Catalysis Today 138 (2008) 124–129

Contents lists available at ScienceDirect

Catalysis Today

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

Low temperature hydrogen production from methane on cerium nickel- and zirconium-based oxyhydrides

L. Jalowiecki-Duhamel *, H. Zarrou, A. D'Huysser

UCCS Unité de Catalyse et de Chimie du Solide, UMR CNRS 8181, Bât. C3, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq Cedex, France

ARTICLE INFO

Article history:
Available online 23 July 2008

Keywords:
Anionic vacancy Ceria
Hydrogen production
Methane partial oxidation
Oxyhydride
Nickel oxide

ABSTRACT

Hydrogen production from methane has been obtained at low temperature, in presence of O_2, over cerium nickel and zirconium $CeZr_zNi_xO_y$ ($z = 0$ or 0.5 and $0 < x \leq 3$) oxyhydrides. A H_2 yield of 100% is obtained at high temperature (650 °C), at 200 °C a yield of 34% is reached with a stable methane conversion at 53% and selectivity in H_2 at 64% when the solid is previously in situ treated in H_2 at 200 °C. Different physicochemical techniques have been used to characterize the catalysts. Depending on the composition and metal loading, a solid solution and/or a highly dispersed nickel oxide in ceria (or ceria–zirconia) can be obtained. Ion sputtering followed by XPS analysis has been very useful for estimating the size of small NiO clusters (10–15 Å) present in the compounds. Correlations among the species present in the solid, and the catalytic performances are discussed, an active site based on the formation of anionic vacancies and a mechanism involving a heterolytic abstraction of a hydride species from methane are proposed.

1. Introduction

Synthesis gas ($H_2 + CO$) is industrially produced through the steam reforming of methane (endothermic reaction) at high temperature. However, catalytic partial oxidation of methane (POM) offers the greatest potential to hydrogen or synthesis gas because adoption of POM would result in energy savings, due to mild exothermicity. Moreover, the hydrogen purified after a CO clean-up process can be used for ammonia synthesis, hydrotreating processes and reduction operations in metallurgical industry. Another very interesting use of hydrogen is based on its conversion into power in fuel cell systems. Recently, there has arisen a strong interest in using H_2-based fuel cells as future energy carrier due to the high conversion efficiency of hydrogen energy to electricity as well as no emissions of pollutant gases.

Ni metal or noble metals, are often used as catalytically active components for POM. Many research groups have developed various Ni catalysts effective for the reaction because of a high cost of noble metals. CeO_2–NiO catalysts have been studied in many oxidation reactions by taking advantage of ceria redox properties that can be enhanced by adding Zr and forming solid solutions (CeO_2–ZrO_2). It has also been reported that a good coking resistance depends on a high dispersion of Ni [1,2]. Therefore, among the important parameters pointed out, the catalysts dispersion and reducibility are often taken into consideration [1–4]. Besides, the catalysts are required to work under various conditions, and improvement in the stability of the catalysts is desired, in particular, in strong reducing conditions. In some cases the results have been ameliorated with a CH_4/O_2 ratio higher than 2 [5]. Moreover, the effect of an activation step has also been noted, Choudhary et al. found that after catalytic reaction at high temperature, NiO–Yb_2O_3 allowed to obtain at 298 °C a methane conversion of 71% with a CO and H_2 selectivity, respectively, of 84 and 88% [6].

In this paper, we investigate the partial oxidation of CH_4 to H_2 and CO in strong reducing conditions ($CH_4/O_2 = 3$) over cerium nickel and zirconium $CeZr_{0.5}Ni_xO_y$ mixed oxides in situ activated in H_2 (oxyhydrides). We report studies of their structural, dispersion and reduction properties in order to find a relationship with catalytic reaction and propose an active site.

2. Experimental methods

The mixed oxides denoted $CeZr_zNi_xO_y$ ($z = 0$ or 0.5 and $0 < x \leq 3$) where x and z are the Ni/Ce and Zr/Ce atomic ratios, respectively, were prepared by coprecipitation of the corresponding hydroxides from mixtures of cerium zirconium and nickel nitrates (0.5 M) using triethylamine (TEA) as a precipitating agent.

