

# Tuning the properties of nickel nanoparticles inside SBA-15 mesopores for enhanced stability in methane reforming



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## ABSTRACT

The properties of nickel nanoparticles inside the mesopores of SBA-15 support were tuned by a careful control of the calcination rate. Ni/SBA-15 catalysts containing 5 wt% nickel were prepared following three different calcination rate values (0.25 – 0.5 – 4.5 °C min<sup>-1</sup>). Their properties were characterized by N<sub>2</sub>-sorption, X-ray diffraction (low and wide angles), temperature programmed reduction and transmission electron microscopy. These catalysts were then tested in dry reforming of methane (DRM). As a result, the catalyst calcined at 0.5 °C min<sup>-1</sup> resulted in the formation of strong interaction between the active phase and the SBA-15 support, high nickel dispersion and accessibility that greatly enhanced its stability in dry reforming of methane.

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## 1. Introduction

Since oil and coal are being depleted, extensive studies are tackled in order to replace them by natural gases as they are plentiful. Moreover, global warming is one of the most dangerous problems that humanity is facing nowadays. In this context, dry reforming of methane (DRM) has been extensively studied since it consumes two greenhouse gases, CO<sub>2</sub> that is extensively produced by burning fossil fuels and CH<sub>4</sub> which is one of the major components of natural gas (both conventional and shale sources) and has a potential of global warming that is 25 times greater than CO<sub>2</sub>. DRM has another benefit since the syngas (H<sub>2</sub> and CO) produced has an equimolar ratio of H<sub>2</sub>:CO = 1 suitable for Fischer Tropsch synthesis, thus increasing its selectivity and yield [1–6]. DRM was performed over different kinds of catalysts such as noble metals (Rh, Ru, Ir, Pt or Pd) that are good candidates with high catalytic performances, but they are very expensive with limited availability [7–9]. Non-noble metal catalysts, Ni-based ones specifically, are considered as good alternative having lower cost and wider availability [9,10]. However, these catalysts show serious deactivation due to carbon deposition and/or sintering of the active phase. In order to improve their stability, various methods have been applied like the use of additives [11], change of support type [12,13] and altering the interaction between Ni and its support [14–

16]. Recent studies have revealed that nickel-based SBA-15 catalysts show promising behavior in DRM and their mesoporous support SBA-15 plays a prominent role in stabilizing Ni nanoparticles inside the pores, thus reducing sintering and coke deposition [17–19]. For this, further improvement of nickel properties inside mesopores is required in order to get higher stability under more severe conditions that resemble more to industrial ones. Calcination treatment during catalyst preparation has an important impact on non-noble metals dispersion (Ni, Cu) over SBA-15 support [20–22]. Even though re-dispersion of copper nanoparticles was successfully established during conventional catalyst activation under air by De Jong group [22], authors reported that nickel re-dispersion was impossible under conventional heat treatment because of the decomposition of Ni<sub>3</sub>(NO<sub>3</sub>)<sub>2</sub>(OH)<sub>4</sub> during calcination that caused sintering [20–22]. Thus, the aims of this paper, never reported in literature before, and successfully established here were multiple: i) to re-disperse the nickel inside the porosity of SBA-15 by using the simple and cheap calcination atmosphere (air calcination) rather than H<sub>2</sub> or NO/He; ii) to control the properties (particle size, accessibility and interaction with support) of nickel by a variation of calcination heating rate and iii) to check the effect of such properties on the stability in DRM under severe conditions of reaction (at high gas hourly space velocity, GHSV). All these objectives lead to a better understanding of the properties affecting the stability of nickel inside mesoporous support that differ from the stability of non-porous supports largely known. Also, this study enabled the design of a stable mesoporous catalyst under severe conditions of DRM.

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## 2. Experimental

### 2.1. Catalysts preparation

Commercially available mesostructured silica (SBA-15, Sigma Aldrich 777242) was used as support in this study. The impregnation of 5 wt% nickel followed the “two-solvents” loading method described by Lopes et al. [23]. Briefly, 2 g of the support were stirred with 40 ml of *n*-hexane for 15 min. Nickel nitrate salt (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), Sigma Aldrich 72253, was used as nickel precursor. Then, 2 ml of the aqueous nickel nitrate solution carrying 0.05 g of Ni were added drop by drop to the solution of SBA-15 and hexane. The final solution was left to dry for 24 h at room temperature. After drying, impregnated catalysts were calcined in a muffle furnace under air at 450 °C for 5 h (thin bed conditions) in order to remove nitrates. Three different heating rates (0.25, 0.5, and 4.5 °C min<sup>-1</sup>) were used during calcination to reach the required temperature (450 °C) and the obtained catalysts were marked as Ni<sub>5</sub>/SBA-15<sub>(0.25)</sub>, Ni<sub>5</sub>/SBA-15<sub>(0.5)</sub>, and Ni<sub>5</sub>/SBA-15<sub>(4.5)</sub>. The SBA-15 support was calcined in absence of nickel at 0.25, 0.5, or 4.5 °C min<sup>-1</sup> for comparison purposes and to check if the heating rate has any influence on its structural and textural properties. These supports were denoted as SBA-15<sub>(0.25)</sub>, SBA-15<sub>(0.5)</sub>, and SBA-15<sub>(4.5)</sub> respectively.

### 2.2. Catalysts characterization

Textural properties (surface area, pore volume, pore size) were calculated from N<sub>2</sub> adsorption-desorption isotherms obtained at –198 °C using ASAP 2020 Micromeritics apparatus. BET (Brunauer, Emmett, Teller) equation was applied for relative pressures within the range of 0.05 and 0.3 to get the BET surface area. The relative pressure of 1 was used in the N<sub>2</sub>-sorption isotherm to calculate the pore volume. Similar conditions of degas and analysis with respect to the ones reported in our previous study were used in this work [17].

