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Influence of Ce/Zr molar ratio on catalytic performance of hydrotalcite-derived catalysts at low temperature CO₂ methane reforming

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ABSTRACT

Zr and Ce promoted hydrotalcite-derived materials were tested as a catalysts for dry reforming of methane. Zirconium species were introduced into hydrotalcite brucite-like layers, while cerium species were deposited on the external surfaces of crystallites. Three catalysts with Ce/Zr molar ratio of 1.2, 0.6 and 0.3 were synthesized, tested in dry reforming at 550 °C and subsequently characterized with the aid of XRD, XRF, FTIR, H₂-TPR, CO₂-TPD and TG techniques. Promotion with both Ce, Zr resulted in decrease catalytic activity, however, stability of materials was significantly increased, which could be attributed to increased concentration of strong basic sites. The effect of Ce/Zr molar ratio was mainly dependent on the position of Zr species in brucite-like layers or in mixed ceria–zirconia on catalyst surface and influenced materials basicity, reducibility and stability in DRM.

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Introduction

The growing emissions of carbon dioxide forced implementation of various CO₂ emissions reduction strategies, from which the very beneficial approach might be realized via chemical utilization of carbon dioxide. Such processes would not only decrease emission levels of harmful pollutant – CO₂, but also might be the source of industrially important

chemicals, among others hydrogen [1–4]. The process of dry reforming of methane (DRM) is considered an essential method for obtaining added-value products from CO₂ [5–7]. It allows to obtain synthesis gas with H₂/CO molar ratio desired for the production of organic oxygenated compounds or Fisher-Tropsch synthesis. Moreover, the DRM process is an excellent solution for transport and energy storage in Chemical Energy Transmission and Storage systems (CETS) [8–10]. The commercialization of the process is currently limited due

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to the high endothermicity of the process, low market price of CO₂ and lack of active and stable catalyst [11]. The latter is the most important limiting factor, therefore research for coke-resistant, active and economically available DRM catalyst is still an open question.

The research for DRM catalyst is currently focused on nickel-based materials, as they show similar activity to noble metals, and nickel is more abundant and cheaper material [12,13]. On the other hand, nickel-based materials still exhibit deactivation upon DRM due to the occurrence of C-forming reactions [14]. Much effort has been paid to increase stability of nickel-based catalysts and several approaches have been proposed, including [15–17]: implementation of appropriate catalyst preparation method, application of support with basic properties, addition of second metal, sulfur passivation, change of reaction conditions by the addition of oxidizing agents or application of various promoters. These strategies are mainly aiming at increasing nickel-support interactions which prevents Ni sintering and also results in the formation of small Ni crystallites upon catalyst activation which are more resistant to C-forming reactions [14].

The beneficial performance in DRM reaction was shown by nickel-based catalyst containing, among others, magnesia, alumina, ceria and/or zirconia. Magnesia and alumina supported nickel catalysts exhibit strong interactions between nickel species and support which is ascribed to the formation of NiO–MgO solid solution and NiAl₂O₄ spinel phase respectively [18,19]. The former additionally increases catalyst basicity. The advantage of addition of ceria is attributed to its high mobile oxygen capacity, which enhances basicity and thus removal of carbon deposits [20–24]. Basic properties of ceria supported/promoted catalysts may be further improved by introduction of ZrO₂ [25,26]. Moreover, Ni species may be incorporated into the lattice of ceria increasing in this way metal-support interactions [20,27,28]. Among various materials containing nickel, magnesia and alumina, hydrotalcite-derived catalysts showed very promising performance in DRM [29–38].

