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MgO and Nb_2O_5 oxides used as supports for Ru-based catalysts for the methane steam reforming reaction

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ABSTRACT

A comparative analysis of Ru catalysts for low temperature (400–750 °C) methane steam reforming reaction has been performed on magnesia, niobic acid and niobia supports. Ru from chloride or nitrosyl nitrate precursors was deposited by incipient wetness impregnation method on supports calcined in different ways. All of the MgO-supported catalysts were calcined at 400 °C whilst the niobia-based catalysts underwent different calcinations regimes. The catalytic activity towards the methane steam reforming reaction was assessed in a fixed bed quartz reactor with an overall flow rate of 100 N cm^3 min^{-1} (weight space velocity WSV of 33 N cm^3 min^{-1} g_{cat}^{-1} and steam-to-carbon S/C ratio equal to 4). All of the catalysts showed comparable results, especially the magnesia- and the niobic acid-supported catalysts resulted in high activity at 700 °C, whereas a few of the niobia-supported catalysts achieved complete CH_4 conversion. The best performing catalysts were characterized by BET, CO chemisorption, XRD, XPS and SEM analyses.

1. Introduction

Hydrogen has to face many challenges from current commercial scale to future fuel for fuel cells (FCs). Due to the absence of hydrogen delivery and storage systems, the primary challenge in this context is the hydrogen production directly on board vehicles or on stationary mode using fuel processors [1–3]. Commercially hydrogen is produced alongside CO and CO_2 through catalytic methane steam reforming (MSR) process usually with a steam-to-carbon (S/C) ratio of 2–5, over Ni catalyst at 1100 °C [4–6]. The catalytic MSR process is preferred among other catalytic processes like partial oxidation and auto thermal reforming due to its high efficiency, lower emissions and lower cost [7,8].

When hydrogen is produced from MSR process, the product obtained is the syngas, which must be cleaned up to remove CO for obtaining a hydrogen-rich gas stream. CO, in fact, acts as a poison for FCs. When the catalytic MSR process is squeezed to small scale due to space shortage for on-board production, a problem of CO separation from hydrogen arises [6–11]. Thus, research focused the attention to develop catalysts which produce minimum CO content without affecting hydrogen production. Nickel-based catalysts are effective industrially, but due to high metal loading, higher operating temperatures and carbon whiskers formation, attention is being focused on noble metal catalysts which operate at much lower temperatures, with low metallic loading and minimum carbon formation [12–16]. In particular, the use of Ru in a highly dispersed state suppresses coke formation in the MRS [17,18].

This manuscript shows a comparative analysis of Ru-based catalysts on different supports to identify highly active and selective catalysts for the MSR process. Magnesia (MgO), niobic acid ($Nb_2O_5 \cdot nH_2O$) and niobia, or niobium pentoxide (Nb_2O_5), were used as support for Ru. Ru/MgO catalyst has been studied for ammonia synthesis [19] but not for MSR reaction. However, MgO has been employed as an additive on Ni/Al_2O_3 catalyst for MSR: it improves the CO_2 selectivity of the process at S/C molar ratio equal to 2 [20]. The niobic acid is known for its acidic nature and no studies regarding MSR reaction are available. The niobic acid is known to facilitate the reaction involving water [20,21], whilst niobia provides strong metal–support interaction [22–26]. Niobia on the other hand has been employed as an active support for ethanol steam reforming with S/C molar ratio varying from 4 to 10 [27–29], but studies involving MSR are unavailable. For this study, the S/C molar ratio for the MRS of methane has been chosen equal to 4. The main goal pursued with the investigation on these catalysts is

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the maximization of the CO_2 formed in the syngas, to minimize the following CO clean-up removal. The CO clean-up process is not taken into consideration here.

2. Materials and methods

2.1. Chemicals

Magnesium(III) nitrate hexahydrate $Mg(NO_3)_2·6H_2O$ (99.999% purity), urea NH_2CONH_2 (≥98% purity), ruthenium(III) chloride hydrate $RuCl_3·xH_2O$ (99.9% purity, degree of hydration, ≤1), and ruthenium(III) nitrosyl nitrate $Ru(NO)(NO_3)_3$ (Ru 1.5%, in dilute nitric acid) were purchase from Sigma–Aldrich. Niobic acid ($Nb_2O_5·nH_2O$, type HY-340, water content ≈20 wt.%) was supplied by the Companhia Brasileira de Metalurgia e Mineracão (CBMM, Brazil). Ultrapure water obtained from a Millipore Milli-Q system with a resistivity > 18 MΩ cm^{-1} was used for preparing aqueous solutions and steam. Pure methane, hydrogen and nitrogen gases (99.999% purity) were supplied in cylinders provided by SIAD and used as received.

2.2. Preparation of the catalysts

Three types of supports were prepared. MgO was synthesized by using a simultaneous combustion synthesis technique [12,30] with $Mg(NO_3)_3·6H_2O$ and urea at 350 °C, followed by a 3 h calcination at 650 °C in static air. Niobic acid was used to prepare Nb_2O_5 in two different ways:

- as received (hereafter labelled as Nb_2O_5);
- washed with deionized water four times, dried at 90 °C for 72 h and calcined in furnace at 500 °C for 5 h in static air (hereafter labelled as Nb_2O_5_500) [28,31].

