Current Catalysis, 2012, *1*, 215-220

Ni-Fe Catalysts Derived from Perovskite Precursors for Partial Oxidation of Methane

Camila R. B. Silva, Nielson F.P. Ribeiro and Mariana M.V.M. Souza*

Escola de Química – Universidade Federal do Rio de Janeiro (UFRJ), Centro de Tecnologia, Bloco E, sala 206, CEP 21941-909, Rio de Janeiro/RJ, Brazil

Abstract: $LaNi_{1-x}Fe_xO_3$ perovskites (x= 0, 0.2 and 0.4) were synthesized by the combustion method with urea and used as catalyst precursors in the partial oxidation of methane (POM). $LaNiO_3$ was obtained as a single phase, while NiO and $La(OH)_3$ were also detected in Fe-doped samples. The substitution of Ni by Fe in $LaNiO_3$ perovskite resulted in a decrease in the specific surface area and an increase in the reduction temperature. The perovskite structure was completely decomposed by reduction, with formation of Ni°-Fe° and La_2O_3 phases. Activity cycles between 400 and 800°C revealed that the introduction of Fe decreased the catalytic activity for POM reaction at high temperatures. The catalysts showed great stability during 24 h on stream at 750°C without carbon deposition.

Keywords: Ni-Fe catalysts, perovskites, partial oxidation, methane, syngas.

1. INTRODUCTION

In a near future, natural gas is expected to become an increasingly important raw material for the synthesis of clean fuels and chemicals. Production of synthesis gas, a mixture of CO and H_2, from methane followed by its conversion to a wide range of fuels and chemicals is of particular interest as the worldwide reserves of crude oil are being depleted [1]. Generally, methane is converted to synthesis gas by steam reforming, but it requires a large energy supply due to the strong endothermicity and the H_2/CO ratio obtained (about 3) is too high for fuel synthesis via Fischer-Tropsch reaction [2].

Partial oxidation of methane (POM- Eq. I) is an advantageous route for syngas 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 [3, 4].

$$CH_4 + \frac{1}{2} O_2 \Leftrightarrow CO + 2H_2 \quad \Delta H_{298K} = -36 \text{ kJ/mol} \quad (I)$$

Many catalysts have been studied in the POM reaction, most of them are based on noble (Pt, Ru, Rh, Pd) or non-noble (Ni, Co, Fe) metals deposited over porous supports, as reviewed by Enger *et al.* [5]. 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 [6].

A particularly attractive option of a Ni-based catalyst for POM is to use precursors with perovskite structure. The general formula of these oxides is ABO_3, in which the cation A of larger size is responsible for the thermal resistance whereas the cation B of smaller size accounts for the catalytic performance. These compounds produce small metallic particles after reduction, with high dispersion on the surface of the oxide support, reducing sintering and avoiding coke formation [7]. 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 [7]. In particular, studies performed with $LaNiO_3$ evidenced that nickel into this type of structure is stabilizing against sintering and limits the coke formation [8, 9].

Optimizing the catalytic properties requires detailed studies of the perovskite composition and the preparation methods. Provendier *et al.* [10] showed that substitution of Ni by Fe in $LaNi_xFe_{1-x}O_3$ perovskite catalysts prepared by sol-gel route decreased both activity and selectivity for partial oxidation of methane; however, Fe tends to stabilize the structure in testing conditions and limits the mobility of the active nickel. Lima and Assaf [11] observed that the addition of iron in $LaNiO_3$ perovskites prepared by precipitation increased the stability of the catalysts for dry reforming of methane, while causing a decrease in the catalytic activity.

Combustion synthesis is characterized by fast heating rates, high temperatures and short reaction times. It is a straightforward preparation process to produce homogeneous, crystalline and nano-sized oxide powders, without intermediate decomposition steps [12, 13]. The most common fuel used in the combustion process for the perovskite synthesis is glycine; this fuel was used by Gallego *et al.* [6, 14] to synthesize $LaNiO_3$ and $LaNi_{1-x}Co_xO_3$ perovskite catalysts for dry reforming of methane. We have shown recently that urea is an adequate fuel to synthesize different perovskites, with good phase formation because the combustion reaction is slower than using glycine, which promotes increased formation of gases, producing materials of high crystallinity with nanometric dimensions [15, 16]. The combustion synthesis has not been used to prepare Ni-Fe catalysts for POM reaction yet.

---

*Address correspondence to this author at the Escola de Química – Universidade Federal do Rio de Janeiro (UFRJ), Centro de Tecnologia, Bloco E, sala 206, CEP 21941-909, Rio de Janeiro/RJ, Brazil; Tel: 55-21-25627598; Fax: 55-21-25627596; E-mail: mmattos@eq.ufrj.br

2211-5455/12 $58.00+.00