction was evaluated in a fixed bed flow reactor under atmospheric pressure in a range of temperatures from 413 K to 563 K. The feed gas stream contained a volume composition of 1.87% CO, 35.92% H_2O, and He balance, with a total flow of 100 mL min-1. Activity tests were performed using 0.150 g of catalyst diluted with SiC, at a volume ratio of 1:2, to avoid thermal effects. Prior to the reaction, catalysts were reduced during 1 h at 623 K with flowing H_2 (50 mL min^{-1}). Reaction at each temperature was stabilized for 2 h, and the composition of the gas stream exiting the reactor was determined by on-line mass spectrometry (Pfeiffer, OmniStar GSD 301). The catalytic activity will be expressed by the degree of CO conversion.

3. Results and discussion

3.1. Characterization

Representative TEM images of the reduced catalysts (H_2, 623 K, 1 h) are shown in Fig. 1. In general, samples presented wrinkled layers as well as some transparent areas corresponding to exfoli-