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Hydrogen production from oxidative reforming of methane on supported nickel catalysts: An experimental and modeling study

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HIGHLIGHTS

- Autothermal reforming of methane was studied using nickel based catalysts.
- A kinetic model from the literature was used to compare the obtained results.
- Catalysts containing alumina presented better metallic dispersions.
- Higher dispersions led to superior methane conversions and H_2 yield the reaction.
- Literature model predicted well the general behavior of the reaction.

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ABSTRACT

Nickel catalysts supported on Al_2O_3, CeO_2/Al_2O_3, $Ce_{0.5}Zr_{0.5}O_2/Al_2O_3$, and $Ce_{0.5}Zr_{0.5}O_2$ were investigated for methane oxidative reforming. BET surface area results showed that the catalysts containing alumina presented higher surface area which favored better nickel dispersion. This was confirmed by X-ray diffraction (XRD) data from the reduced samples. XRD analysis of the calcined catalysts also showed the formation of a ceria–zirconia solid solution. In fact, the addition of CeO_2 and $CeZrO_2$ to alumina provided higher oxygen storage capacities as observed by CO_2 formation during CO-TPD. Temperature Programmed Reduction and Diffuse Reflectance Spectroscopy experiments revealed that samples containing alumina showed higher interaction between metal and support. Samples supported on alumina showed similar methane conversions during oxidative reforming, which could be related to similar nickel dispersions. A literature based kinetic model was used to compare data predicted by this model with the experimental behavior. The model results of methane conversions and composition profiles indicated that high temperatures should be used in order to obtain a maximum in H_2 production. The model predicted smaller methane and oxygen conversions, as well as, lower H_2 and CO molar fractions than the ones observed experimentally. This happened probably due to the fact that the kinetic expressions used were obtained at lower temperatures, lower conversions and with a different catalyst. Despite these differences, the general behavior was predicted by the model.

1. Introduction

In recent years, hydrogen has been attracting great interest as a clean fuel for combustion engines and fuel cells [1]. Among all the potential sources of hydrogen, natural gas, which has methane as its main component, has been considered a good option because it is clean, abundant and it can be easily converted to hydrogen [2]. There are three major reforming reaction that are used to produce hydrogen from methane, i.e., steam reforming (SRM), partial oxidation (POM) and oxidative reforming of methane (ORM) [3]. ORM is a good alternative for H_2 production since it integrates energetically the two processes, SRM and OPM [4,5]. Although ORM has an interesting potential in industrial application, there has been only a limited amount of work reported in the field of reactor design and simulation.

The conversion of methane and the selectivity of the reactions to hydrogen or synthesis gas depend on several variables such as temperature, pressure, reagents feed ratio, and the catalyst used, among others [2]. Nickel catalysts supported on alumina are commercially used in reforming of methane mainly due to their low cost. However, these catalysts suffer deactivation, generally because of coke formation [6]. In the search of higher stability, other supports have been studied such as $CeZrO_2$ [7]. In fact, $Ni/CeZrO_2$

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exhibited higher activity and stability than Ni/Al_2O_3 for methane reforming reaction [8]. The reducibility and oxygen transfer capacity of $CeZrO_2$ have been shown to be fundamental to keep the active phase surface free of carbonaceous deposits. Although, ceria–zirconia helps to prevent coke deposition, it usually has higher costs and lower thermal stability than alumina [4].

In this way, the objective of this study is to investigate the performance of nickel catalyst during ORM and to use a literature based kinetic model to compare data predicted by this model with the experimental behavior.

2. Mathematical model

Mathematical model used in this work has been presented and validated by Ávila-Neto et al. [2]. Table 1 shows the reactions that represent the kinetics of oxidative reforming of methane [3] and their respective rates [9,10]. The rate of consumption/formation of each species in the gas phase was determined by summing up the reaction rates of each species in all reactions. A one-dimensional model was proposed to represent a fixed bed reactor, with nickel based catalyst, in small scale, operating in steady state condition. The reactor considered was operated with the same conditions described in catalytic tests.

The model was constituted by a set of ordinary differential equations (ODE's), non-linear, of initial value in length. The initial condition was given by $F_i = F_{i0}$, and the inlet composition in molar ratio was 16.7% CH_4: 1.7% O_2: 41.6% H_2O: 40% N_2. The ODE system was integrated numerically using the function "ode" of free software Scilab© INRIA-ENPC [2]. The model was validated comparing the results with literature data [1], showed by Ávila-Neto et al. [2]. With this validations step done, the model was tested with the actual experimental conditions used in the present work ($2CH_4$:$1H_2O$:$0.5O_2$).

