



# Biogas to syngas conversion without carbonaceous deposits via the dry reforming reaction using transition metal catalysts



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## ARTICLE INFO

### Article history:

Received 28 October 2014

Received in revised form 8 January 2015

Accepted 9 January 2015

Available online 6 March 2015

### Keywords:

Methane dry reforming

Syngas

Ceria-zirconia

Nickel

Selectivity

Coking

## ABSTRACT

This study investigates how morphology, active metal content and oxygen storage capacity of various bimetallic NiCo/CeZrO<sub>2</sub> materials influence their catalytic activity and stability in the methane dry reforming reaction. Catalyst preparation procedure and chemical composition were steered to finally obtain materials, which do not accumulate carbon during the CH<sub>4</sub>/CO<sub>2</sub> reforming reaction. Oxygen storage capacity of the CeZrO<sub>2</sub> catalyst support was identified to play a vital role in retarding carbon accumulation over the tested NiCo/CeZrO<sub>2</sub> materials. This property can be fully developed when a nanocrystalline solid solution of CeO<sub>2</sub> and ZrO<sub>2</sub> is formed. Secondly, a high dispersion of nickel and cobalt is crucial for two reasons: (i) catalysts which contain larger NiCo bimetallic particles (for example with 12–18 wt.% active metal loading) exhibit a low metal-support interphase that results in enhanced coke formation rates; (ii) additionally, only a marginal gain in methane reforming rates are achieved at higher loadings, compared to catalysts with a 3–6 wt.% active metal content. We demonstrated that a NiCo/CeZrO<sub>2</sub> catalyst under relevant operating conditions after 400 h TOS maintains 79 and 84% conversion of CH<sub>4</sub> and CO<sub>2</sub>, with negligible coke accumulation.

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## 1. Introduction

Rapidly decreasing fossil fuel reserves [1] and continuously increasing stringency of environmental regulations for CO<sub>2</sub> emissions [2] are stimulating us to seriously consider renewable resources as alternatives for syngas (mixture of H<sub>2</sub> and CO) production and its further catalytic transformation via established industrial processes into numerous base, specialty chemicals and also synfuels, such as Fischer-Tropsch hydrocarbons, methanol, DME, higher alcohols, etc. [3].

Beside biomass gasification, biogas reforming (Eq. (1)) could in the near future represent a meaningful complementary source of syngas without involvement of fossil resources. Biogas production in the EU27 states has increased from 4.9 to 10.1 Mtoe from 2006 to 2011 [4], which represented about 2% of annual European natural gas consumption in 2011. Main components of biogas are CH<sub>4</sub> (50–70%) and CO<sub>2</sub> (30–50%) with remaining impurities such as NH<sub>3</sub>, H<sub>2</sub>S, organic sulfur containing contaminants and water vapor. Methods for biogas purification (catalytic HDS, followed by H<sub>2</sub>S adsorption) can be adopted from natural

gas conditioning processes, thus making biogas an interesting carbon source for reforming processes, either with or without steam addition, depending on the final syngas utilization. Purified biogas streams can be mixed with CO<sub>2</sub>-rich streams, for example from coal-fired power plants, in order to adjust the CH<sub>4</sub>/CO<sub>2</sub> ratio before the reforming reaction.



Methane reforming with CO<sub>2</sub>, due to much more thermodynamically favored conditions for coke formation [5], requires development of new catalysts that can operate without coke accumulation. Industrially employed Ni/Al<sub>2</sub>O<sub>3</sub> based formulations for methane and naphtha steam reforming are unfortunately not up to the task due to fast coke buildup, followed by an increased pressure drop across the catalyst bed and catalyst deactivation [6]. If biogas reforming to produce syngas is to become a meaningful pathway for syngas production, transition metal based catalysts are most appropriate candidates because of their considerably lower price compared to noble metal based (Ru, Rh) counterparts. Amongst transition metals, nickel is the most active for reforming-type reactions; however, when used as the only supported active component, the catalyst is rapidly fouled by coke deposition. There are several known strategies how to decrease coke accumulation over transition metal-based catalysts in the

