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Low-temperature CO₂ reforming of methane over Ni supported on ZnAl mixed metal oxides

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ABSTRACT

Ni catalysts supported on mixed ZnO–Al₂O₃ and on pure ZnO and Al₂O₃ were prepared, characterized by XRD, TPR, and XPS, and tested in long-term methane dry reforming at low temperature (400 °C). Depending on Zn/Al ratio in the supports, the catalysts varied in their physico-chemical properties and exhibited different trends in their on-stream catalytic activity. Catalysts with high alumina content consist of a mixture of alumina and zinc aluminate phases with metallic Ni particles on their surface. These samples show medium activity for reforming and high on-stream stability. The catalysts on mixed Zn-rich supports were more active than those on Al-rich supports and exhibited maxima in their activity after 30–40 h on stream, while Ni on pure ZnO possessed very low activity. Such contrast in performance of Zn-rich catalysts was explained by detected transformation of initially formed NiZn alloy to a mixture of Ni and Ni₃ZnC_{0.7} particles that are assumed to have higher activity for reforming. Moreover, the size of Ni-containing particles on Zn-rich supports decreased under reaction conditions resulting in higher Ni dispersion.

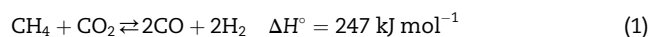
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Introduction

Dry reforming of methane (DRM) is a method of natural gas and carbon dioxide conversion into synthesis gas. Although not a commercial process yet, catalytic DRM is being intensively studied because it allows redial conversion of large volumes of CO₂ [1–5], which is especially important in light of increasing greenhouse gases emission. DRM is also seen as a viable alternative to steam reforming of methane since DRM-derived synthesis gas has the H₂/CO ratio of 1 which makes it valuable for the processes needing not as high H₂/CO ratio as produced by steam reforming [6].

Typically, DRM is carried out over supported catalysts containing noble metals [7–16], Ni [1,17–21] and Co [22–25] as a catalytically active phase. Noble metal-based catalysts have

high resistance to coking and thus extended lifetime. Ni-based catalysts are less resistant to coking and deactivate faster, but are more economical than the noble metal-based ones. Since the reaction is strongly endothermic (Eq. (1)), industrially relevant conversions are achieved at temperatures in excess of 700 °C.



However, DRM may become economical even at moderate degrees of CH₄/CO₂ conversion, i.e. when operated at lower temperatures. Removing the formed hydrogen in a membrane reactor can shift the equilibrium and thus higher conversion can be achieved at low temperature [26,27]. Reports on DRM catalysts being tested at low temperatures (≤550 °C) are found in literature [23,28–37], but they are by far less numerous than

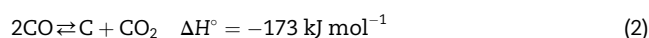
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on DRM performed at high temperatures. In contrast to high-temperature DRM, the choice of catalyst support is not restricted to those that are stable at high temperature which opens more opportunities for a catalyst design. One of the side reactions running concomitant with DRM is coke formation via Boudouard reaction (Eq. (2)). Being exothermic, this reaction is favored at low temperatures and thus may become the main pathway of coke formation at low temperature compared to methane decomposition being the coke forming reaction at high temperature. Due to this difference in coke formation mechanism, for low-temperature DRM other catalyst features may be responsible for coke resistance and thus, developing new catalysts for such operation conditions is a challenge.



In our previous study, we explored the influence of the support chemistry and morphology on the size of formed Ni particles and subsequently, on the catalysts coking behavior in low-temperature DRM [32]. It was found that Ni supported on mesostructured $\text{La}_2\text{O}_3\text{--ZrO}_2$ possesses the best activity and on-stream stability in a broad series of tested Ni-based catalysts. However, one potential candidate for a DRM catalyst support was not investigated in this reaction yet. $\text{ZnO--Al}_2\text{O}_3$ is capable of anchoring CO_2 [38], while $\text{Ni/ZnO--Al}_2\text{O}_3$ are viewed as promising catalysts for methanol [39] and ethanol [40] steam reforming as well as ethanol partial oxidation [41]. Ni metallic particles were suggested to have strong interaction with $\text{ZnO--Al}_2\text{O}_3$ support [42] which makes the catalyst resistant to deactivation by coking in reforming reactions.

