



# Structured Reactors as an Alternative to Fixed-bed Reactors: Influence of catalyst preparation methodology on the partial oxidation of ethanol



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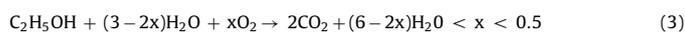
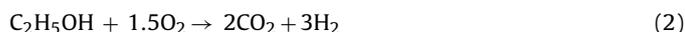
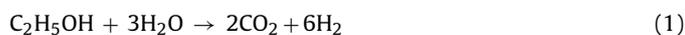
## ABSTRACT

This work studied the effect of the preparation of monolithic catalysts for partial oxidation of ethanol. Cordierite monoliths coated with 10Ni/CeSiO<sub>x</sub> catalyst were prepared by washcoating with two different binders (PVA and Ludox) and a direct sol–gel techniques. Scanning electron microscopy and transmission electron microscopy analyses and adherence tests revealed that structured washcoated monoliths prepared by the slurry with Ludox and direct synthesis using citrate method exhibited excellent dispersion and adherence of catalyst coatings. For the washcoated monolith obtained by slurry with PVA, large agglomerates of catalyst over the wall were observed. The tests with the monolith without catalyst revealed that POX of ethanol only takes place in the presence of the Ni-based catalysts. The monolith catalysts synthesized by slurry with Ludox and direct synthesis using citrate method exhibited a high formation of syngas. However, the preparation method of the monolithic catalysts affects product distribution at low temperature. The addition of Pt to the NiCeSiO<sub>x</sub> monolith catalyst synthesized by citrate method significantly improved the partial oxidation of ethanol reaction.

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## 1. Introduction

Hydrogen production through ethanol conversion reactions has been extensively studied in the literature [1–7]. Different technologies can be used for the production of hydrogen from ethanol, including steam reforming (SR) (Eq. (1)), partial oxidation (POX) (Eq. (2)), and oxidative steam reforming (OSR) (Eq. (3)) [5]:



The partial oxidation (POX) of ethanol is an exothermic reaction that exhibits quick start-up and response times. Furthermore, the POX reactor is more compact than that of a steam reformer since the indirect addition of heat is not needed. Therefore, POX of ethanol provides the desired features for vehicle fuel cell applications [8]. In addition, POX of ethanol is also very attractive for solid oxide

fuel cell (SOFC) because further purification steps are not required, which reduces the costs of the fuel processor [9,10].

Several catalysts have been studied for the POX of ethanol [8–18]. However, the majority of the studies about POX of ethanol used catalysts in powder form and fixed-bed reactors and then, hot-spot formation may occur, which makes the reaction control difficult. Alternatively, the monolithic structures can be used as a support to obtain catalytic reactors with high structural and thermal stability. Monolithic reactors offer the advantage of thin walls, high geometric surface area with enhanced heat and mass transfer, low pressure drop and rapid response to transient operations [19–21]. In addition, the easy scale-up and reduced costs of a compact catalyst design contribute to the large potential of monolith catalysts with respect to their application in hydrogen production technologies.

Monolithic catalyst is well known from automotive and industrial applications as exhaust gas converter. Structured reactors have been used for SR and OSR of ethanol [22–25] but their application for POX of ethanol is more scarce [19,20]. The extremely low contact time makes monoliths suitable for POX of ethanol at high temperature. Hotspots can be eliminated, improving the selectivity of the reaction. POX of ethanol was carried out on Co<sub>3</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> and

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NiO/Al<sub>2</sub>O<sub>3</sub> catalysts washcoated on a cordierite monolith [19,20]. After 30 of time on stream (TOS), a large formation of carbon filaments was observed, which was responsible for catalyst degradation. Therefore, the development of stable structured catalysts for POX of ethanol at high temperature is still a challenge.

One crucial point for the development of structured reactors is the deposition of a suitable and stable catalytic layer on the ceramic support. The most known method to coat monolithic supports is the washcoating procedure, by dipping and removing the monolith from a solution containing the catalyst. It is probably the most versatile of the methods because any kind of solution can be applied, as suspension, colloidal or sol-gel containing the solid or precursors of catalysts. The characteristic of the final coating depends on the monolith properties, solution properties and preparation conditions [21,26]. Several parameters must be controlled for obtaining uniform, reproducible and mechanically stable washcoat; such as: pH of the solution, particle size, viscosity, slurry concentration, primers and binders used, etc.

For coating ready-made catalysts on a monolith, a slurry of particles with controlled size (about 5 μm) has to be used, with a properly solvent and a binder agent. The first step is to ball mill the ready catalyst to a small size, producing an easily accessible coat layer. According to the literature [21,27,28], the adhesion of the washcoated layer on the porous support is improved with the reduction of particle size down to colloidal dimensions. Another way to improve the catalyst adhesion is increasing the contact surface between the particles and the support, by binding agent addition. The binder is preferably colloidal silica or alumina, depending on the application. Alumina has the advantage that is more thermostable than silica, because high-temperature applications silica binder can be lost by steaming. It is worth noting that the binder must be made by the same material as the support, because it could influence the physical and acid/base properties of catalysts causing a strong influence on the catalytic performance. The amount of binder to be used is preferably kept minimal, even 1%wt of total solids is sufficient to properly attach the ready catalyst to the support, avoiding the coverage of active phase or channel blocking [27,29–31].

