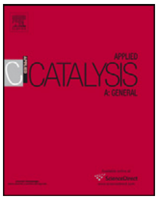
Applied Catalysis A: General 392 (2011) 36–44

Contents lists available at ScienceDirect

Applied Catalysis A: General

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



Effect of Ce/Zr composition and noble metal promotion on nickel based $Ce_xZr_{1-x}O_2$ catalysts for carbon dioxide methanation

Fabien Ocampo[a], Benoit Louis[a,∗], Lioubov Kiwi-Minsker[b], Anne-Cécile Roger[a,∗]

[a] Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse LMSPC, UMR 7515 du CNRS, Université de Strasbourg, 25 rue Becquerel, 67087 Strasbourg Cedex 2, France
[b] Group of Catalytic Reaction Engineering (GGRC-ISIC), Station 6, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

ARTICLE INFO

Article history:
Received 8 July 2010
Received in revised form 4 October 2010
Accepted 20 October 2010
Available online 30 October 2010

Keywords:
Methanation
Carbon dioxide
Mixed oxides
Ceria–zirconia
Synthetic fuels

ABSTRACT

Carbon dioxide methanation was carried out over a series of Ni–$Ce_xZr_{1-x}O_2$ catalysts prepared by a pseudo sol–gel method. The influence of CeO_2/ZrO_2 mass ratio and noble metal addition was investigated. The catalysts were subsequently characterized by means of XRD, TPR, BET, H_2-TPD and SEM-EDX. The modification of structural and redox properties of these materials was evaluated in relation with their catalytic performances. All catalysts gave impressive CO_2 conversion and extremely high selectivity to methane (superior to 98%). Ni^{2+} incorporation into the CZ structure was proved to enhance catalysts specific activity. The global performance of the studied systems depended not only on the surface of available metallic nickel but also on the composition of the support and on its modification by Ni^{2+} doping. As a result of these two phenomena, the Ni-based mixed oxide having a CeO_2/ZrO_2 = 60/40 exhibited the highest catalytic activity, owing to an optimal Ni^{2+}/Ni^0 ratio. Noble metal addition led to higher Ni dispersion, resulting in a raise of both activity and catalyst life-time. It did not modify the support intrinsic activity. The deactivation was shown not to be due to carbon deposits but rather to nickel particles sintering. The investigated parameters thus allowed an improvement of the previously studied 5 wt% Ni–$Ce_{0.72}Zr_{0.28}O_2$ system.

1. Introduction

Human activities have resulted in an impressive raise in carbon dioxide emissions in the atmosphere, estimated to reach 30 Gt worldwide in 2008 [1]. Because of its impact on the environment through the greenhouse effect [2], its fixation has gained a lot of interest in recent years and has become a world challenge and priority. Among the viable solutions to mitigate CO_2 emissions, many studies focused on two strategies: its capture and storage [3–5] and its chemical recycling [6–13]. Indeed, raising attempts are made by industries to consider CO_2 as a valuable resource rather than a waste [13–15]. Hence, a compound without any value (or even negative value when considering carbon taxes) is converted into commercial chemicals or fuels. Furthermore, such companies involved in environmental issues now beneficiate from this growing positive image, thus leading to a further increase in their benefits. It is noteworthy to add that increasing amounts of low-cost and concentrated CO_2 will be available from carbon sequestration and storage units in a nearly future. Taking into account that the consumption of fuels is two orders of magnitude higher than chemicals' one, CO_2 has to be mainly converted into energy carriers such as methane [8–10,16], methanol or dimethylether [11–13].

CO_2 methanation remains the most advantageous reaction with respect to thermodynamics when compared to other hydrocarbons or alcohols production [17]. This reaction has been mainly investigated using Ni-based catalysts on various oxide supports [8–10,18–21]. In our previous work [16], Ni based catalyst on $Ce_{0.72}Zr_{0.28}O_2$ mixed oxides (80% of CeO_2 in weight), *i.e.*, Ni(80–20), were investigated for the first time in CO_2 methanation reaction. They turned out to be greatly efficient in terms of activity and stability. Their astonishing performances were attributed to their high oxygen storage capacity [22,23] and to their ability to highly disperse nickel [24]. Ni^{2+} cations insertion into the Ce–Zr (CZ) structure improved the redox properties [25] of the material and restricted the metal sintering, leading thus to a further improvement in their catalytic performance. 5Ni(80–20) (5% Ni in weight) presented the highest specific activity, however it also exhibited the smallest degree of CO_2 conversion and the lowest stability on stream during 150 h while 10Ni(80–20) was the most efficient. In this study, we focused on 5 wt% Ni loaded material with the aim of enhancing both its catalytic activity and stability.

