Controlling the impregnation of nickel on nanoporous aluminum oxide nanoliths as catalysts for partial oxidation of methane

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HIGHLIGHTS

- NiO incorporation into AAO nanoliths pores has been successfully achieved.
- The three impregnation methods tested can incorporate NiO into the nanoliths pores.
- A low Ni^{2+} concentration (0.14 M) during the impregnation is a key factor.
- The addition of NiO into the pores entails the incorporation of the nanolith faces.

GRAPHICAL ABSTRACT
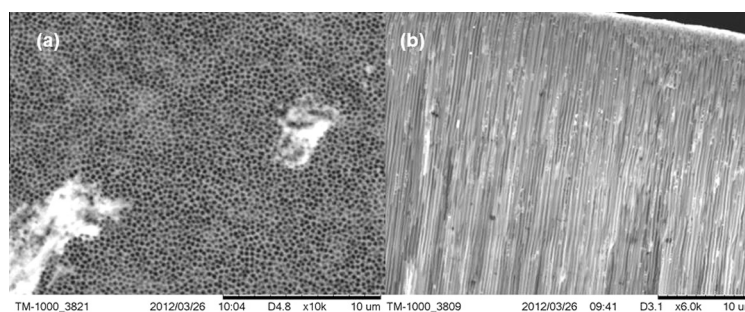
ABSTRACT

Three different conventional impregnation methods were studied in order to elucidate the effect of impregnation variables on the homogeneity in the incorporation of Ni species into the nanoporous structure of the aluminum oxide nanoliths. From results obtained in this study, two factors seem to control the Ni incorporation onto the aluminium oxide nanostructure: (i) the methodology used in the impregnation: incipient wetness impregnation, wet impregnation, or forced wet impregnation, and (ii) the Ni precursor concentration used during the impregnation process. Both the nickel loading and the nickel distribution entities inside the porous structure of aluminium oxide nanoliths depend on the method and concentration of the Ni impregnating solution used in the impregnation. The distribution of the NiO loaded on nanoliths was not uniform as SEM analyses demonstrated. Segregation of NiO entities on surface of AOO nanolith was observed in all samples. For impregnation with Ni solution of low concentration, only incipient wetness impregnation and forced wet impregnation allows the deposit of nickel entities on the porous structure of the AAO nanoliths. By increasing the Ni concentration in the impregnating solution, a larger degree of pore coverage was obtained for all impregnation methods used.

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1. Introduction

Hydrogen is used in the chemical industry for both oil refining processes such as hydrotreating and hydrocracking and for the production of bulk chemicals such as methanol, ammonia and syn-thetic hydrocarbons (Fischer–Tropsch synthesis) [1,2]. In next years is expected that hydrogen demand grows because hydrogen is contemplated as efficient and attractive energy carrier for the future [3]. Nowadays, the most important industrial route to produce hydrogen is the steam methane reforming (SMR), which is the most economical process for its massive production.

Nevertheless, steam reforming is a very energy-intensive process with high investment costs and in which overheated steam in a H_2O/CH_4 molar ratio slightly higher than stoichiometric value

is used to avoid carbon deposition [4,5]. In this context, new processes for the syngas production, at lower energy costs, are needed. The partial oxidation process (Eq. (1)) is an attractive alternative because it avoids the need of large amounts of superheated steam and they need smaller reactors because the faster oxidation reactions.

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \qquad \Delta H^0_{298} = -36 \text{ kJ/mol} \qquad (1)$$
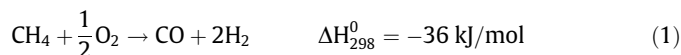
The active catalysts for partial oxidation are very similar to the supported metals used in steam reforming. The high reaction temperatures associated with partial oxidation reaction requires the use of catalysts with extreme thermal stability. This requirement puts strenuous demands on the catalyst materials in their agglomeration and vaporization resistances and structural/morphological stabilities. Additionally, the carbon formation is also key challenge for partial oxidation catalysts. At present, the state-of-the-art partial oxidation catalysts consist of metals from Groups 8, 9 and 10 (Ni, Co, Fe, Pd, Pt, Ru and Rh) supported onto various high surface area oxide substrates such as modified α-Al$_2$O$_3$, stabilized ZrO$_2$ or mixed metal oxides [6–14]. Although, the noble metal-based catalysts present highest activity, their high cost limits their industrial application. The much lower cost of Ni-catalysts makes them good candidates for oxidative reforming reactions. It has been shown that Ni catalyst deactivation by carbon is influenced by the cluster size of the active metal, showing the larger metal clusters a much stronger interaction with carbon, than smaller, well-dispersed metal particles.

