



# Highly active and stable Ni/SBA-15 catalysts prepared by a “two solvents” method for dry reforming of methane



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## ABSTRACT

Two series of Ni (2.5–7.5 wt%) and Ce (6 wt%) containing SBA-15 catalysts were prepared and tested in dry reforming of methane, a promising route for the production of syngas. Both Ni and Ce species were introduced in the organized mesoporous silica support in the form of nitrate salts using the “two solvents” procedure that is known to favor metal dispersion inside the porosity. Samples characterizations by N<sub>2</sub> sorption, SAXS, XRD, SEM and TEM indicate good preservation of the porosities after Ni deposition and calcination as well as formation of NiO nanoparticles entrapped in the porous channels. In the cerium-enriched samples, the CeO<sub>2</sub> nanoparticles are also highly dispersed. After reduction, all the catalysts show high activity and selectivity towards H<sub>2</sub> and CO at atmospheric pressure with full CH<sub>4</sub> conversion below 650 °C. In these conditions, there is no significant promotional effect by ceria. Moreover, prolonged tests performed at 500 °C for 12 h reveal a high stability of the catalysts. The absence of deactivation throughout the catalytic run at this temperature agrees with the low carbon amount detected after test and with the limited sintering of the Ni nanoparticles in the used catalysts. The positive effect of the SBA-15 mesoporous channels towards stabilization of the supported particles is discussed.

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## 1. Introduction

Fischer–Tropsch Synthesis (FTS) is an important process for the production of liquid hydrocarbons from syngas. The latter is a gaseous mixture primarily composed of CO and H<sub>2</sub> in a ratio that varies depending on its method of production. The three main processes for syngas production are steam reforming of methane (reaction of H<sub>2</sub>O with CH<sub>4</sub>), CO<sub>2</sub> reforming of methane (reaction of CO<sub>2</sub> with CH<sub>4</sub>) and partial oxidation of biomass, methane, coal, or petroleum naphtha [1]. Among these reactions, CO<sub>2</sub> reforming of methane has the strong advantage of producing a clean CO and H<sub>2</sub> mixture in an equimolar ratio (1:1) best suited for subsequent FTS reaction [2–4]. The obtained H<sub>2</sub>/CO ratio is on the contrary near 3

(i.e. too high for FTS) when syngas is produced from steam reforming of methane. It is around 2 with direct oxidation of methane but the process is then highly exothermic, being thus risky and insecure due to the formation of hot spots, particularly at high space velocities, leading to difficulties in process control. Based on these considerations, dry reforming of methane (DRM) arises as one of the most promising methods for syngas production. Moreover, an important advantage is that syngas is then produced from the consumption of methane and carbon dioxide that are two gases with strong greenhouse effect, thus offering an additional environmental benefit.

In the process of dry reforming of methane by carbon dioxide, the main reaction (CH<sub>4</sub> + CO<sub>2</sub> → 2H<sub>2</sub> + 2CO) occurs in the gas phase. Secondary reactions can also take place especially reverse water gas shift (RWGS, CO<sub>2</sub> + H<sub>2</sub> → CO + H<sub>2</sub>O), methane decomposition (CH<sub>4</sub> → 2H<sub>2</sub> + C), and CO disproportionation known as Boudouard reaction (2CO → CO<sub>2</sub> + C). The last two reactions produce carbon that can contribute to catalyst deactivation by forming carbonaceous deposits on the inner and/or outer catalytic surfaces [5]. Besides, both Boudouard and RWGS reactions occur at low

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temperatures while DRM (main reaction) and methane decomposition require high temperatures. Therefore, a reasonable goal for reaching more efficient and energetically less demanding reforming processes is to design heterogeneous catalysts able to perform the reaction at moderate temperatures where carbon formation is inhibited.

As recently reviewed [6], supported catalysts containing noble metals such as Rh, Ru, Pt or Pd are active catalysts for DRM. They are also stable at the high temperatures (>600 °C) classically needed to achieve high conversions [7,8]. However, due to economic and environmental constraints, the substitution of noble metals by transition ones, especially nickel [9–16], is nowadays attractive. In this context, Hou et al. reported that nickel nanoparticles well-dispersed on alumina can provide high CH<sub>4</sub> and CO<sub>2</sub> conversions close to those obtained on Rh based catalysts [11]. Similarly, Jozwiak et al. found good and comparable performances towards DRM using catalysts with either Ni, Rh or bimetallic Ni–Rh nanoparticles supported on SiO<sub>2</sub> [12]. However, the Ni containing catalysts suffered from heavy coke deposition [11–14]. Therefore, increasing coke resistance appears as a key parameter to develop new efficient Ni-based catalysts for DRM. Ni particles' sintering during activation and reaction is also an important drawback that should be avoided.

In a recent study, Zhang et al. succeeded in stabilizing nickel particles in phyllosilicate nanotubes and obtained catalysts with excellent DRM performances and coke resistance [17]. Similarly, Ma et al. found that nickel nanoparticles located inside carbon nanotubes are more reducible and resistant to sintering as well as catalytically more active and stable than those loaded outside the nanotubes [18]. Besides, various authors reported a promoting effect of ceria in these catalysts due to (i) higher availability of oxygen atoms that inhibit coke formation and (ii) enhancement of the Ni nanoparticles dispersion and stability [19–23]. It was also proposed that the performances of ceria-doped mesoporous Ni/SBA-16 in DRM were increased through metal-support interactions [24].