It is well admitted that the use of bimetallic systems [26] or noble metals as rhodium and ruthenium generally has the specific ability to achieve this goal. According to the literature, they pro-

---

∗ Corresponding author. Tel.: +33 3 6885 27 60; fax: +33 3 6885 27 61.
E-mail addresses: blouis@unistra.fr, blouis@chimie.u-strasbg.fr (B. Louis), annececile.roger@unistra.fr (A.-C. Roger).

0926-860X/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2010.10.025

mote oxide-based catalysts such as $LaCoO_3$ [27] or Ni/MgO [28–29] in hydrocarbon reforming reactions. Our group has observed the same effects on Co or Ni based $Ce_xZr_{1-x}O_2$ (CZ) systems for ethanol and methane reforming reactions respectively [30–31]. Therefore, the H_2 spillover from noble metals should restrict Ni oxidation in the CO_2 methanation reaction. It is known that Ce/Zr composition is another factor that strongly influences the catalytic activity of CZ like systems in all types of reactions such as NO reduction in three-way catalysts [32], methane partial oxidation [33] or ethanol and methane reforming [31,34].

In this work, noble metal and Ni based CZ catalysts were prepared in a powder form by a sol–gel like method [35]. Ni–CZ with several CeO_2/ZrO_2 (C/Z) mass ratios was prepared to determine the influence of structural modifications on catalytic activity and selectivity. In order to evaluate the impact of noble metal addition, Rh and Ru were loaded on 0 and 5Ni(80–20) systems. All catalysts were tested in a fixed-bed down-flow reactor under the optimal reaction conditions settled down in our previous study [16]. Long-term experiments were performed during 150 h at 350 °C to investigate the deactivation of the catalysts.

2. Experimental

2.1. Preparation of the catalysts

The fluorite oxides Ni–CZ, Ni–Rh–CZ and Ni–Ru–CZ were synthesized by a pseudo sol–gel method, based on the thermal decomposition of propionate precursors. Ni loading was 5 wt% (coded 5Ni) and noble metal loading was 0.5 wt%. In addition, several C/Z mass ratios were prepared: 4, 1.5 and 0.25 referenced (80–20), (60–40) and (20–80) and referring to $Ce_{0.72}Zr_{0.28}O_2$, $Ce_{0.5}Zr_{0.5}O_2$ and $Ce_{0.14}Zr_{0.86}O_2$ in terms of molar composition respectively. The starting materials were cerium(III) acetate sesquihydrate, zirconium(IV) acetylacetonate, nickel(II) acetate tetrahydrate, rhodium(II) acetate, ruthenium(III) acetylacetonate. These starting salts were individually dissolved in boiling propionic acid in a concentration of 0.12 mol L^{-1} in cation, at 100 °C for 1 h, leading exclusively to propionate precursors. The boiling solutions were mixed during 2 h under reflux and then the solvent was evaporated until a resin was obtained. Finally, the resin was calcined under air at 500 °C for 6 h, with a heating ramp of 2 °C min^{-1}.

2.2. Characterization of the catalysts

The obtained metal contents in CZ mixed oxides were determined by Inductively Coupled Plasma (ICP) for elemental analysis (Service Central d'Analyse de Vernaison, CNRS, France).

Specific surface areas (SSA) of the different catalysts were determined by N_2 adsorption–desorption measurements at 77 K by employing the Brunauer–Emmet–Teller (BET) method (Micrometrics sorptometer Tri Star 3000). Prior to N_2 adsorption, the sample was outgassed at 200 °C overnight to desorb moisture adsorbed on the surface and inside the porous network.

X-ray diffraction patterns (XRD) were recorded on a Bruker D8 Advance diffractometer with a VANTEC detector side and Ni filtered Cu Kα radiation (1.5418 Å) over a 2θ range of 10–90° and a position sensitive detector using a step size of 0.05° and a step time of 1 s. The crystallite size of the samples was evaluated from X-ray broadening by using the well-known Debye–Scherrer equation [36].