---

* Corresponding author. Tel.: +33 3 20 33 77 35; fax: +33 3 20 33 65 61.
E-mail address: louise.duhamel@univ-lille1.fr (L. Jalowiecki-Duhamel).

0920-5861/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2008.06.011

After filtration, the solids are dried at 100 °C and calcined in air at 500 °C for 4 h [7]. The loading has been measured by microanalysis.

The catalytic partial oxidation of CH_4 was performed with 0.2 g of catalyst under atmospheric pressure in a fixed-bed stainless-steel tubular reactor by cofeeding the nitrogen-diluted reaction gases ($CH_4/O_2/N_2 = 3/1/3$). Each catalyst was diluted with SiC (1:1). The total flow rate was $3\ L\,h^{-1}$ (down flow) and the reaction temperature, measured in the catalytic bed with a thermocouple, was in the range of 50–700 °C. The experimental details have been published previously [8]. The gases at the outlet of the reactor were analyzed by FID and TCD gas chromatography. Conversion (CH_4, O_2) and selectivity (H_2, CO, CO_2) were collected after about 5 h of reaction when the steady state conversion and selectivity were obtained for each temperature. Carbon and H_2O are also formed but the quantity has not been analyzed. Conversion (X), selectivity (S) and yield (Y) were calculated as follows:

$$X_{CH_4} = \frac{CH_4^{in} - CH_4^{out}}{CH_4^{in}}, \qquad X_{O_2} = \frac{O_2^{in} - O_2^{out}}{O_2^{in}},$$

$$Y_{H_2} = \frac{H_2^{out}}{2CH_4^{in}}, \qquad S_{H_2} = \frac{Y_{H_2}}{X_{CH_4}}, \qquad S_{CO} = \frac{Y_{CO}}{X_{CH_4}}, \qquad S_{CO_2} = \frac{Y_{CO_2}}{X_{CH_4}}$$

X-ray powder diffraction (XRD) analysis was carried out with a D 5000 Siemens diffractometer using a copper target and a secondary beam monochromator. The XRD patterns were registered in the 2θ domain (15–80°) with a measured step of 0.02°. The $K\alpha_2$ contribution was eliminated from the diffraction by computer post-processing; the patterns obtained were not subjected to other treatments. The crystallites size was calculated using the Scherrer equation, from the most intense reflections observed for the NiO and CeO_2 crystallographic structures: (1 1 1), (2 0 0), and (2 2 0).

Temperature-programmed reduction (TPR) was performed on a Micrometrics Autochem 2920 analyser, and hydrogen consumption was measured by a TCD detector: 25 mg of the sample was treated in the 5% H_2–95% Ar gas mixture (2 L/h). The temperature was increased to 800 °C at a heating rate of 10 °C/min. To calibrate the amount of H_2 consumption, the AgO powder was used.

The X-ray photoelectron spectroscopy (XPS) spectra of the samples were obtained on a VG Escalab 220 XL instrument using Al $K\alpha$ radiation ($h\nu = 1486.6$ eV). The anode was operated at a power of 300 W and the fixed retardation ratio (FRR) was applied. The base pressure attained during the analysis was 1.33×10^{-6} Pa. The calcined samples, lightly pressed on an Au-holder, were applied to a sample rod. For calibration of the binding energy (E_B) scale of photoemission features, the Ce 3d u‴ peak at 916.7 eV was taken as an internal reference. In our experimental conditions, the reproducibility of E_B was estimated at ±0.2 eV. As for atomic ratios, they were calculated by assuming a homogeneous distribution of the catalyst components. The details of the spectrometer and the experimental procedure are given in Ref. [9].

The spectrometer allows ions to be bombarded directly onto the surface of compounds. For this, the solids were thinly pressed on an indium-holder and measurements were performed with the same analysis conditions as those previously described. Ions sputtering conditions were carried out with an ionic energy of 2000 eV and an applied tension of 580 V. The cumulated time of sputtering treatment under argon ions was varied from 1 to about 5000 s.