The three supports (MgO, Nb_2O_5, and Nb_2O_5_500) were impregnated with Ru by incipient wetness impregnation (IWI) method using aqueous solution of a $Ru(NO)(NO_3)_3$ or $RuCl_3$ to obtain a nominal 1.5 wt.% of Ru as active element. An aqueous solution of the metal precursor was prepared and deposited drop by drop on the support, meanwhile thoroughly mixing the whole mass at about 130 °C in order to let the water evaporate together with N_2. The samples obtained were labelled as Ru_n/support and Ru_c/support, respectively. All of the impregnated samples were further divided into two groups: the first group was used as catalyst without any further calcination treatment whilst the second group was calcined at 400 °C for 3 h in calm air [32]. The list of all of the synthesized catalysts along with the various preparation conditions is tabulated in Table 1.

2.3. Catalytic activity

Catalytic activity tests on MSR were conducted in a fixed-bed quartz micro-reactor with inner diameter of 4 mm at atmospheric pressure. Each sample, 0.3 g in powder diluted with 0.5 g of SiO_2 (0.2–0.7 mm), was placed between two quartz wool plugs in the centre of the quartz tube and inserted into a furnace heated to the reaction temperature. A K-type thermocouple was inserted into the reactor to measure the temperature of the catalytic bed. Before experiments, each catalyst was reduced with a mixture of 50% H_2 in N_2, 100 N cm^3 min^{-1}, by heating from room temperature to 200 °C, and by maintaining that temperature for 1 h. The MSR was performed by feeding the fixed bed with an overall flow of 100 N cm^3 min^{-1}, maintaining the S/C molar ratio equal to 4, with a weight space velocity (WSV) of 33 N cm^3 min^{-1} g_{cat}^{-1}. The reaction temperature was varied from 400 to 750 °C. The outlet gas stream was analysed through a gas chromatograph (Varian CP-3800) equipped with a thermal conductivity detector (TCD) and two Molsieve 5A columns. For all of the tests performed, repeated at least three times for assuring the repeatability of the measures, the carbon balance was respected within ±2%. All of the measures were performed after condensing the remaining water in the reformate: the reported values refer thus to dry gas composition.

The methane conversion and carbon dioxide selectivity were calculated as follow:

$$X_{CH_4} = \frac{F_{CH_{4,in}} - F_{CH_{4,out}}}{F_{CH_{4,in}}} \times 100\%$$

$$S_{CO_2} = \frac{F_{CO_2,out}}{F_{CO_2,out} + F_{CO_{out}}} \times 100\%$$

$$S_{CO} = 100 - S_{CO_2}$$

As CO and CO_2 selectivity are interrelated and the goal of this study is to maximize the CO_2 selectivity and the H_2/CO molar ratio of the system to reduce the CO clean-up section (not considered here), only the CO_2 selectivity is reported throughout the text.

2.4. Characterization

The specific surface areas (S_{BET}) of the catalysts were determined using the Brunauer–Emmet–Teller (BET) method within the relative pressure range of 0–1 on an ASAP 2020M Micromeritics Instrument. N_2 adsorption isotherms were recorded at −196 °C. Prior to adsorption, approximately 0.05 g of solid powder was placed in the cell and degassed at 350 °C for 3 h under high vacuum. The pore diameter distribution was evaluated by the Barrett–Joyner–Halenda (BJH) method, calibrated for cylindrical pores according to the improved Kruk–Jaroniec–Sayari (KJS) method, with the corrected form of the Kelvin equation, from the desorption branches of the isotherms.

By using the same apparatus the chemisorption analysis was carried out to evaluate the active metals dispersion on supports and the size of crystallites. H_2 saturation was firstly performed (20 N cm^3 min^{-1} for 2 h at 350 °C) followed by He treatment (20 N cm^3 min^{-1} for 1.5 h at 370 °C). Then, at room temperature, a mixture of 10% CO in He was injected in pulses of 500 N μl each, till the fulfilment of constant outlet peaks. The amount of adsorbed gas was determined as difference between the total volume injected and the residual one escaped. The metal dispersion on the carrier surface was determined as follows:

$$D\% = 100 \cdot S_f \cdot \frac{V_{ads} \cdot M_{Ru}}{V_g \cdot F_{Ru}}$$

considering a stoichiometric factor S_f equal to 1 (i.e., each Ru atom adsorbed one CO molecule), the total volume of CO chemisorbed referred to the mass of the support used for the analysis in N cm^3 g^{-1} (V_{ads}), the metal atomic weight M_{Ru} (101.07 g mol^{-1}), the total mass fraction of the metal on the catalyst (F_{Ru}, expressed as g_{Ru} g^{-1} of support) and that one gas g-mole, V_g, occupies 22,414 cm^3 at normal conditions.

The X-ray diffraction (XRD) patterns were collected using a Philips X-Pert MPD X-ray diffractometer equipped with a Cu Kα radiation at 40 kV and 30 mA to verify the effective composition of the samples and derive qualitative indications of the presence of comparatively large noble metals crystallite from its eventually visible peaks. All of the catalysts were scanned over 2θ range between 20° and 70° over 1 h. The peaks were assigned according to the PCPFWIN database.

The morphology of catalysts was examined by scanning electron microscopy (SEM) coupled with energy-dispersive X-ray