



# Catalytic performance of ordered mesoporous carbons modified with lanthanides in dry methane reforming

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## ABSTRACT

The catalytic activity of Ce- and La-based catalysts supported on mesoporous carbons was studied in dry methane reforming reaction (DMR). Mesoporous carbons were prepared by hard template method using ordered silica (SBA-15 and KIT-6) as templates and sucrose as carbon precursor. After sucrose pyrolysis samples were washed with 5 wt% hydrofluoric acid at room temperature to remove the silica template. Catalysts and supports were characterized by small- and high-angle X-ray diffraction (XRD), scanning and transmission electron microscopy (SEM/TEM), acid-basic surface oxygen functional groups and N<sub>2</sub> adsorption-desorption isotherms. Catalytic tests were performed at 1:1 molar ratio of methane and carbon dioxide at continuous flow in a bed-fix stainless-steel reactor under atmospheric pressure and 650 °C. Catalysts were pretreated in situ under hydrogen flow from ambient to temperature of reaction. Preliminary results showed that Ce- and La-based catalysts supported on mesoporous carbons exhibit higher activity and a better stability in comparison of analogous catalysts supported on SBA-15 and KIT-16.

## 1. Introduction

An important change is expected in the global energetic matrix with the contribution of natural gas in the following years [1]. Natural gas is not only important for developing countries [1] but also for developed ones [2]. At 2014, natural gas achieved up to 26% of the global energy matrix [2]. So, besides the increase in the production of renewable energies such as solar and eolic [3–5], an increasing attention is being given to hydrogen production from methane [6–12] because this molecule is the main component of natural gas.

Hydrogen is the most abundant element in Universe and it can be obtained from different sources and by several processes. Hydrogen has the highest theoretical specific energy (c.a. 33,500 kWh/ton) and the lowest energy density (c.a. 600 kWh/m<sup>3</sup> at 200 bar gas pressure and 2380 kWh/m<sup>3</sup> as liquid) [13] in comparison to other conventional sources of energy such as natural gas, oil, or conventional capacitors based on Pb, NiCd, NiH, or ionic Li or Na [13]. Accordingly, hydrogen is an economic and clean alternative source of energy to be used in fuel cells for locomotion of vehicles or for fuel plants [14–16].

Hydrogen can be also produced by water splitting via heterogeneous photocatalysis under UV–vis irradiated carbon-based catalysts [17,18] but despite this way is fully eco-friendly. The low cost favors the catalytic conversion of methane.

Methane cracking has being extensively studied [19,20] but besides the high cost of process the main disadvantage is the fast deactivation of catalysts by coke deposits [19,20]. Partial oxidation of methane (POM) is a widely used process to convert hydrocarbons and alcohols to valuable oxygen-containing chemicals [21]. However, it is a very exothermic reaction leading to ultrafast coking and deactivation of catalysts [22]. Also, despite autothermal reforming (ATR) that involves the combination of partial oxidation and steam reforming, is a very promising technology. This process can be easily affected by parallel reactions [23,24]. As consequence, dry methane reforming (DMR) is being receiving a considerable attention as a promising alternative to steam reforming for synthesis gas (H<sub>2</sub> and CO) production [25–28]. Dry methane reforming yields a syngas with a H<sub>2</sub>/CO ratio close to 1. So, this high CO content which could be industrially advantageous for the synthesis of valuable oxygenated chemicals [29,30]. In addition, dry methane reforming features also some potential environmental implications, utilizing the main greenhouse effect contributors (CH<sub>4</sub> and CO<sub>2</sub>) and transforming them into high added value products.

