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Short Communication

Partial oxidation of methane over Ni–Co perovskite catalysts

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ABSTRACT

A series of $LaNi_{1-x}Co_xO_3$ compounds (x = 0, 0.2 and 0.4) was synthesized by the combustion method with urea and used as catalyst precursors in the partial oxidation of methane (POM). Only $LaNiO_3$ was obtained as a single phase. The substitution of Ni by Co in $LaNiO_3$ perovskite caused formation of secondary phases and resulted in a decrease in the specific surface area and an increase in the reduction temperature. After the reduction treatment, the perovskite structure was completely decomposed and the only phases detected were Ni^0, Co^0 and La_2O_3. Activity cycles between 400 and 800 °C revealed that the introduction of Co decreased the catalytic activity for POM reaction at high temperature. No apparent deactivation was observed during 24 h on stream at 750 °C for all catalysts.

1. Introduction

There has been substantial interest in alternative routes for conversion of natural gas (methane) to synthesis gas, a mixture of CO and H_2, which can be used to produce chemical products with high added values, such as hydrocarbons and oxygenated compounds. Generally, methane is converted to synthesis gas by steam reforming, but it requires a large amount of heat addition and the H_2/CO ratio obtained (about 3) is too high for fuel synthesis via Fischer–Tropsch reaction [1].

Partial oxidation of methane (POM — Eq. 1) is an advantageous route for synthesis gas production for both economical and technical reasons: it makes the process less energy and capital cost intensive because of its exothermic nature and the lower H_2/CO ratio (about 2) is more favorable with respect to downstream processes such as methanol synthesis and Fischer–Tropsch synthesis of higher hydrocarbons [2,3].

$$CH_4 + {}^1/_2O_2 \Leftrightarrow CO + 2H_2 \qquad \Delta H_{298K} = -36\,kJ/mol \tag{1}$$

Many catalysts have been studied in the POM reaction, most of them based on noble (Pt, Ru, Rh, and Pd) or non-noble (Ni, Co, and Fe) metals deposited over porous supports, as recently reviewed by Enger et al. [4]. Industrially, the metal of choice is nickel due to its high activity for reforming/oxidation reactions, interesting redox properties and relatively low cost. However, it is difficult to prevent sintering of nickel and coke deposition at high temperatures.

An attractive option of a Ni-based catalyst for POM is to use perovskite-type oxides (ABO_3), which are well defined structures that produce small metallic particles after reduction, with high dispersion on the surface of the oxide support, reducing sintering and avoiding coke formation [5].

Perovskite-type oxides offer the possibility of partial substitution of both A and B cations, modifying their oxidation state, the mobility of lattice oxygen and the redox properties, which modify the catalytic performance [5]. In particular, studies performed with $LaNiO_3$ evidenced that nickel into this type of structure is stabilized against sintering and limits the coke formation [6,7].

Optimizing the catalytic properties requires detailed studies of the perovskite composition and the preparation methods. Choudhary et al. [8] showed that substitution of Ni by Co decreased both activity and selectivity for oxidative conversion of methane. However, Co tends to stabilize the structure under a reducing environment, limiting the metal particle growth [9].

In this work, perovskites of general formula $LaNi_{1-x}Co_xO_3$ (x = 0, 0.2 and 0.4) were synthesized by the combustion method with urea and used as catalyst precursors in the POM reaction. The effect of Co addition was investigated on the catalytic activity and stability, as well as on the structure and reducing behavior of the catalyst.

2. Experimental

2.1. Catalyst preparation

The materials used in the synthesis were metal nitrates, La $(NO_3)_3 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$, and urea as the propellant. All reagents were from Vetec, Brazil. In the combustion method, the metal nitrates were dissolved with the fuel (Table 1) in

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