Low angle XRD measurements were performed on a Brüker D8 Advance diffractometer (CuKα = 1.5418 Å) using a step size of 0.01° at 1 s per step and operating at 20 KV and 10 mA.

An X-Ray diffractometer (PANalytical X'pert Powder) was used to identify crystalline phases through international center for diffraction data (ICDD) and to calculate average particle size by Scherer equation:  $D = K\lambda/\beta\cos\theta$ , where *K* is a constant (*K* = 0.9),  $\lambda$  is the X-ray wavelength ( $\lambda$  = 1.5405 nm for Cu Kα),  $\beta$  is the full width at half maximum (FWHM) of the diffraction peaks, and  $\theta$  is the peak position.

Temperature-programed reduction (TPR) experiments were performed with an Autochem 2920 Micromeritics apparatus. 50 mg of calcined catalysts were carried on quartz wool in a U-shaped quartz sample tube and heated from room temperature to 800 °C at a rate of 10 °C min<sup>-1</sup> under a gaseous mixture flow (25 ml min<sup>-1</sup>) of 5% H<sub>2</sub> diluted in Ar. The gas flow was passed through an ice bath to remove any water product formed during reduction before reaching the thermal conductivity detector (TCD). In order to determine the percentage of reducible Ni species, we have assumed that the reduction is taking place following the reaction:



Hydrogen uptake was obtained by an integration of the area under the curves in the TCD vs. temperature graph. Each area is then converted to a number of mol of hydrogen based on the active gas concentration and TCD calibration. Eq. (1) was then used to calculate the number of mol of NiO and its corresponding reducible Ni considering an initial theoretical nickel content of 5 wt%.

High resolution transmission electron microscopy (TEM) images of the fresh and spent catalysts were obtained using JEOL JEM-200 electron microscope operating at 200 KeV. For observations, the powder catalysts were suspended in ethanol then deposited on a copper grid coated with carbon membrane.

### 2.3. Reactivity measurements

The catalysts were tested in a Hastelloy-X tubular reactor with an internal diameter of 9 mm. A Microactivity reference catalytic reactor (MAR, PID Eng and Tech Spain) was used under conditions similar to the ones reported in our previous work [24]. Catalysts were loaded into the reactor and reduced in situ at 650 °C for 2 h in a 5% H<sub>2</sub>/Ar flow (30 ml min<sup>-1</sup>). After pretreatment, the temperature was cooled down to 200 °C and dry reforming of methane was conducted under atmospheric pressure where CH<sub>4</sub>/CO<sub>2</sub> = 1:1 and a total GHSV = 180 L g<sup>-1</sup> h<sup>-1</sup> (20 mg of catalyst were used for each test). Good reproducibility of catalytic results under these conditions was obtained. For activity measurements, the reaction temperature was increased from 200 °C (5 °C min<sup>-1</sup>) up to 750 °C followed by a decrease of temperature till 650 °C that was maintained for 12 h. The gaseous products were then analyzed online by an Inficon micro GC equipped with a thermal conductivity detector and two columns in parallel (Plot U and Molecular sieves columns). The conversions of methane, carbon dioxide, and H<sub>2</sub>/CO ratio corresponding for the activity and stability test were calculated as follow in Eqs. (2)–(4):

$$\text{CH}_4 \text{ conversion \%} = \frac{\text{CH}_{4(\text{in})} - \text{CH}_{4(\text{out})}}{\text{CH}_{4(\text{in})}} \times 100 \quad (2)$$

$$\text{CO}_2 \text{ conversion \%} = \frac{\text{CO}_{2(\text{in})} - \text{CO}_{2(\text{out})}}{\text{CO}_{2(\text{in})}} \times 100 \quad (3)$$

$$\text{H}_2/\text{CO} = \frac{\text{mol of H}_2}{\text{mol of CO}} \quad (4)$$

## 3. Results and discussion

### 3.1. Textural and structural properties of Ni<sub>5</sub>/SBA-15 catalysts

TEM images of the SBA-15 support as received are presented in Fig. S.1. The grains are elongated with an average length of 1 μm. The channels are parallel and seem to be uniform. N<sub>2</sub> adsorption-desorption isotherms (Fig. 1 and Fig. S.2) for all SBA-15 supports

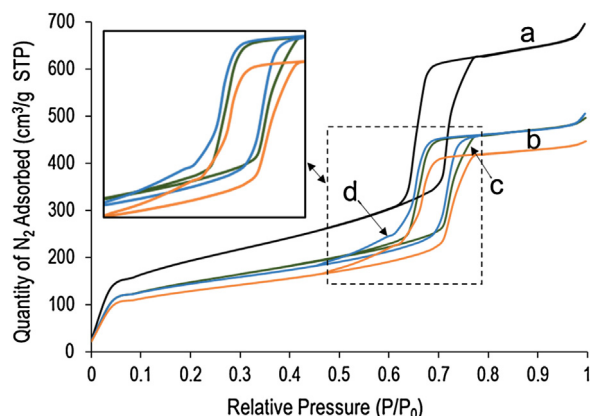


Fig. 1. Adsorption-desorption isotherms for different calcination rate catalysts: (a) SBA-15, (b) Ni<sub>5</sub>/SBA-15<sub>(0.25)</sub>, (c) Ni<sub>5</sub>/SBA-15<sub>(0.5)</sub>, (d) Ni<sub>5</sub>/SBA-15<sub>(4.5)</sub>.

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