Syngas production by the CO_2 reforming of CH_4 over Ni–Co–Mg–Al catalysts obtained from hydrotalcite precursors

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ABSTRACT

The catalytic performance of the Ni, Co, Mg, and Al mixed-oxide solids, synthesized via hydrotalcite route, was investigated towards the dry reforming of methane for hydrogen production. The hydrotalcite structure was successfully obtained upon the synthesis. After calcination at 800 °C under an air flow, this structure was completely decomposed and the resulting oxides ($Co_xNi_yMg_zAl_2800$, x and y = 0; 1; 2; 3; 4, z = 2; 4, x + y + z = 6, x, y, and z are the molar ratios) were used as catalysts and were characterized using X-ray diffraction and Temperature-Programmed Reduction. The dry reforming of methane was carried out using a mixture of CH_4:CO_2 (1:1) after 2 h of reduction under an H_2 flow at 800 °C. $Co_2Ni_2Mg_2Al_2800$ showed the highest catalytic activity in the studied series, ascribable to an interaction between Ni and Co, which is optimal for such Co/Ni ratio. The post-reaction characterization of the catalytic samples by X-ray diffraction and Differential Scanning Calorimetry evidenced a better resistance towards carbon deposition for the catalysts where Co molar ratio is higher than Ni.

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Introduction

The depletion of the conventional fuel reserves with the increasing in the energy demand has captured the attention of all societies [1]. Actually, energy has an irreplaceable status, but the use of fossil fuels contributes to global warming due to greenhouse gases emission [2]. Recent researches have rationally shifted towards the development of a clean, sustainable, and renewable source of energy. In that regard, hydrogen is particularly attractive since it can be stored and transported efficiently, and it burns cleanly producing only water as a byproduct [3,4]. Hydrogen can be obtained from the conversion of biogas which is mainly composed of methane (CH_4) and carbon dioxide (CO_2) and produced by anaerobic decomposition of organic material. In this context, the dry reforming of methane (DRM) has been investigated as a promising route providing a renewable source of energy [5]. In fact, the syngas produced has an equimolar mixture of hydrogen (H_2) and carbon monoxide (CO) which is suitable to prepare a large variety of chemicals such as acetic acid, ammonia, methanol, Fischer–Tropsch chemicals [6]… In addition, DRM (1) reduces simultaneously CH_4 and CO_2, the two important greenhouse gases and provides the opportunity of using natural gas resources, avoiding the gas separation process.

$$CO_2 + CH_4 \rightarrow 2\ CO + 2\ H_2, \Delta H^0_{298K} = 247\ kJ \cdot mol^{-1} \qquad (1)$$
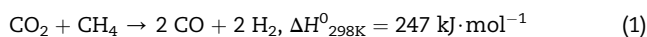
This is an endothermic reaction but even at higher temperatures, it needs suitable catalysts to induce sufficient conversions [7]. The most active components used for the reforming of methane by carbon dioxide are the transition elements in group VIII such as Ru, Rh, Pt and Ir. Nevertheless, applying cheap and abundant metals such as Co and Ni, which are also active for this process, is certainly preferred [8–11]. However, the deactivation caused by the potential carbon deposition on the catalysts of DRM reaction is a major barrier for commercial application in the chemical industry. Carbon is produced by secondary reactions and leads to catalyst deactivation [6].

Mixed oxides-based catalysts containing transition metal cations are often used to overcome this problem. They can be easily obtained by a controlled thermal decomposition of the layered double hydroxides (LDHs), which are also known as hydrotalcite-like compounds. Various approaches have been developed to synthesize LDHs powder including co-precipitation, sol gel, ion exchange and hydrothermal treatment [12]. Among these methods, co-precipitation is the most favorable because it allows controlling several parameters such as temperature, stirring speed, pH and nature of precursors…. LDHs are natural or synthetic laminar materials, whose structure is similar to brucite ($Mg(OH)_2$) and natural hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$) [13]. Their chemical composition may be presented by the general formula $[M^{II+}_{1-x}M^{III+}_x(OH)_2]^{x+}\ (A^{n-})_{x/n} \cdot y\ H_2O$ where M^{II+} and M^{III+} are divalent and trivalent metal cations, respectively, x is the mole fraction of the trivalent cation, A^{n-} is the anion of compensation, and y is the degree of hydration. Generally, M^{II+} may be Ni^{2+}, Co^{2+}, Zn^{2+} or Cu^{2+}, M^{III+} may be Al^{3+}, Ce^{3+} or Fe^{3+}, and A^{n-} may be CO_3^{2-} or NO_3^- [14]. The calcination of

these materials results in the formation of solid basic oxide that exhibit excellent catalytic performances such as small crystal size, basic character, high dispersion and large specific surface area, required for heterogeneous catalysts [14,15]. Cobalt and nickel are widely recognized for their catalytic activity in the reforming of methane. Ni-based catalysts have been reported as effective catalysts for DRM with low cost and desirable performance [7,9]. They present high activity in terms of methane conversion but they are affected with severe deactivation due to their coking and sintering problems [16–18]. On the other side, Co-based catalysts have showed catalytic stability and coke resistance when increasing the Co loading which probably arises from the higher affinity of Co for oxygen species [8,19,20]. Co–Ni based systems seem to be very promising as they combine the high activity of nickel with the high resistance of cobalt towards carbon deposition. In fact, these advantages appear in the literature, where few studies [10,15,21] corroborate that the presence of such co-cations in the solids will modify the catalytic properties, in particular the redox behavior and the resistance to catalyst deactivation. According to Munoz et al. [15], the mixed Ni–Co system exhibits better redox behavior and stronger basic centers in comparison with the Ni or Co isolated systems. Other contributions such as Zhang et al. [22] and Zhu et al. [23] report that the bimetallic catalyst of Ni–Co had a great tolerance to coke formation resulting from synergetic effects as well as highly dispersed active metal and strong metal-support interactions. This better performance of the Ni–Co bimetallic catalyst is attributed by Long et al. [14] to its higher metal dispersion, smaller metal particle size and to the interaction effect between Ni and Co.

Thus, the aim of this present work is the preparation of catalysts by incorporating Co and Ni with different Ni/Co contents in the LDH structure in order to improve their catalytic properties. Calcination is employed to decompose these precursors to obtain the corresponding oxides whose catalytic properties are evaluated in the DRM reaction. Finally, physicochemical characterization was carried out on the series of the prepared catalysts before and after test.

Experimental section

Preparation of catalysts

Co, Ni, Mg and Al based mixed oxides were synthesized by hydrotalcite route with a molar ratio $M^{(II+)}/Al^{3+} = 3$. A solution containing appropriate quantities of $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, and $Al(NO_3)_3 \cdot 9H_2O$ was added drop wise under vigorous stirring to NaOH (2 M) and Na_2CO_3 (1 M) aqueous solution. The pH was maintained at 9 and the temperature at 60 °C. The resulting slurry was heated at 60 °C for 18 h to slowly crystallize the hydrotalcite phase. Then, the precipitate was filtered, washed several times with hot deionized water (60 °C) until a neutral pH and dried at the same temperature for 48 h. The precipitate was ground to obtain fine powders and then calcined at 800 °C for 4 h under flow of air (2 L h⁻¹, 1 °C·min⁻¹). The solids calcined at 800 °C were named: $Co_2Mg_4Al_2800$, $Ni_2Mg_4Al_2800$, $Co_1Ni_1Mg_4Al_2800$,