The objective of our current work was to study the influence of $\text{ZnO--Al}_2\text{O}_3$ composition on physicochemical properties of $\text{Ni/ZnO--Al}_2\text{O}_3$ catalysts and consequently on their performance in low-temperature DRM. To this end, a series of supported $\text{Ni/ZnO--Al}_2\text{O}_3$ catalysts with varying Zn:Al ratio but similar loading of Ni were prepared, their phase composition and redox properties were examined and catalytic tests comparing activity and on-stream stability of the catalysts over extended period of time were performed.

Experimental

Preparation of the support materials and catalysts

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (ACROS) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck) were used as metal precursors. Mixed $\text{ZnO--Al}_2\text{O}_3$ oxides with Zn/Al ratios of 0.09, 0.15, 0.33, 1.28, 1.78 as well as pure ZnO and Al_2O_3 were synthesized by aqueous ammonia (25 vol.%) co-precipitation; washed and dried precipitates were calcined in air at 650°C for 5 h. The catalysts were prepared in a synthesis robot (Zinsser, Germany) by excess impregnation of the supports with aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (8 mg of Ni per mL). After drying under vigorous shaking at 90°C , the catalyst precursors were calcined in air at 650°C for 4 h. The catalysts are denoted according to their composition determined by elemental analysis, e.g. $\text{Ni/ZnAl}_{0.78}\text{O}_x$ describes Ni supported on a support containing 0.78 Al atoms per Zn atom.

Characterization

The specific surface area of the materials was measured by nitrogen adsorption on BELSORP-mini II (BEL Japan, Inc.) and calculated applying the Brunauer, Emmet and Teller (BET) equation for the N_2 relative pressure range of $0.05 < P/P_0 < 0.30$. The elemental composition of the supports and catalysts was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Varian 715-ES).

XRD powder patterns were recorded on a Panalytical X'Pert diffractometer equipped with a RTMS detector (X'Celerator), automatic divergence slits and $\text{Cu K}\alpha_{1/2}$ radiation (40 kV, 40 mA). Scan mode: continuous, step range: $5\text{--}80^\circ 2\theta$, step size: 0.0167° , counting time: 25 s/step. Cu beta-radiation was excluded by using nickel filter foil. $\text{Cu K}\alpha_2$ radiation was removed arithmetically using the Panalytical HighScore Plus software package. Peak positions and profiles were fitted with Pseudo-Voigt function using the WinXPow software package (Stoe). Phase identification was done by using the PDF-2 database of the International Center of Diffraction Data (ICDD).

Temperature-programmed reduction in hydrogen (TPR) was carried out on 30 mg of each fresh catalyst (sieve fraction $310\text{--}710 \mu\text{m}$). The samples loaded in quartz reactors were installed in a computer-controlled in-house developed 8-channel instrument with 8 independent ovens [43] and heated consecutively at 10 K min^{-1} to 900°C in 5 vol.% H_2/Ar mixture flowing at 7 mL min^{-1} . Hydrogen consumption and water formation were monitored by an on-stream quadrupole mass spectrometer (Pfeiffer OmniStar 200). Morphology of coke and Ni species on spent catalysts was examined by scanning electron microscopy (SEM) on JEOL 7401F instrument operated between 4.0 and 10.0 kV.

X-ray photoelectron spectroscopy (XPS) was performed at an ESCALAB 220iXL (ThermoFisher) with a monochromatic Al $\text{K}\alpha$ radiation source ($E = 1486.6 \text{ eV}$). For the charge compensation, a flood gun with low energy electron (10 eV) was used. The electron binding energy was referred to adventitious carbon at 284.8 eV. The samples reduced externally at 650°C were additionally reduced at 350°C in hydrogen in a reaction chamber in the lock of the XPS equipment and then transferred into the UHV chamber without any air contact. The peaks were fitted with a Gaussian–Lorentzian curve after background subtraction and in this form used for the calculation of the peak areas and determination of the binding energy. For the determination of the amount of the elements in the near surface region, the peak area was divided by the element-specific Scofield factor and the spectrometer-specific transmission function.

Catalytic test

Catalytic tests were performed in an in-house developed parallel reactor system containing 50 single fixed-bed continuous flow reactors (quartz tubes, inner diameter of 4 mm) installed in an oven. 100 mg of a calcined catalyst with a particle size of $310\text{--}710 \mu\text{m}$ were diluted with silicon carbide particles (750 mg, $500\text{--}710 \mu\text{m}$) to ensure isothermic and plug-flow conditions and loaded into a quartz reactor. Before the test, all catalysts were reduced in a 10 vol.% H_2/N_2 mixture at

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