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methane dry reforming reaction. These include partial passivation by sulfur [7], alkali and earth alkali metal doping [8], bimetallic catalysts [9] and utilization of catalyst supports that exhibit substantial oxygen mobility (reducibility), such as titania [10], ceria [11] and ceria-zirconia [12,13]. Sulfur passivation and bimetallic catalyst approaches improve resistance to coke accumulation by partial nickel surface blockage or alloy formation that in turn partly deactivates or decreases the nickel surface ensemble size, which is still able to perform the methane reforming function, but the rate of carbon precursor polymerization to coke is strongly decreased. In both approaches, a reasonable trade-off in catalyst activity should be taken into account in order to achieve stable operation with decreased selectivity for carbon growth. However, providing an additional transitional metal does not require additional steps in the synthesis procedure, as opposed to sulfur based passivation. Dilution of Ni within the Ni-Co alloy decreases the effective particle size of Ni [14,15], resulting in considerable suppression of formation of precursors to filamentous carbon [16,17] and the growth of carbon nanotubes, which is greatly affected by the size of the active metal grain size [15].

Furthermore, the catalyst performance may also be improved greatly by the properties of the support. Reducible metal oxide catalyst supports retard coke accumulation through maintaining a high active metal dispersion via the strong metal-support interactions and supply of active oxygen species to the metal-support interface, where they act as oxidizing scavengers for coke precursors.

In this work we focused on the synthesis of thermally stabilized ceria-zirconia mixed oxides, which were used as supports for bimetallic nickel-cobalt clusters. Reaction conditions, effect of synthesis method on catalyst morphology, oxygen storage capacity and active metal loading were studied in order to obtain information on their contribution to stable and selective catalytic performance in the CH<sub>4</sub>-CO<sub>2</sub> reforming reaction.

## 2. Experimental

Several methods were used for CeO<sub>2</sub>-ZrO<sub>2</sub> support preparation (CeO<sub>2</sub>/ZrO<sub>2</sub> molar ratio of 4:1), which are noted in the following text as EG (Ethylene Glycol), HT (HydroThermal), HP (Homogeneous Precipitation) and PE (Pechini), respectively.

During a typical EG synthesis, Ce(NO<sub>3</sub>)<sub>3</sub> × 6H<sub>2</sub>O (Fluka, p.a.) and ZrO(NO<sub>3</sub>)<sub>2</sub> × 5.82H<sub>2</sub>O (Sigma Aldrich, >99% purity) with 1 g total mass were dissolved in 1 mL of ultrapure water and mixed with 1 mL of propionic acid (Merck, >99% purity) and 30 mL of ethylene glycol (Merck, >99% purity). The solution was transferred to PTFE-clad autoclaves and aged for 3.3 h at 453 K. After the appointed aging period, the precipitated solids were separated from the esterified solution by centrifugation at 8950 rpm in 15 min cycles. The obtained solid was washed with ultrapure water and ethanol and dried overnight in a laboratory drier at 343 K.

During the HT method, Ce(NO<sub>3</sub>)<sub>3</sub> × 6H<sub>2</sub>O and ZrO(NO<sub>3</sub>)<sub>2</sub> × 5.82H<sub>2</sub>O were dissolved in 100 mL of ultrapure water. The solution was added drop-wise to 250 mL of 25% aqueous ammonia solution (Merck, p.a.) while stirring intensively using a magnetic stirrer. The obtained suspension with 0.12 M total Ce and Zr ion concentration was transferred to PTFE-clad autoclaves and aged for 6 h at 393 K. The aged product was filtered, consecutively washed with distilled water and ethanol and dried overnight in a laboratory drier at 343 K.

During the homogeneous coprecipitation (HP) method, Ce(NO<sub>3</sub>)<sub>3</sub> × 6H<sub>2</sub>O and ZrO(NO<sub>3</sub>)<sub>2</sub> × 5.82H<sub>2</sub>O were dissolved in 100 mL distilled water to achieve 0.16 M total Ce and Zr ion concentration and urea (1 M) was added. Continuous mixing on the magnetic stirrer ( $N = 130 \text{ min}^{-1}$ ) and heating to 363 K, with a slow ramp (1 K/min) followed by 22 h of refluxing resulted in

homogeneous co-precipitation of both cerium and zirconium hydroxides. The obtained precipitate was filtered and washed several times with distilled water and absolute ethanol.