In this context, the purpose of the present work was to prepare efficient and stable Ni/SBA-15 catalysts with and without CeO<sub>2</sub>. The organized SBA-15 mesoporous silica was selected as support because of its ordered channel system with high internal surface area and high pore volume that gives high capability to disperse and stabilize oxide and metal nanoparticles. This choice was also established from recent results reporting promising behaviors of Ni based SBA-15 catalysts in DRM [20,21,25]. In these works, however, the catalysts were prepared by classical incipient wetness impregnation [20,21] and nickel depositions both inside and outside the pores were observed. Therefore, our purpose in this work was to prepare improved Ni(Ce)/SBA-15 catalysts with active Ni (and Ce) nanoparticles highly dispersed all over the support and predominantly (if not fully) located at the interior of the mesoporous channels. To this end, we used a “two solvents” method that consists in suspending the mesoporous silica in a hydrophobic solvent (e.g. hexane) before mixing it with the aqueous metal precursor solution. Indeed, it was shown that this facilitates the homogeneous penetration of the impregnating metal precursor solution inside the channels while simultaneously avoiding excessive local impregnation at the external surface of the silica grains [26–31]. As a result, higher deposition of the supported active phases inside the pores compared to classical impregnation is obtained, which should be strongly beneficial to both the activity and stability of the catalysts during DRM reaction. The addition of ceria in some samples was carried out to check if the above mentioned promoting effect reported by various authors remains in our preparation conditions.

## 2. Experimental part

### 2.1. Catalyst preparation

The SBA-15 silica supports were synthesized according to a standard procedure adapted from the recipe described by Zhao et al. [32]. Thus, 8 g of P123 were dissolved in 252 mL HCl (1.9 M) at 35 °C for 24 h then 18.4 mL of TEOS were added drop by drop and the resulting solution was kept under heating at 35 °C for another 24 h. The syntheses were carried out without applying a condensation hydrothermal treatment. After recovery by filtration, the powders were calcined at 500 °C (heating rate 2 °C min<sup>-1</sup>) for about 9 h in a muffle furnace (Nabertherm, LE6/11) to eliminate the structuring organic agent and the Cl ions. In order to have sufficient amount of support, two silica batches were prepared (denoted SBA-15<sub>1</sub> and SBA-15<sub>2</sub>), with close textural properties (see results section). For both preparations, we checked that the calcined mesoporous silica were almost chlorine free.

The deposition of the precursor nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) or cerium nitrate (Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O) salts (from Sigma–Aldrich) inside the pores of the SBA-15 supports was carried out using the “two solvents” procedure detailed elsewhere [26–28]: briefly, 1 g of support was suspended in 20 mL of n-hexane for about 15 min, then a volume of water set equal to the silica porous volume (as determined by N<sub>2</sub> sorption) and containing the appropriate amount of metal salt precursor was added dropwise. Afterwards, the impregnated samples were left to dry overnight under air. The cerium content was identical in all Ce-containing catalysts (6 wt%) while the concentration of nickel varied (2.5, 5.0 or 7.5 wt%). For the Ce-containing samples, the Ce loading was carried out first, followed by calcination in air for 5 h at 450 °C (thin bed conditions, heating rate 0.5 °C min<sup>-1</sup>), then Ni addition and calcination were conducted as above. The obtained samples are designated Ni<sub>x</sub>/SBA-15<sub>1</sub> and Ni<sub>x</sub>Ce<sub>6</sub>/SBA-15<sub>2</sub>, where x is the Ni wt%. A Ni free sample (Ni<sub>0</sub>/SBA-15<sub>2</sub>) was also prepared by submitting the SBA-15<sub>2</sub> mesoporous silica to the “two solvents” preparation (including calcination) but without adding nickel nitrate. Finally, a reference sample was similarly prepared (Ni<sub>5</sub>/SiO<sub>2</sub>), using fumed silica (Sigma–Aldrich) as support.

### 2.2. Characterization techniques

The textural properties were determined from N<sub>2</sub> adsorption–desorption isotherms recorded on an ASAP 2020 (Micromeritics) apparatus. Prior to experiments, the samples were degassed under vacuum for 2 h at 250 °C. X-ray Diffraction (XRD) studies were carried out using a Brüker D8 diffractometer (Bragg–Brentano, Copper  $\alpha = 1.5418$  Å). Coherent crystallographic domains were determined by standard analysis of FWHM (Full Width at Half Maximum) using the Scherrer equation applied with a Warren correction. The Small angle X-Ray scattering (SAXS) measurements were recorded on the SWING beamline of synchrotron SOLEIL using experimental conditions detailed elsewhere [33]. The morphologies of the silica grains and oxides/metal nanoparticles were determined by transmission electron microscopy (TEM) on a 2010 JEOL TEM microscope operating at 200 keV (LaB<sub>6</sub> gun) equipped with an energy dispersive spectroscopy (EDS) probe for local chemical analyses. The mean particle sizes were evaluated by counting at least 500 particles. Scanning electron microscopy (SEM) micrographs were registered on a Hitachi SU-70 SEM-FEG that did not necessitate covering the sample with a carbon or gold conducting film previous to observations. The images were recorded in a mixed mode to obtain simultaneous information on the surface morphology of the grains (70% of secondary electrons signal) and on the external Ni-based species, if present (30% of retro-diffused signal).

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