The aim of this work is to investigate the performance of Ni/CeSiO<sub>x</sub> and PtNi/CeSiO<sub>x</sub> washcoated monolithic catalyst for the POX of ethanol. The monolithic catalyst was prepared by two different methods: (i) the traditional dip-coating procedure for the monolith washcoat with addition of two different binders and (ii) the direct synthesis of the mixed oxide on the monolith itself by one step citrate route.

## 2. Material and methods

### 2.1. Catalyst preparation

CeSiO<sub>x</sub> catalyst support was synthesized by co-precipitation method. An aqueous solution of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Sigma-Aldrich)(0.31 mol L<sup>-1</sup>) was added to a suspension containing 3 g of SiO<sub>2</sub> (Aerosil 300) solubilized in a NaOH (Aldrich 98%) solution (C<sub>NaOH</sub> = 0.34 mol L<sup>-1</sup>) with continuous stirring at 840 rpm for 1 h. Finally, the solvent was removed by filtration and the solid was washed with hot water until reach pH 7. The solid was dried at 100 °C for 16 h and then, calcined at a heating rate of 1.7 °C min<sup>-1</sup> from room temperature to 500 °C, and kept for 5 h in a muffle furnace. The nominal CeO<sub>2</sub>:SiO<sub>2</sub> weight ratio is 8.6.

The Ni/CeSiO<sub>x</sub> catalyst in powder form was prepared by incipient wetness impregnation of the support CeSiO<sub>x</sub> with an aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Sigma Aldrich) in order to obtain 10 wt.% of Ni. After impregnation, the samples were dried and calcined at

the same thermal treatment described for the support. The final powder catalyst was sized in a particle range of 0.4–0.5 mm.

Monolithic catalysts were prepared using two different methods. The first one involved the washcoating by slurry, and the second one was the co-precipitation by citrate method. Before incorporation of catalyst into monoliths, they were washed in isopropanol, calcined for 2 h at 800 °C; and weighted for obtaining the start pure monolith amount. A commercial 400 cells per square inch (cpsi) cordierite monolith cylinder with a diameter of 2 cm and a length of 6 cm from Rauschert was used.

The Ni/CeSiO<sub>x</sub> catalyst prepared in powder form and two different binders were used to investigate the effect of coating procedure on the dipcoating preparation method of monolithic catalyst. PVA (polyvinyl alcohol, 95%, hydrolyzed, average MW = 100,000, Fluka) or Ludox HS-40 (colloidal silica, 40 wt.% in water, Aldrich) were employed as a binder. For the preparation of the washcoat slurries, the catalyst in powder form was ground by hand into coarse powder (particle size < 100 μm) in a mortar and pestle. A suspension with 10 wt.% of catalyst and 5 wt.% of binder in distilled water was prepared. In the first step, the binder was dissolved in water in a 250 mL graduated bottle by stirring smoothly with a magnetic stir bar at 65 °C and 150 rpm for 3 h in a water bath, and left without stirring overnight (about 16 h). An homogeneous clear solution was obtained [32]. After dipcoating in the slurry containing the catalyst/binder and drying, the impregnated washcoats monoliths were calcined at a heating rate of 1.7 °C min<sup>-1</sup> from room temperature to 500 °C, and kept for 5 h in a muffle furnace. The coating procedure was finished when the monolith contains 2 g of catalyst before monolith calcination.

A NiCeSiO<sub>x</sub> monolith catalyst was also prepared by the citrate method (NiCeSiO<sub>x</sub> (CM)). Citric acid was added to an aqueous solution that contained all the required precursor salts of the support (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> and SiO<sub>2</sub> (Aerosil 300), in a 9:1CeO<sub>2</sub>:SiO<sub>2</sub> weight ratio, and of the active phase Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Sigma Aldrich), as described elsewhere [9,10]. The final solution was stirred for 10 min, and then the temperature was raised to start boiling, which was continued for 30 min to form a homogeneous chelate between the metal cations and the citrate anions. Then the solution was concentrated by evaporation at 80 °C until a viscous liquid was obtained. After dipcoating the monolith into the suspension containing the catalyst and drying, the impregnated washcoated monolith was calcined. The coating procedure was finished when the monolith contains 2 g of catalyst before monolith calcination. Then, the monolithic catalyst was calcined following the same procedure previously described.

A 1Pt10NiCeSiO<sub>x</sub> monolith catalyst was also prepared by citrate method (PtNiSiO<sub>x</sub> (CM)). In this case, an aqueous solution containing Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Sigma Aldrich) and 8 wt.% H<sub>2</sub>PtCl<sub>6</sub> in water solution (Sigma Aldrich) was added to a citric acid aqueous solution with all the required ions of the support. The preparation method was similar to the one previously described.

### 2.2. Adhesion test

Catalyst layer adhesion to the monolith ceramic walls was tested with an ultrasonic bath treatment according to the method described elsewhere [33], to verify the weight loss caused by mechanical stress. After 10 min, the sample was dried and the weight loss measured.

### 2.3. Characterization

The specific surface area of the powder samples was measured by N<sub>2</sub> adsorption-desorption isotherms at –196 °C on an ASAP 2420 Micromeritics instrument. Prior to the measurements, the samples were dried at 100 °C for 24 h, and then, submitted to *in situ*

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