

Dry reforming of biogas over mixed oxides derived from hydrotalcite catalysts

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Introduction

Biogas or landfill gas is produced by anaerobic digestion of organic matter, such as animal waste. Biogas is composed mainly by CH₄ and CO₂ and therefore its emission to the atmosphere may contribute significantly to the greenhouse gas effect. The conversion of biogas into a high value-added product such as synthesis gas by dry reforming of methane (DRM) is a promising technology for energy generation [1]. Ni-based catalysts have been extensively studied for DRM due to its high activity and low cost, but these catalysts are prone to coking [2]. Different strategies have been proposed to prevent carbon formation, such as: (i) the control of ensemble size; (ii) the use of supports with high rate of CO₂ dissociation. Hydrotalcite (HT)-type compounds have been reported as promising precursors for DRM catalysts. The calcination and reduction of these materials produce highly dispersed metallic particle, high surface area and basic properties which improve CO₂ dissociation [3]. Therefore, the aim of this work is to study the performance of Ni-based catalysts derived from hydrotalcite precursor for the dry reforming of biogas.

Materials and Methods

Three HTs precursors were synthesized by co-precipitation method, varying the Ni loading (5, 10 and 15 wt%). Aqueous solution of mixed metal nitrates (Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, Ni(NO₃)₂·6H₂O) was added dropwise into a solution with Na₂CO₃ and NaOH, under stirring at pH 10 and kept at room temperature for 21h. Then, the precipitated was vacuum filtered and dried overnight at 383 K, followed by calcination at 823 K for 2 h. Three mixed oxides were obtained: 5NiMO, 10NiMO and 15NiMO. The samples were characterized by X-ray diffraction (XRD), CO₂-temperature programmed desorption (CO₂-TPD), temperature programmed reduction (TPR), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). Prior to reaction, the catalysts were reduced under H₂ at 1023 K for 1 h. DRM was performed in a fixed-bed reactor at 1073 K and atmospheric pressure, using a CH₄:CO₂ molar ratio of 1.0 and 1.2.

Results and Discussion

The diffractograms of the mixed oxides revealed the formation of a NiMgAl solid solution for all samples, in agreement with the TPR profiles. After reduction, all catalysts exhibited the same Ni crystallite size (5 nm). The total density of basic sites calculated from the CO₂-TPD profiles was approximately the same for all samples. However, the distribution of basic sites depended on the Ni content. 15NiMO showed a higher fraction of strong basic

sites. The CH₄ and CO₂ conversion remained constant during 24 h time on stream (TOS) for all catalysts. In addition, the CO₂ conversion was higher than CH₄ conversion, indicating the occurrence of reverse of water-gas shift (RWGS) reaction. 15NiMO catalyst exhibited the highest H₂/CO molar ratio (0.79). SEM images showed the formation of carbon filaments (Fig. 1a). The amount of carbon deposited over all samples during DRM was determined by TGA (Fig. 1b). The catalyst 15NiMO was more resistant to coke formation (0.04 mgC.g_{Ni}⁻¹.h⁻¹.mol reacted CH₄⁻¹), which is likely due the higher amount of strong basic sites. According to the literature [4], increasing basicity decreased the amount of carbon deposits due to the increase of carbon gasification rate. Increasing the CH₄:CO₂ molar ratio led to a higher formation of carbon (0.26 mgC.g_{Ni}⁻¹.h⁻¹.mol reacted CH₄⁻¹) due to the increase in the rate of CH₄ decomposition [5].

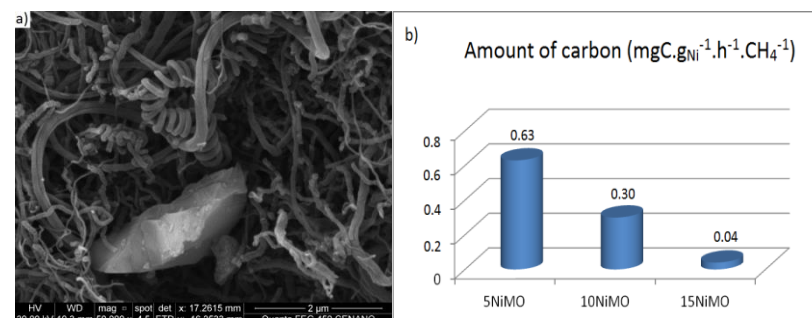


Figure 1. (a) SEM image of carbon filaments after the reaction; (b) Amount of carbon after the reaction measured by TGA.

Significance

The development of a catalyst that is stable for the DRM is one of main challenges for the commercialization of this technology. In our work, we demonstrate that the hydrotalcite-type oxides are promising catalyst precursor for the conversion of biogas into syngas for energy generation. The mixed oxide containing 15%wt. Ni exhibited high activity with low carbon formation for DRM.

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