Supported Ni-Co bimetallic catalysts for syngas production from model biogas streams with varying CH₄/CO₂ ratio

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Introduction

Development of catalytic processes for efficient and clean conversion of renewable and waste resources into synfuels is gaining importance because they can provide alternatives for fossil based hydrocarbons. Available reserves of the latter are limited, their consumption rates are increasing rapidly and regulations for greenhouse gas emissions are becoming increasingly severe. Therefore, the need for minimization of our dependence on fossil fuels is urgent. Anaerobic digestion of organic material to produce biogas (mixture of CH₄ and CO₂) represents an environmentally friendly pathway with up to 85 % carbon efficiency. Biogas production in Europe currently accumulates to about 2 % of total natural gas consumption and is expected to grow about 4-fold until 2020 [1]. Biogas mixtures can be catalytically transformed into syngas via the dry reforming reaction (CH₄ + CO₂ \rightarrow 2CO +2H₂) and further into various synfuels through established syngas-based technologies (Fischer-Tropsch, methanol, DME etc.). This work deals with development of active and stable transition metal catalysts for methane dry reforming, which are not prone to coke buildup during the reaction conditions of variable CH₄ and CO₂ feed composition.

Materials and Methods

Nickel and cobalt (Ni:Co=40:60 w/w, total loading 3 wt. %) were deposited over the high surface area $CeZrO_2$ solid solution [2]. Catalyst samples were analyzed by SEM, Raman, CO chemisorptions, TEM, XRD, N₂ sorption and H₂-TPR methods.

Prior to all catalytic tests, powdered catalyst samples were reduced in-situ in a 20 % H_2/N_2 mixture (50 Nml/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. Catalytic tests were performed at 1.2 bar in a tubular quartz reactor (I.D.= 10 mm). Reactor was fed with CH₄ and CO₂ at 100 NmL/min total flow. Catalyst bed comprised of 150 mg catalyst, diluted with 850 mg of SiC (WHSV= 37 L/g_{cat}.h). Gases leaving the reactor were analyzed by GC.

Results and Discussion

The prepared bimetallic catalyst exhibited BET surface area of 38.1 m²/g and finely dispersed bimetallic nickel and cobalt active phase. Their average size was estimated at 5.8 nm from CO chemisorption results. XRD analysis confirmed high dispersion of the active metal components with no apparent diffraction peaks, which could be attributed to the presence of ordered nickel or cobalt particles. XRD and Raman analysis confirmed effective substitution of Ce⁴⁺ with Zr⁴⁺ ions in the FCC structure of ceria, resulting in the formation of a solid solution.

 H_2 /CO ratio in produced syngas was during performed tests improved significantly (from 0.72 to 1.34) with the increase of n(CH₄+H₂O)/n(CO₂) feed ratio (Table 1 and Figure 1).

Characterization of spent catalyst after 115 h TOS revealed only 0.24 wt. % of carbon deposits on its surface, which is due to high oxygen mobility of the CeZrO₂ support. During the H₂-TPR experiment, 67 % of Ce⁴⁺ to Ce³⁺ transformation was achieved.

Table 1.	Molar	feed	gas	compositions	in	the	performed	tests	of	biogas	reforming	using
NiCo/CeZ	ZrO ₂ cat	alyst.										

Component	1	2	3	4	5	6	7	8	9
CH_4	40	40	40	45	45	45	50	50	50
CO_2	50	45	40	45	40	35	40	35	30
H_2O	10	15	20	10	15	20	10	15	20

High water content in the feed did not result in catalyst deactivation. This is very encouraging since cobalt-based methane reforming catalysts are usually reported as very susceptible to oxidation (by water produced via RWGS reaction) and consequent deactivation. Improved stability of the developed catalyst probably originates from alloy formation between nickel and cobalt.



Figure 1. H₂/CO molar ratios obtained with various feed gas compositions (Table 1) using the 3NiCo/CeZrO₂ catalyst at 1023 K.

Significance

Results obtained over the NiCo/CeZrO₂ catalyst revealed that this solid can be very effectively used for catalytic transformation of simulated moist biogas streams into syngas with a H₂/CO ratio above 1. When feed gas composition is oxidant rich, *i.e.* $n(H_2O+CO_2)/n(CH_4) \ge 1$, coke accumulation on the catalyst surface can be completely avoided.

References

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