Temperature-programmed reduction (TPR) was conducted on a Micromeritics AutoChem II to study the reducibility of the catalysts. TPR measurements were carried out on 100 mg of catalyst, loaded in a quartz U-tube and heated from room temperature to 900 °C at a heating rate of 15 °C min^{-1} under 10% H_2/Ar with a total gas flow of 50 mL min^{-1}. TPR profiles were presented as a function of temperature herein, but H_2 consumptions were calculated using the profiles expressed as a function of time for which the baseline returns to its initial value.

Scanning electron microscopy (SEM) micrographs were recorded on a JEOL FEG 6700F microscope working at 9 kV accelerating voltage. EDX spectra were acquired at an accelerating voltage of 15 kV.

The surface of metallic Ni (m^2) was calculated from the amount of chemisorbed hydrogen, measured by H_2 temperature-programmed desorption (H_2-TPD) on a Micromeritics AutoChem II (performed at GGRC-ISIC-EPFL-Switzerland). Prior to H_2-TPD, the catalyst (200 mg) was pre-reduced at 400 °C at a heating rate of 2 °C min^{-1} and held for 1 h under a 10% H_2/Ar flow and another 90 min in pure Ar flow to desorb any H_2 that might have been spilled over the support. The catalyst was then cooled down to room temperature and H_2 chemisorption pulses were performed. The sample was then purged with pure Ar to remove the reversibly adsorbed H_2. The TPD analysis was carried out from room temperature to 800 °C at a heating rate of 15 °C min^{-1} under pure Ar flow. The calibration of the system was based on mass 44 (corresponding to CO_2).

Carbon deposits formed during long test runs were carried out by means of temperature-programmed oxidation (TPO) on a Micromeritics Autochem II equipped with a mass spectrometer (at GGRC-ISIC-EPFL-Switzerland). Prior to TPO, a TPD was performed up to 600 °C under pure He, with a heating ramp of 15 °C min^{-1}, using 50 mg of catalyst having reacted for 150 h in the CO_2 methanation reaction in order to clean up the catalyst surface. Temperature was then cooled down to room temperature. The TPO analysis was carried out up to 900 °C, at a heating ramp of 15 °C min^{-1} under a 2% O_2/He flow.

2.3. Catalytic activity

The catalysts were reduced in situ before reaction in a 80% H_2/N_2 stream for 6 h with a total gas flow of 45 mL min^{-1} at 400 °C with a heating ramp of 2 °C min^{-1}.

Carbon dioxide methanation was conducted at atmospheric pressure in a fixed-bed down-flow reactor within the temperature range from 150 to 400 °C. Five injections were performed within 25 min and an average value was calculated each 50 °C. A thermocouple was inserted in the furnace to measure the pretreatment and reaction temperatures in situ. The reactor was heated in a tubular furnace monitored by a temperature controller.

The flow of reactants was regulated by calibrated mass flow controllers (Brooks). H_2 and CO_2 were mixed at a H_2:CO_2 ratio of 4:1 and N_2 was added as an internal standard. They were introduced into the reactor at a molar ratio of $H_2:CO_2:N_2 = 36:9:10$ and the total flow rate was set to 55 mL min^{-1}. 150 mg of catalyst was loaded into the reactor. The gas hourly space velocity was kept fixed at 43,000 h^{-1}. The feed and products were analyzed on-line by a micro gas chromatograph (Hewlett Packard, Quad Series Micro GC) equipped with TCD: alumina, poraplot and molecular sieve 5 Å columns. CO_2 conversion and CH_4 selectivity were defined as follows:

$$X_{CO_2}(\%) = \left(1 - \frac{CO_2}{CO_2+CH_4+CO+2C_2H_6}\right) \times 100 \quad \text{(carbon balance)}$$

or

$$X_{CO_2}(\%) = \left(1 - \frac{CO_2 \times (N_2)_{in}}{N_2 \times (CO_2)_{in}}\right) \times 100 \quad \text{(internal standard)}$$

$$X_{H_2}(\%) = \left(1 - \frac{H_2 \times (N_2)_{in}}{N_2 \times (H_2)_{in}}\right) \times 100$$