For achieving industrially relevant conversions at relatively moderate temperatures, the use of a catalyst with high activity and selectivity for the DMR reaction is required [26,27]. Noble metal-based catalysts have been studied for this reaction [31–33]. However, the high cost and deactivation by coking of these catalysts has lead the attention to low-

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cost metals. Our group has studied microporous activated carbon-supported Ni-based catalysts [34–38] for DMR reaction. It has been reported that coke deactivation can be controlled by working under kinetic regime [34,35] and by using soft experimental conditions [36,37]. On the other hand, lanthanides have been used as catalytic promoters both for dry reforming reactions of hydrocarbons [39,40] and for Fischer-Tropsch synthesis [41] where carbon-based and silica-based mesoporous supports have received an important attention in DMR [42].

In this sense, the main objective of the present work was to synthesize mesoporous silica to be employed as templates to prepare mesoporous carbon materials to be used as supports for lanthanides (La and Ce). A preliminary study of the catalytic activity and stability of Ce- and La-based catalysts in dry methane reforming reaction was performed and results were related with the physical and chemical properties of the silica and carbon supports.

## 2. Experimental

### 2.1. Synthesis of silica-based materials

The synthesis of SBA-15 [43,44] was performed by mixing 0.5 g of triblock polyoxyethylene-polyoxypropylene-polyoxyethylene copolymer (Pluronic P123, BASF) with 19 mL of 1.6 M HCl (37%, Chempur) and 1.1 mL of TEOS (tetraethyl orthosilicate, 98% wt., Aldrich). The copolymer was dissolved in a solution of hydrochloric acid at 35 °C. Then, TEOS as a source of silicon was dropwise added under stirring for 8 h. The mixture was placed in a polypropylene bottle and heated in an oven under static air (Memmert, UF-110) for 24 h at 35 °C and for 6 h at 100 °C. After this time, the solid product was filtered, washed with water and dried at 100 °C for 12 h. The copolymer template was removed by calcination at 550 °C for 8 h under static air conditions.

KIT-6 sample was prepared [43,44] as follows. 4.0 g of Pluronic P123 (BASF) was dissolved in 144 mL of distilled water and 7.9 g of hydrochloric acid (37%, Chempur) upon stirring at 35 °C. After complete dissolution, 4.0 g of 1-butanol (Sigma-Aldrich) was added. After 1 h stirring, 8.6 g of TEOS was added to the homogeneous clear solution. The mixture was kept under vigorous and continuous stirring at 35 °C for 24 h and then, the reaction mixture was aged at 100 °C for 24 h. The product was filtered off without washing and dried at 100 °C for 24 h in the oven under static air (Memmert, UF-110). Finally, the sample was calcined at 550 °C in the air to remove the template.

### 2.2. Synthesis of mesoporous carbons

Fig. 1 shows a scheme for the synthesis of carbon mesoporous materials (Fig. 1A) and for La- and Ce-based catalysts (Fig. 1B). The ordered mesoporous carbon denoted as C<sub>SBA-15</sub> was synthesized by replication using SBA-15 as template and sucrose (Sigma-Aldrich) as carbon source [45–47]. The pores of SBA-15 were filled with sucrose by diffusion in the solution. In a typical synthesis, 1.0 g of SBA-15 was impregnated with an aqueous solution obtained by dissolving 1.25 g of sucrose and 0.14 g of H<sub>2</sub>SO<sub>4</sub> (98%, Chempur) in 5.0 g of deionized water. The mixture was placed in the drying oven for 6 h at 100 °C, and subsequently the oven temperature was raised to 160 °C and maintained there for 6 h. The silica sample, containing partially polymerized and carbonized sucrose was treated again at 100 °C and 160 °C using the same drying oven steps after the addition of 0.8 g of sucrose, 0.09 g of H<sub>2</sub>SO<sub>4</sub> (98%, Chempur) and 5.0 g of H<sub>2</sub>O. The sucrose/silica composite was then heated at 900 °C for 6 h in Ar atmosphere with a flow rate of 170 mL/min to complete the carbonization. The silica template was dissolved with a 5 wt% solution of hydrofluoric acid at room temperature.

In the next step, mesoporous carbon was filtered, washed with ethanol, and dried at 105 °C for 12 h.