3. Results and discussion

3.1. XRD

Fig. 1 reports the diffraction patterns obtained with different $CeZr_{0.5}Ni_xO_y$ solids. Only a ceria like phase is apparent in every solid analyzed (34-0394 JCPDS file) while crystallized NiO (4-0835 JCPDS file) appears when $x \geq 0.5$. No phase related to the presence of Zr has been observed. The $CeNi_xO_y$ mixed oxides were classified in two families, depending on the nickel content: the first family with $x \leq 0.5$ corresponds to a solid solution with the substitution of Ni^{2+} ions in the CeO_2 lattice and the second family with $x > 0.5$ concerns compounds in which crystallized NiO and solid solution coexist [10–12]. The size of the nickel oxide varies considerably from clusters to a crystallized material depending on the x-value and the experimental conditions (preparation conditions, calcination temperature, etc.). As already reported in previous studies for $CeNi_xO_y$ compounds, a careful examination of the patterns shows that the addition of nickel affects not only the broadness of the ceria peaks, but also their position (Fig. 2), attributed to the substitution of Ce^{4+} cations by Ni^{2+} cations inside the CeO_2 lattice and interpreted by the formation of a cerium–nickel solid solution [12]. As a matter of fact, the nickel ionic radius (Ni^{2+}: 0.7 Å), is smaller than the cerium ionic radius (Ce^{4+}: 0.9 Å). It has been reported on binary mixed oxides, that the highest proportion of solid solution has been obtained for the $CeNi_{0.5}O_y$ compound, as also observed here when the molar ratio $Ni/M_T = 0.3$ (M_T = Ni + Ce + Zr, $Ni/M_T = x/(1 + z + x)$ with $z = 0$ or 0.5). The results obtained on $CeZr_{0.5}Ni_xO_y$ compounds reported in Fig. 2 show clearly that the presence of Zr affects even more drastically the ceria phase forming a well-known solid solution allowed by the size of Zr^{4+} cations (0.84 Å).

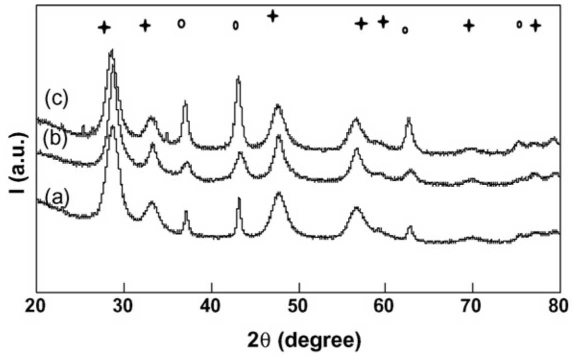

Fig. 1. XRD patterns of (a) $CeZr_{0.5}Ni_1O_y$ (b) $CeZr_{0.5}Ni_2O_y$ and (c) $CeZr_{0.5}Ni_3O_y$ compounds: CeO_2 (✦) and NiO (○).

The grain size (d) has been estimated from the XRD line widths taking into account the (1 1 1), (2 0 0) and (2 2 0) peaks, for both NiO and CeO_2. The average dimensions obtained for $CeZr_{0.5}Ni_1O_y$ and $CeNi_1O_y$ oxides are summarized in Table 1. The size of the crystallites of the mixed oxides is found smaller than the size measured for the pure oxides [12]. This phenomenon has been

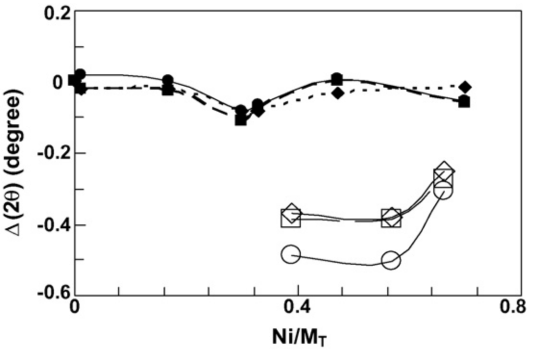

Fig. 2. Shift of the CeO_2 diffraction peaks in $CeZr_{0.5}Ni_xO_y$: (○) (1 1 1), (□) (2 0 0), (△) (2 2 0) and $CeNi_xO_y$: (●) (1 1 1), (■) (2 0 0), (▲) (2 2 0). $\Delta(2\theta)$ = (peak position of the reference oxide CeO_2) − (peak position of the CeO_2-like phase in the mixed oxide). ($Ni/M_T = x/(1 + z + x$; $z = 0$ or 0.5).