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Effect of synthesis parameters on morphology and activity of bimetallic catalysts in CO_2–CH_4 reforming

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HIGHLIGHTS

- ▶ CeO_2–ZrO_2 powders were obtained by two solvothermal approaches.
- ▶ CeO_2–ZrO_2 supported NiCo catalysts were prepared for CH_4 dry reforming.
- ▶ Glycothermal synthesis yields catalyst supports with superior redox properties.
- ▶ Large active metal particles stimulate catalyst coking via methane dehydrogenation.
- ▶ Catalysts with small active metal particles are resistant to carbon accumulation.

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ABSTRACT

High surface area CeO_2–ZrO_2 (80/20 wt.%) mixed oxide supports with superior reducibility were synthesized by two solvothermal approaches, hydrothermal aging in NH_4OH aqueous solution and glycothermal aging in ethylene glycol. The materials aged in alkaline water at elevated temperature and pressure exhibit large crystallite sizes (roughly 30–40 nm), and structural segregation of the CeO_2 and ZrO_2 crystal phases. The materials synthesized by reduction in ethylene glycol show properties of homogeneous solid solutions with highly developed nanocrystalline structure (an average crystallite size was estimated at about 6 nm). Bare CeO_2–ZrO_2 supports were selected mostly on grounds of their reducibility for the subsequent homogeneous deposition coprecipitation with nickel and cobalt (3, 6, 12, 18 wt.%) loadings. The bimetallic catalysts were thoroughly characterized and then examined in the catalytic CO_2–CH_4 reforming reaction. The materials which exhibited both small crystallite sizes of the employed support and small active bimetallic particles, demonstrated high catalytic activity and good resistance to carbon accumulation on the catalyst surface. Dry reforming process over catalysts bearing glycothermally aged supports revealed the simultaneous occurrence of reverse water gas shift reaction, whereas the hydrothermally prepared supports stimulate methane dehydrogenation reaction at higher temperatures; the occurrence of both reactions is influenced by the dispersion of active metal species.

1. Introduction

Catalytic dry reforming of methane is rapidly gaining the interest of the scientific community and practitioners [1], since the process enables simultaneous utilization of two broadly accessible carbonaceous gases, CO_2 and CH_4 (Eq. (1)). Utilization of biomass-sourced CO_2 and CH_4 mixtures (e.g. biogas, decarboxylized organic acids, etc.) in dry reforming is particularly prospective.

$$CH_4 + CO_2 \leftrightarrow 2\,CO + 2\,H_2 \quad \Delta H^{\circ}_{298\,K} = +247\ \mathrm{kJ/mol} \tag{1}$$

The main engineering challenge of methane reforming with carbon dioxide is the suppression of carbon deposition on the catalyst surface. Traditional reforming catalysts based on nickel are especially prone to carbon accumulation and can cause undesirable pressure drops or complete choking of the reformer. Excessive carbon deposition can be avoided: (i) by the use of highly active and expensive noble metal catalysts [2] and (ii) by the use of bimetallic transition metal alloys that are more commonly applied due to their low cost and high availability. Dilution of Ni in a bimetallic solid solution generates a number of beneficial interactions, such as prevention of carbide and graphite formation [3–6] and the suppression of filamentous carbon growth, the latter mostly due to decrease of Ni particle size [7,8]. Zhang et al. [9] examined the performance of Ni bimetallic catalysts with Co, Fe, Cu and Mn

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and reported high activity and stability of Ni–Co catalyst for carbon dioxide reforming of methane. Surplus of Co in the Ni–Co alloy is reflected in lower levels of deactivation, suppressed carbon formation and improved H_2 yields [10,11]. On the other hand, supported monometallic Co catalysts show very low catalytic activity and are prone to active metal deactivation by oxidation. Therefore, the activity of Ni–Co catalysts depends mostly on the content of Ni [12]. A reasonable trade-off in catalyst activity should be expected in order to design a catalyst with attainable stable operation in the absence of active metal oxidation and carbon deposition.

Moreover, general catalyst performance in the dry reforming of methane is influenced by the properties of the support. Mixed oxide supports with good redox properties enable good dispersion of the active metal, formation of a strong metal/support interface and minimize carbon accumulation on the catalyst surface [2]. Due to the endothermic nature of dry reforming reaction and consequential high operational temperatures in the reformer, endurable catalytic supports with good refractory properties are required. Ceria (CeO_2) is well known for its superior reducibility and highly developed surface area [13], yet these properties are greatly diminished by exposing the material to elevated operation temperatures. Mixed ceria–zirconia oxides exhibit higher levels of reducibility than pure ceria or zirconia, an effect that is associated with the formation of structural defects formed during incorporation of zirconium atoms into ceria lattice structure, as the distorted O_2-sublattice allows reduction of the bulk oxygen. Thermal stability of the material increases with rising zirconium content, which also improves the oxygen storage capacity of the material, as long as the cubic phase of the solid solution is maintained and phase segregation of the ceria and zirconia is prevented [14–16].

In this study, we investigated the activity and stability of Co promoted Ni catalysts supported on thermally stable high surface area CeO_2–ZrO_2, prepared by two solvothermal synthesis approaches. Synthesis time and temperature were finely tuned in order to achieve desirable properties of the support. The effect of Ni and Co loading on the active phase dispersion, catalytic performance and carbon-deposition on the catalyst surface was evaluated.