The procedure of C<sub>KIT-6</sub> material synthesis (Fig. 1A) was similar to

preparation of the C<sub>SBA-15</sub> except that the KIT-6 template was used in place of SBA-15 and the amount of water was adjusted to the pore volume of KIT-6.

### 2.3. Synthesis of Ce- and La-based catalysts

Cerium and lanthanum catalysts were prepared by incipient wetness impregnation method [45–47]. Cerium(III) chloride (CeCl<sub>3</sub>, Aldrich) or lanthanum(III) chloride (LaCl<sub>3</sub>, Aldrich) were dissolved in water and added to the silica-based or carbon-based supports. Fig. 1B shows a scheme of Ce- and La-based catalysts. The amount of lanthanides salts were calculated to achieve a final metal loading of 5 wt%. Water was removed on a rotary evaporator at 100 °C. The impregnated samples were dried at 100 °C for 5 h under static air and finally heated under argon flow with a flow rate of 170 mL/min for 3 h at 400 °C. The catalysts were not calcined. The samples were denoted as 5-Ce/SBA-15, 5-La/SBA-15, 5-Ce/KIT-6, 5-La/KIT-6, 5-Ce/C<sub>SBA-15</sub>, 5-La/C<sub>SBA-15</sub>, 5-Ce/C<sub>KIT-6</sub>, 5-La/C<sub>KIT-6</sub>.

### 2.4. Characterization of materials

Catalysts and supports were characterized by X-ray diffraction (XRD), scanning (SEM) and transmission electron microscopy (TEM), acid-basic surface oxygen functional groups according to Boehm method, and nitrogen adsorption-desorption isotherms.

X-ray diffraction (XRD) patterns at small- and high-angle were obtained on a D8-Advance diffractometer (Bruker) by using a CuK $\alpha$  radiation,  $\lambda = 0.154$  nm, with a step size 0.02° in the small-angle range and 0.05° in the high-angle range.

For TEM measurements, powdered samples were deposited on a grid with a carbon film and analyzed in a JEOL 2000 electron microscope operating at 80 kV. SEM images were obtained in a PHILIPS equipment (Netherlands) in the following conditions: working distance of 14 mm, accelerating voltage of 15 kV and digital image recording by DISS.

The content of the acid and basic surface oxygen functional groups was determined by standard neutralization–titration with HCl and NaOH, according to Boehm method [48,49]. For the acidic groups, 0.25 g of dry sample powder was shaken for 24 h in 25 mL of 0.1 N NaOH solution. After that time, the suspension was filtrated through a membrane filter and titrated with 0.1 N HCl solution. For the basic groups, the converse procedure was applied.

Textural analysis of samples was performed based on low-temperature (–196 °C) nitrogen adsorption–desorption isotherms measured on a sorptometer (Quantachrome Autosorb iQ). Prior to adsorption measurements, the samples were degassed under vacuum at 300 °C for 2 h. Surface area and pore size distribution were calculated by BET [50] and BJH [51] methods, respectively.

### 2.5. Catalytic tests

Dry methane reforming (DMR) was followed at mild experimental conditions (650 °C, 0.101 MPa) in a continuous flow system with a bed-fix reactor [26,34,35]. Before activity test, the samples were submitted to in situ pre-treatments [26] under H<sub>2</sub> flow (50 mL/min, 0.101 MPa) from room temperature to 650 °C by 1 h (heating rate of 10 °C/min). DMR conditions employed were 100 mg of catalyst; 80 mL min<sup>–1</sup> flow of both CH<sub>4</sub> and CO<sub>2</sub> (50 vol%, 0.101 MPa); reaction temperature 650 °C. Methane analysis was carried out in a Perkin Elmer Clarus 500 gas chromatography with FID detection. Catalytic activities were estimated by Eq. (1):

$$Activity_{(t)} = \frac{n_{Conv,CH_4(t)}}{Mass_{(Catalyst)}} \quad (1)$$

being  $n_{Conv,CH_4(t)}$  the methane conversion mols obtained from Eq. (2):

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