3. Experimental

3.1. Catalysis preparation

The support, $Ce_xZr_{(1-x)}O_2$, with Ce/Zr atomic ratio equals to 1 was prepared by co-precipitation technique as described elsewhere [11]. The supports 12 wt%CeO_2/Al_2O_3 or 12 wt%$Ce_{0.5}Zr_{0.5}O_2/Al_2O_3$ were prepared by wet co-impregnation on γ-Al_2O_3 (Catapal A – Sasol) pre-calcined at 1173 K during 6 h. The addition of nickel (15 wt%) was done by incipient wetness impregnation using an aqueous nickel nitrate solution. The samples were calcined in air flow at 723 K by 4 h. Therefore, four catalysts were obtained: Ni/Al_2O_3 (NiA), $Ni/Ce_{0.5}Zr_{0.5}O_2$ (NiCZ), $Ni/CeO_2/Al_2O_3$ (NiCA), $Ni/Ce_{0.5}Zr_{0.5}O_2/Al_2O_3$ (NiCZA).

3.2. Catalysts characterization

BET surface areas were measured using a Quantasorb Jr. apparatus equipped with a thermal conductivity detector. The adsorption isotherms were determined by nitrogen adsorption at 77 K.

X-ray diffraction measurements, for calcined and passived samples, were made using a RIGAKU diffractometer with a Cu Kα radiation. The XRD data were collected between $2\theta = 25$ and 75°, at 0.04°/step with integration times of 1 s/step. For passivation, after the reduction (as described CO-TPD), the samples were cooled to room temperature under He flow. Still under He flow, then samples were cooled to 273 K. After this the samples were submitted to a flow of a 5% O_2/He mixture during 15 min for the passivation to occur. Unit cell volume of CeO_2 and $CeZrO_2$ were calculated by averages of software UNITCELL [12] for calcined samples through main peaks and their respective plans of reflection.

Temperature Programmed Reduction (TPR) measurements were carried out in a micro-reactor coupled to a quadrupole mass spectrometer (Balzers, Omnistar). A mixture of 2% H_2 in Ar flowed through the sample (300 mg) at 30 mL/min, raising the temperature at a heating rate of 10 K/min up to 1273 K. The sample was kept at this final temperature for 20 min.

CO Temperature Programmed Desorption (CO-TPD) measurements were carried out in a micro-reactor coupled to a quadrupole mass spectrometer (Balzers, Omnistar). The samples were reduced under H_2 flow (30 mL/min), increasing the temperature up to 773 K at 10 K/min. The temperature remained at 773 K for 3 h, the H_2 flow was replaced by He and the sample was heated up to 1073 K. Then, the samples were cooled to room temperature and the He flow was replaced by CO for chemisorption. After CO chemisorption was completed, the reactor was purged with He and CO-TPD measurements were carried out increasing the temperature up to 1073 K at 20 K/min.

Oxygen storage capacity measurements (OSC) also were carried out in a multipurpose unit connected to a quadrupole mass spectrometer. The samples (100 mg) were reduced as described in the CO-TPD. Then, the samples were cooled to 723 K and a 5% O_2/He mixture was passed through the catalyst until the oxygen uptake was finished. The reactor was purged with He and the dead volume was obtained by switching the gas to the 5% O_2/He mixture. Finally the amount of oxygen consumed on the catalysts was calculated taking into account a previous calibration of the mass spectrometer.

Table 1
Reactions and rates that prevail in the kinetics of oxidative reforming of methane.

Reactions		Rate
$CH_4 + H_2O \rightarrow CO + 3H_2$	(1)	$R_1 = \frac{k_1}{p_{H_2}^{2.5}}\left(p_{CH_4}p_{H_2O} - \frac{p_{H_2}^3 p_{CO}}{K_I}\right) \times \frac{1}{\Omega^2}$
$CO + H_2O \rightarrow CO_2 + H_2$	(2)	$R_2 = \frac{k_2}{p_{H_2}^{3.5}}\left(p_{CH_4}p_{H_2O}^2 - \frac{p_{H_2}^4 p_{CO_2}}{K_{II}}\right) \times \frac{1}{\Omega^2}$
$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$	(3)	$R_3 = \frac{k_3}{p_{H_2}}\left(p_{CO}p_{H_2O} - \frac{p_{H_2} p_{CO_2}}{K_{III}}\right) \times \frac{1}{\Omega^2}$
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	(4)	$R_4 = \frac{k_{4a}p_{CH_4}p_{O_2}}{\left(1+K_{CH_4}^C p_{CH_4}+K_{O_2}^C p_{O_2}\right)^2} + \frac{k_{4b}p_{CH_4}p_{O_2}}{\left(1+K_{CH_4}^C p_{CH_4}+K_{O_2}^C p_{O_2}\right)}$
		$\Omega = 1 + K_{CO}p_{CO} + K_{H_2}p_{H_2} + K_{CH_4}p_{CH_4} + K_{H_2O}\frac{p_{H_2O}}{p_{H_2}}$