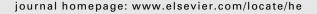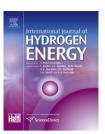Available online at www.sciencedirect.com

SciVerse ScienceDirect

Stability of Ni and Rh–Ni catalysts derived from hydrotalcite-like precursors for the partial oxidation of methane

Deborah V. Cesar [a,b], Maria A.S. Baldanza [a], Cristiane A. Henriques [a,b], Francisco Pompeo [c], Gerardo Santori [c], John Múnera [d], Eduardo Lombardo [d], Martin Schmal [a], Laura Cornaglia [d], Nora Nichio [c,*]

[a] UFRJ/COPPE/NUCAT Núcleo de Catálise -Programa de Engenharia Química - Universidade Federal do Rio de Janeiro - Caixa Postal 68502 Rio de Janeiro 21945-970, RJ, Brazil
[b] UERJ/IQ/PPGEQ — Programa de Pós-graduação em Engenharia Química — Instituto de Química — Universidade do Estado do Rio de Janeiro, Rio de Janeiro, RJ, Brazil
[c] CINDECA, y Facultad de Ingeniería, UNLP-CONICET, 47 No. 257, 1900 La Plata, Argentina
[d] INCAPE (FIQ, UNL-CONICET), Santiago del Estero 2829, 3000 Santa Fe, Argentina

ARTICLE INFO

ABSTRACT

In this work, NiMgAl and RhNiMgAl catalysts prepared from HTLCs precursors were investigated for the Partial Oxidation of Methane (POM) at 550 and 750 °C. Samples have been characterized by XRD, TPR, H_2 chemisorption, TPSR analyses, XPS, field emission scanning electron microscopy and Raman spectroscopy. NiMgAl catalysts with high Ni content (40 and 16 wt%) showed high stability and high methane conversion for POM. On the other hand those with lower Ni content (NiHT15 and NiHT25, with 6 and 4 wt%) exhibited low catalytic activity with low H_2/CO ratio (<2) and fast deactivation. In RhNiHT25 (0.6 wt. % Rh), the Ni reducibility was improved, increasing the methane conversion and hydrogen selectivity. In addition, the noticeable increase in stability was related to the absence of carbon deposition after 30 h on stream at 550 °C. These results show that RhNiHT25 is promising for application in membrane reactors to produce high purity hydrogen.

1. Introduction

In the last few years, there has been a significant progress in the study of hydrogen generation from alternative sources other than fossil fuels. However, natural gas has proven to be increasingly competitive in relation to various other fuels, either in the industrial sector or in power generation. According to the International Energy Agency (IEA) [1], the demand for natural gas in energy production will keep expanding until 2020. Methane is the main component in natural gas and due to its economic feasibility it has become the main source of synthesis gas and hydrogen produced from steam reforming. Partial oxidation (POM) is a promising substitute for the steam reforming process since it is economical, shows high conversion and selectivity to hydrogen besides the production of H_2 and CO in a ratio of 2, which is suitable for the Fischer Tropsch synthesis [2]. Moreover, the low endothermicity and the short contact time of the process are interesting features if small or medium-sized plants are projected [3]. On the other hand, due to the high temperatures

and space velocities, the development of new active and stable catalysts for POM is an issue of interest. Among the different catalysts that have been analyzed, those based on nickel are the most widely studied ones for this reaction and their main advantage is the low cost. However, these catalysts are susceptible to carbon deposition and the active Ni metallic particles can be oxidized even at low temperatures of reaction. This justifies increasing efforts in the study of catalyst formulation in order to obtain stable systems based on Ni. The preparation method and the synthesis parameters are important features since they influence the interactions between the metal and the support playing an important role on the catalytic performance including the prevention of carbon deposition and sintering [4–7].

Thermally treated hydrotalcite-like compounds (HTLCs) lead to mixed oxides with high surface area, thermal stability, basic properties and highly homogeneous dispersion of the elements into the oxide matrix. Many catalytic applications have arisen since the 1990s and are based on basic and/or redox properties, which are associated with stable metallic particles [8–10]. The use of Ni based or noble metal mixed oxides derived from HTLCs as active catalysts for H_2 production has been extensively studied, not only for the partial oxidation of methane but also for steam reforming [11], dry reforming [12] and autothermal reforming of methane [13] at reaction temperatures higher than 650 °C [14–17]. However, only a few papers have reported the activity and stability of these materials at low temperatures (T ∼ 550 °C), which may allow their application on membrane reactors. In the literature, Rh has been studied as a good promoter that increases the activity of the Ni catalysts and decreases the carbon deposition [6,7]. However, several authors have claimed that Rh–NiMgAl catalysts present higher rates of carbon deposition, in the dry reforming and POM reactions, suggesting that carbon deposition occurred because Rh favors CH_4 decomposition [18].