For the Pechini method, Ce(NO<sub>3</sub>)<sub>3</sub> × 6H<sub>2</sub>O and ZrO(NO<sub>3</sub>)<sub>2</sub> × 5.82H<sub>2</sub>O were dissolved in a water-ethylene glycol mixture ( $n_{\text{H}_2\text{O}}/n_{\text{EG}} = 1.7/1$ ) and glycine was added as fuel, resulting in its concentration of 0.3 M and Ce and Zr ion concentration of 0.65 M. The solution was aged in Teflon-clad autoclaves at 413 K for 30 min, followed by self-ignition.

After drying, the obtained CeZr powders were calcined for 4 h at 673 K in air with the heating ramp of 2 K/min. A systematic analysis of the influence of aging temperature and time on the morphology of the prepared CeZr powders for both EG and HT synthesis methods can be found in the publication from Osojnik et al. [18].

Nickel and cobalt, originating from nitrate precursors (Merck, p.a.), were deposited at the 40:60 weight ratio using homogeneous deposition precipitation method. Briefly, urea (Merck, p.a.) was used to increase the pH value of the aqueous CeZr suspension in a slow, controlled manner, while being heated from room temperature to 363 K under reflux. This temperature was maintained for 22 h in order to allow sufficient time for nickel and cobalt deposition. Afterwards, the suspension was filtered, washed with ethanol and water, and dried overnight in air at 343 K. NiCo/CeZr catalysts were thermally stabilized by 4 h calcination at 923 K in air. Total loadings of nickel and cobalt (3, 6, 12 and 18 wt.%) were deposited over the CeZr O<sub>2</sub> supports, which are in the following denoted as xEG, where  $x$  represents the total active metal content while EG indicates the individual synthesis method, used for the preparation of CeZr support.

Catalyst samples were thoroughly characterized by XRD (X'pert Pro by Panalytical), N<sub>2</sub> sorption (Tristar II 3020 by Micromeritics), H<sub>2</sub>-temperature programmed reduction and CO chemisorption (AutoChem II 2920 by Micromeritics) methods.

X-ray spectra were recorded on a PANalytical X'pert PRO diffractometer using Cu K $\alpha$  radiation ( $\lambda = 0.15406 \text{ nm}$ ). The scanned  $2\theta$  range was between 15 and 80° with 0.034° increment and 100 s dwell time at each increment. Unit cell size was calculated according to equation:  $a = (\lambda/2) \times (\sqrt{h^2 + k^2 + l^2} / \sin \theta)$ . In the latter, variable  $a$  represents the unit cell size,  $\lambda$  the X-ray irradiation wavelength,  $\theta$  the apex position of (1 1 1) reflection, with  $h$ ,  $k$  and  $l$  being the Miller indices of the (1 1 1) crystalline plane. The  $2\theta$  values, belonging to the reflection from (1 1 1) crystalline plane of different CeZrO<sub>2</sub> supports and pure CeO<sub>2</sub>, were obtained by fitting the corresponding signal with Pearson VII function in Origin 7.5 software.

H<sub>2</sub>-TPR measurements were performed in a Perkin Elmer Pyris 1 TGA apparatus. Prior to measurements, the samples were *in-situ* degassed in a flow of 10% O<sub>2</sub>/N<sub>2</sub> (50 N mL/min) while heated from RT to 573 K, followed by an isothermal step in N<sub>2</sub> (50 N mL/min, 60 min at 573 K). After pretreatment, the temperature was lowered to 323 K in N<sub>2</sub> flow, followed by a 15 min stabilization period. H<sub>2</sub>-TPR analysis was performed using 50 N mL/min of 5% H<sub>2</sub>/N<sub>2</sub> from RT to 1073 K with a 5 K/min ramp.

Extent of CeO<sub>2</sub> reduction was calculated based on the mass loss during the H<sub>2</sub>-TPR experiment. Ni and Co were assumed to be completely reduced and ZrO<sub>2</sub> did not contribute to the observed mass loss.

Elemental analysis (Perkin Elmer 2400 Series II CHNS elemental analyzer) was performed on the catalyst samples before and after the reforming reaction in order to evaluate the amount of deposited carbon during the catalytic runs.

CO chemisorption was used to evaluate the average NiCo bimetallic cluster size. Before analysis, the sample was *in-situ* reduced in a flow of 20% H<sub>2</sub>/N<sub>2</sub> (50 N mL/min) by heating from RT to 1023 K with a 10 K/min ramp, followed by an isothermal step at 1023 K for 1 h. Chemisorption was performed at 303 K. For the

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