

Abstract

Dry reforming also known as CO₂ reforming of methane (DRM) is a process that simultaneously transforms these two greenhouse gases into syngas (H₂, CO) with high economic and environmental benefit. This reaction was firstly studied over catalysts with low Ni content supported on various Mg-Al mixed oxides to identify different deactivation mechanisms and to develop stable and competitive DRM catalysts at either mild (stoichiometric) or severe (CH₄-rich) conditions with the latter having the perspective to mimic the direct conversion of biogas or specific natural gases.

Named Ni catalysts supported on Mg-Al mixed oxides were prepared from hydrotalcite precursors with various compositions and structures. The final catalysts were then obtained by wet impregnation followed by calcination at high temperature. The precursor Ni²⁺ was either complexed with citric acid (CA) and/or co-impregnated with La³⁺, Sc³⁺ or Gd³⁺ and the Ni content in final catalyst was fixed at 2.5 wt%. The solids were characterized using N₂ physisorption, X-ray diffraction, temperature-programmed reduction, X-ray photoelectron spectroscopy, UV-Vis diffuse reflectance spectroscopy, and scanning transmission electron microscopy with energy-dispersive X-ray spectroscopy.

DRM runs at temperatures above 600 °C, and the catalysts deactivate due to metal particle sintering or coking (methane decomposition, CO disproportionation). The latter effect may lead to reactor blockage. The deactivation pathways depend on the reaction conditions and can be differentiated well on low Ni content catalysts. Ni/Mg_{1.3}AlO_x with Ni species embedded in a solid solution of MgO and Al₂O₃ shows high DRM activity even at low temperature (500 °C). However, this catalyst was prone to carbon deposition, in stoichiometric DRM at low temperature or in CH₄-rich DRM, and suffered from metal agglomeration due to poor Ni dispersion and low metal support interaction (MSI).

By applying different modification routes catalysts with exceptional performance and stability at different DRM conditions were developed. In stoichiometric DRM, the Ni catalyst modified with La and CA-assisted synthesis showed the highest stability against both Ni re-oxidation and agglomeration. This catalyst revealed low coking rate and maintained high activity over 160 h with outstandingly high productivity of hydrogen (118 L/(g_{cat}×h)). In severe CH₄-rich DRM, the La- and CA-modified Ni catalyst supported on thermally pre-treated Mg_{1.3}AlO_x at 1000 °C revealed highest coking resistance. Likewise, Gd.Ni/Mg_{1.3}AlO_x exposed good carbon suppression and both catalysts accomplished high and quite stable activity over 100 h on stream with limited carbon deposition (approx. 6 wt%). These results are promising for Ni catalyst development for industrial-scale DRM.