2. Experimental

2.1. Materials

CeO_2–ZrO_2 (80/20 wt.%) mixed oxide supports were prepared either by hydrothermal approach (precipitation in NH_4OH at 100, 120, 140 and 160 °C, followed by 6, 12, 26, 48 and 90 h of aging; marked as "CeZr HT", followed by temperature and time) by tailoring the method presented by Raju et al. [17], or by glycothermal approach (reduction in ethylene glycol for 3.3, 6.7 and 10 h at 160, 180 and 200 °C; marked as "CeZr EG", followed by temperature and time) with variations of the synthesis conditions presented by Liang et al. [18] for the preparation of CeO_2 spheres. Solvothermal aging was performed in PTFE-lined stainless steel autoclaves. Prepared solid solutions were washed with ethanol and water, dried in air at 70 °C overnight, and subsequently calcined for 4 h at 400 °C.

One CeO_2–ZrO_2 powder from each synthesis approach, exhibiting the best characteristics (high surface area and good reducibility) was selected as the designated support material for subsequent deposition coprecipitation with nickel and cobalt in a broad loading range (3, 6, 12 and 18 wt.%; appropriately marked as "NiCo EG" or "NiCo HT" preceded by a numerical denotation of the active metal loading). Nickel and cobalt were deposited on the selected CeO_2–ZrO_2 mixed oxides by progressive thermal hydrolysis of urea, as it has been thoroughly reviewed by de Jong [19]. Nickel and cobalt nitrate precursors with 40:60 metal weight ratio were dissolved in the aqueous suspension of CeO_2–ZrO_2 (0.3 M urea). The suspension was mixed rapidly, heated gradually to 90 °C and refluxed. After 22 h of refluxing, the suspension was filtered and washed with ethanol and water, dried in air at 70 °C overnight and thermally stabilized in air at 650 °C for 4 h in order to allow the formation of Ni–Co particles [12].

2.2. Catalyst characterization

N_2 physisorption measurements were conducted at −196 °C with the use of Micromeritics TriStar II 3020 apparatus. Prior to measurements, samples were degassed in N_2 stream for 1 h at 90 °C and afterwards for 4 h at 180 °C using the Micromeritics SmartPrep Degasser.

High precision skeletal density measurements were carried out with the use of Micromeritics AccuPyc II 1340 gas displacement density analyzer using a 1 cm^3 sample chamber.

The synthesized catalysts were characterized by XRD technique (PANalytical X'pert PRO diffractometer equipped with the monochromator for Cu Kα1 radiation, $\lambda = 0.15406$ nm). Powdered samples were scanned over the 2θ range between 10° and 80° with the increment of 0.034° and measured for 100 s at each step.

Surface morphology of the prepared materials was characterized by means of a scanning electron microscope (Oxford Instruments, model SUPRA 35 VP equipped with Energy Dispersive X-ray analysis (EDX) hardware).

H_2-temperature programmed reduction (115 Nml/min of 4.5 vol.% H_2/N_2 mixture from 50 to 800 °C with a heating ramp of 5 °C/min), CO chemisorption of pre-reduced solid solutions performed at room temperature (in 115 Nml/min 9 vol.% CO/N_2 mixture) and temperature programmed oxidation (10 vol.% O_2/N_2 mixture from 50 to 800 °C with a heating ramp of 20 °C/min) were carried out with the use of a thermogravimetric analyzer (Perkin Elmer, model Pyris 1 TGA). Active metal particle size was calculated from metal dispersion (%) assuming spherical particles using the equation presented by Fan et al. [20].

The obtained active metal loadings of the prepared catalysts were checked by means of inductively coupled plasma optical emission spectrometry (Varian, model 715 ES). Prior to the measurements, the samples were heated with microwave irradiation (Milestone, model MLS 1200 Mega) and digested in a mixture of concentrated HNO_3 and H_2O_2.

Amounts of carbon, deposited on the catalyst surface after the dry reforming reaction were determined using a CHNS elemental analyzer (PerkinElmer, model 2400 Series II).

2.3. Catalytic runs

The performance of the synthesized catalysts was evaluated in a tubular (I.D. = 10 mm) quartz fixed-bed reactor system (PID Eng&Tech, model MicroActivity Reference). Prior to all catalytic tests, the catalysts were activated in 20% H_2/N_2 atmosphere (50 Nml/min) at isothermal conditions (60 min at 750 °C). After reduction, the reactor was cooled to 500 °C in the dry reforming reactant stream, composed of undiluted equimolar gaseous mixture of CH_4 and CO_2 at 50 Nml/min each (WHSV = 37 L $g_{cat}{}^{-1}$ h^{-1}, which corresponds to the residence time of gas phase of about 0.2 s). The fixed bed was comprised of 150 mg catalyst, diluted with 850 mg SiC sand ($d_p = 0.2 - 0.5$ mm, S_{BET} below 0.1 m^2/g, density: 3.19 cm^3/g) and stabilized with two quartz wool flocks. The reaction was carried out at 1.2 atm absolute pressure in the temperature range from 500 to 800 °C in 50 °C temperature increments. Each temperature step was maintained for 2.5 h. The reactor outlet was coupled to GC (Agilent Technologies, model 7890A) via a heated capillary (1/8″, 200 °C) for online analysis of discharged gas stream.