In this work, Ni–Mg–Al catalysts prepared from HTLCs precursors were investigated for the POM reaction at 550 and 750 °C. Since carbon deposition is a key negative factor for use in Pd based membrane reactors, we have also studied the effect of Ni content and Rh incorporation on the catalytic behavior. Special attention was paid to the stability of these formulations in connection with carbon deposition.

2. Experimental

2.1. Catalyst preparation

Hydrotalcite samples were prepared by coprecipitating an aqueous solution of nickel, magnesium and aluminum cations (solution A) with a highly basic carbonate solution (solution B) at room temperature. Solution A, containing $Ni(NO_3)_2 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ dissolved in distilled water was 1.5 mol L^{-1} in (Al + Mg + Ni) with an Al/(Al + Mg + Ni) molar ratio equal to 0.25 and a Ni/Mg molar ratio of 1/1, 1/5, 1/15, and 1/25. Solution B was prepared by dissolving appropriate amounts of Na_2CO_3 and NaOH in distilled water in order to obtain a $[CO_3^{2-}]$ equal to 1.0 mol L^{-1} and a pH equal to 13 during the ageing of the gel. In the synthesis

procedure, solution A was slowly added (60 mL h^{-1}) under vigorous stirring to a B solution placed in a 150 mL PTFE reactor. The gel formed was aged under constant pH (13) for 18 h at 60 °C. The solid obtained was then filtered and washed with distilled water (90 °C) up to pH = 7.

The Ni–Mg–Al-hydrotalcites obtained were dried in air at 80 °C during 12 h and were denoted as "NiHTX-nc", where X is the Mg/Ni molar ratio and nc means not calcined. A Mg,Al-hydrotalcite (HT-nc) was prepared by the same methodology and used as reference in the physicochemical characterization.

The Ni–Mg–Al mixed oxides were obtained through calcination of the HTLCs precursors under dry air, from room temperature to 500 °C, using a heating rate of 5 °C min^{-1}. The calcined samples were denoted as NiHTX, X being defined as above.

The Rh catalysts were prepared by the conventional wet impregnation of $RhCl_3 \cdot 3H_2O$ onto calcined HT and NiHT25 mixed oxides. The impregnated solids were then heated at 80 °C to evaporate the water, and dried at 110 °C overnight. The catalysts were calcined for 6 h at 500 °C in flowing air. The bimetallic solid presented a molar ratio of Ni/Rh = 10 with 0.6 wt. % of Rh in all samples.

2.2. Physicochemical characterization

The chemical composition of the samples was determined by X-ray fluorescence analysis (XRF), using a Rigaku spectrometer, model Rix 3100, controlled by software Rix 3100, with an X-ray tube of Rh anode. The textural characteristics, specific surface area and pore volume (BJH method) were determined by N_2 physisorption at −196 °C in a Micromeritics ASAP 2000. Prior to the analyses, the samples were outgassed for 20 h at 200 °C (as-synthesized) or at 450 °C (mixed oxides).

X-ray diffraction (XRD) was performed in a Miniflex/Rigaku diffractometer, using CuKα radiation, with a voltage of 30 kV and a current of 15 mA. The diffractograms of calcined and reduced samples were registered in Bragg angles (2θ) from 2° to 90° with steps of 0.05° at 1 s/step. The evaluation of the metallic phases was done after the reduction of the samples ex-situ at 900 °C with pure H_2 (30 mL min^{-1}; 10 °C min^{-1}) for 60 min. Afterwards, the sample was cooled down under Ar (30 mL min^{-1}) until room temperature was achieved. Then, the passivation process was carried out flowing a stream of 5% O_2/He (30 mL min^{-1}) for 30 min through the sample kept at −80 °C, followed by a treatment under Ar (30 mL min^{-1}) for 15 min at this temperature and for 30 min at room temperature. The Rietveld method was used to quantify the NiO and Ni phases formed [19].

The temperature-programmed reduction tests (TPR) were performed in a conventional dynamic equipment, with a H_2/N_2 ratio in the 1/9 feed and heating at 10 °C min^{-1} from room temperature to 900 °C.

The H_2 chemisorption was performed in a dynamic equipment with a TCD detector. The calcined samples were reduced under hydrogen at 700 °C for 1 h, and then they were cooled down under hydrogen flow (50 mL min^{-1}) to 400 °C and then treated under Ar (50 mL min^{-1}) during 2 h at 400 °C. Finally, the samples were cooled down to room temperature under Ar (50 mL min^{-1}) and pulses of pure hydrogen were applied until saturation was achieved. Nickel dispersion was