Hydrotalcites (HTs) or Layered Double Hydroxides (LDHs) are a group of synthetic layered minerals, which possess the structure of brucite and may be described by a general formula [39–41]: $[M^{2+}_{1-x}M^{3+}_x(OH)_2]([A^{n-}_{x/n}) \cdot mH_2O]$, where the part $[M^{2+}_{1-x}M^{3+}_x(OH)_2]$ describes the composition of brucite-like layers and the part $[(A^{n-}_{x/n}) \cdot mH_2O]$ the composition of inter-layer spaces. HTs brucite-like layers are built of octahedral units in which metal cation is placed in the centre of an octahedron and six OH⁻ groups are placed in the corners of the octahedron. Similarly as in brucite, the octahedral units are linked by edges, forming in this way parallel layers. Into the brucite-like layers various di-, tri- or even mono- and tetra-valent cations with ionic radii similar to those of Mg²⁺ and Al³⁺ can be introduced. The composition of interlayer spaces can be also controlled, and there is practically no limitation on the type of anion present between brucite-like layers, which compensates the positive charge of the layers. Such structure and properties of HTs allow to design the material with a desired composition, and thus to tailor their catalytic properties. After thermal decomposition of HTs a homogenous mixture of oxides is obtained. Moreover, HTs-derived materials possess basic character which increases CO₂ adsorption capacity, and thus are desired in DRM [39–42].

In our previous studies we established an optimal Ni content in brucite-like layers for DRM, which was ca. 20 wt.%. The material with such Ni content exhibited the highest basicity and concentration of strong basic sites on the catalyst surface, which enhanced its catalytic activity towards CO₂. Moreover, such nickel content in brucite-like layers resulted in the formation of Ni crystallites with an average size of ca. 6 nm, which was sufficient to partially eliminate C-forming reaction. Unfortunately, sintering of Ni species was observed, which resulted in the formation of carbon deposits [43]. Therefore, the tested sample was promoted with Zr, Ce or both (Ce and Zr) species [44].

The ceria promotion was intensively studied by Daza et al. who investigated the effect of the method of cerium introduction [45], of Ce loading [46–48], and hydrotalcite preparation method [49]. The authors observed increased catalytic activity of Ce-promoted samples with respect to unpromoted catalyst. This effect was attributed to the increase of reducibility of nickel species without simultaneous reduction in the size of the formed Ni particles. Moreover, as reported also in our previous paper [50], ceria addition enhanced basicity of HTs-derived materials, which promotes oxidation of carbon deposits via Boudouard reaction. Similar results were lately reported by Ren et al. [51].

Zirconia promotion over Ni-containing HTs-derived catalyst for DRM has not been yet thoroughly examined. In our previous paper, we showed that the addition of Zr species into brucite-like layers greatly increased the stability of the catalyst, by the inhibition of C-forming reactions, especially direct CH₄ decomposition. The most stable performance was shown by the catalyst promoted with both ceria and zirconia [44]. Therefore in this study, the influence of Ce/Zr molar ratio over HTs-derived Ni(Mg,Al)O mixed oxides was investigated.

Experimental

Catalyst preparation

The catalyst precursors were obtained by co-precipitation method from an aqueous solution of Mg, Ni, Al and Zr nitrates (Sigma Aldrich), using a 0.05 M sodium carbonate (Acros Organics) and 1 M NaOH (POCH) as precipitating agents. The nitrates solution with (Mg,Ni)/(Al,Zr) molar ratio equal to 3 and 1 M NaOH were added dropwise into the Na₂CO₃ solution kept at 65 °C. The velocity of adding the nitrates and base solutions were adjusted in order to work at fixed pH of 10 ± 0.2. The obtained suspension was maintained under vigorous stirring for 3 h at 60 °C, then filtered and dried overnight at 80 °C. Three hydrotalcite-like materials with Ni and Zr species introduced into brucite-like layers were obtained. The content of Zr species introduced into HTs structure was determined by a nominal value of Al/Zr molar ratio in brucite-like layers and was equal to 9:1, 8:2 and 6:4. In order to promote the obtained materials with Ce-species, the synthesized hydrotalcite powders were kept in contact with 3 wt.% aqueous solution of [Ce(EDTA)]⁻ complexes for 24 h at room temperature. The solution of [Ce(EDTA)]⁻ was prepared by a simultaneous addition of equimolar solution of cerium nitrate and disodium EDTA

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