It is widely accepted that in partial oxidation mechanism, methane is first oxidized to CO$_2$ and water in the initial part of the catalyst bed until oxygen is exhausted and in the following part of the bed, the reforming reactions of remaining methane with CO$_2$ and water steam formed initially [15,16] occur. However, at extremely high temperatures and very short contact time, hydrogen may be formed directly [17,18]. In this case, hydrogen is obtained by letting the reactants pass for a few milliseconds inside a small-volume catalytic bed. This approach has been widely investigated both in its fundamental [19–23] and technological aspects [24]. Most of the works in the literature of short contact time in the catalytic partial oxidation of methane were carried out on monolithic reactors [25]. To improve the diffusion control in this type or reaction, the use of nanostructured materials [26–28], mainly the use of nanoliths [29], a nanometer scale version of monoliths, could be interesting. Conceptually, the nanoliths consist of an assembly of parallel pores with diameters at the length scale of 10–250 nm. With these nanoliths, the dimensions and topology of its pore structure can influence the reagent flow, the sequencing of catalytic active sites, and the contact between reagents and catalyst [30,31]. In principle, with this kind of structured nanoliths each molecule must traverse an identical pore resulting in more uniform (and controllable) contact times than are possible with conventional monolithic reactors. Nanoporous anodic aluminum oxides (AAO) present a highly ordered array of straight pores with uniform distribution and thermal stability. These properties are of particular interest for the use of these nanoporous AAO as supports for the production of nanoliths [31,32]. Coating the AAO with catalytically active materials requires the development of preparation methods that allow the control of the incorporation and spatial distribution of active catalytic materials. Methods used to uniformly incorporate the active materials on AAO-nanoliths are electrochemical or atomic layer deposition methods [30]. However, the cost and complexity of these methods require the search of more accessible methods to incorporate the active phases (metals) on AAO-nanoliths. In this sense, the classical wet impregnation method could be an alternative taking into account the knowledge gained with this method in the preparation of highly dispersed active phases on nanoporous supports [33–34].

With this background, in this contribution we study the incorporation of Ni particles on AAO nanoliths by different wet impregnation methodologies, analyzing the effectiveness of each methodology to the incorporation of Ni onto the porous structure of AAO substrates. Careful investigation of the texture and structure of the nanoliths were done in an attempt to establish a relationship between the influence of the impregnation parameters on the spatial distribution of active Ni catalytic species onto the porous structure of AAO nanoliths.

2. Experimental

2.1. Impregnation of AAO-nanoliths

Commercial nanoporous aluminum oxides used as nanolith substrates (*Whatman*, pore diameter = 200 nm and pore length = 60 μm), were impregnated with aqueous Ni-salt solutions (Ni[NO$_3$]$_2$·6H$_2$O from *Sigma–Aldrich*). For the impregnation, two different concentrations of the Ni-impregnating solutions were used: [Ni^{2+}] = 0.14 M and 0.35 M. Both Ni-concentrations correspond to the theoretical Ni loading necessary to achieve half (0.14 M) and one monolayer (0.35 M), respectively on the porous volume of the AAO nanoliths taking into account the reported nickel surface loading for monolayer covering on alumina [35,36].

Incorporation of Ni onto the pore structure of AAO nanoliths was carried out using three different impregnation methodologies: (i) incipient wetness impregnation by dripping (IWI), (ii) wet impregnation by immersion (WII) and, (iii) forced wet impregnation passing the solution through the pores of AAO nanoliths (FWI). The incipient wet impregnation method by dripping method consists on the addition of 200 μl (pore volume of the AAO nanoliths) of the aqueous Ni-solutions (0.14 and 0.35 M) drop by drop on the AAO nanolith until complete coverage of its surface. The wet impregnation by immersion consists on the immersion of the AAO nanolith into the aqueous Ni solutions (0.14 and 0.35 M) for 1.5 min. The impregnated AAO nanoliths were dried after immersion at room temperature in horizontal position. The forced wet impregnation method implies the flow of 5 ml of the aqueous Ni-solutions through the AAO nanoliths forcing the flow by the use of a conventional vacuum filtration system. The contact time of the solution through the nanopores was lower than 1 s. The mother liquor collected still maintain the green color characteristic of the presence of Ni^{2+} ions, although the color intensity was, in all cases, lower than the original solutions. After the impregnation step, all wet Ni-impregnated AAO nanoliths were dried by a dried stage at room temperature (RT) for 12 h. The dried Ni/AAO nanoliths were calcined under static air at 400 °C for 10 h at $\Delta T/\Delta t$ = 2 °C min^{-1} with two temperature plateau of 2 h at 60 °C and 120 °C. Table 1 shows the nomenclature and the aqueous Ni-solutions concentrations.

Table 1
Nomenclature of Ni/AAO nanoliths and EDX-SEM analyses corresponding to perpendicular surfaces of Ni/AAO nanoliths.

Sample	Method	[Ni^{2+}] (M)	EDX-SEM (wt%)
			Ni in perpendicular surfaces
IWI-L	IWI	0.14	21–17
IWI-H	IWI	0.35	35–30
WI-L	WI	0.14	18–8
WI-H	WI	0.35	32–25
FWI-L	FWI	0.14	30–24
FWI-H	FWI	0.35	28–24