



Full Length Article

Catalytic activity of electrodeposited cobalt oxide films for methane combustion in a micro-channel reactor

José M. Rodrigues^{a,*}, M. Filipa Ribeiro^b, Edgar C. Fernandes^a^a IN+, Centro de Estudos em Inovação, Tecnologia e Políticas de Desenvolvimento, Técnico Lisboa, Universidade de Lisboa, Avenida Rovisco Pais, 1049-001 Lisboa, Portugal^b CQE, Centro de Química Estrutural, Técnico Lisboa, Universidade de Lisboa, Avenida Rovisco Pais 1, 1049-001 Lisboa, Portugal

ARTICLE INFO

Keywords:

Catalytic combustion
Electrodeposition
Cobalt oxide (Co₃O₄)
Micro-channel reactor
Methane combustion

ABSTRACT

This paper studies the catalytic combustion of a methane-air mixture inside a micro-channel reactor coated with cobalt oxide (Co₃O₄) film. The Co₃O₄ was coated on the reactor channels by an inexpensive electrodeposition method. A cohesive film with large accessible surface area was fabricated with the method described, which allowed the control of the film thickness. Complete combustion of methane was achieved at 760 °C. The catalytic activity profiles obtained suggest that the reaction is carried only via catalytic combustion up to 600 °C, while both gas-phase and catalytic combustion might occur simultaneously at higher temperatures. The measured catalytic reaction rate per unit area was aligned with the reaction rate reported for similar reactors and operating conditions. Results showed that the catalytic films did not deactivate after a total of 50 h of cyclic operation. Tests with different reactants concentration revealed a first order dependence of the reaction rates for methane concentration and a near zero-order dependence on the oxygen concentration, at 600 °C. The measured data was successfully fitted by a chemistry model proposed in the literature. Overall, this work highlights the potential of using inexpensive electrodeposited films of Co₃O₄ on micro-channel reactors for combustion of hydrocarbons.

1. Introduction

More than ever, combustion systems manufacturers feel the pressure of government regulations for restriction of pollutant emissions from the products they develop and sell. Consecutive pro-climate agreements between governments culminated recently in the COP21 Paris Agreement, in which governments from most countries showed their commitment to establish reasonable target emissions and avoid the two-degree increase of the Earth's average temperature scenario [1]. Advances in combustion technologies have made possible the reduction of carbon monoxide (CO) and unburnt hydrocarbons (UHC) emissions to levels that are considered safe to the environment. However, nitrogen oxides (NO_x) emission levels are still a challenge for manufacturers of hydrocarbon-fueled systems, either for heating or production of power. NO_x emissions are mostly in the form of NO and result from the oxidation of atmospheric nitrogen at temperatures above 1200 °C as described by the Zeldovich mechanism [2,3]. Catalytic combustion (CC) of hydrocarbons has been proposed as an abatement technology of unburnt emissions of methane and NO_x [4–8]. The activation energy of a catalytic reaction is greatly reduced, meaning that complete combustion is achieved at lower temperatures and NO_x

formation [5] is largely diminished, accordingly. Several studies and new burner concepts using CC have been published and proposed for energy applications [9–11,4,8,12]. However, the use of CC has been under valued by the industry, mainly on the design of compact burners. Micro combustion chambers benefits from CC given the high surface-to-volume ratio and the associated high heat losses. This types of burners might be interesting for applications with high energy density and portability requirements, of which demand increases day-by-day. There has been significant work on catalytically-assisted micro combustion chambers, namely on the investigation of simultaneous gas-phase and surface combustion. Most agree that the heat fluxes across the channel and across the gas and solid phases are critical for combustion stability and for the integrity of catalytic layer [9,13]. When a micro combustion chamber is design to favor gas-phase combustion, the catalytic reactions at the combustion chamber wall may avoid reaction quenching by providing extra heat to the reacting zone, balancing the wall heat losses. In such cases, the catalytic reaction is only accountable for a small fraction of the total combustion reaction rate. In our opinion, there is still large windows for research on combustion of hydrocarbons in micro combustion chambers, namely using alternative non-noble catalytic metals.

* Corresponding author.

E-mail address: jose.neves.rodrigues@tecnico.ulisboa.pt (J.M. Rodrigues).

The high cost of the most active catalytic metals, Pt, Pd and Rh, has hindered the proliferation of CC as a sustainable and competitive combustion technology and other metal or metal compounds must be screened to unlock the potential of the technology. As an alternative to single-metal catalysts with Platinum, Palladium or Rhodium, several authors had proposed and studied CC of methane over variety of compounds from transition metal oxides in a pure form [14–19] or doped with noble metals [20–24] to perovskites and zeolites [25–27]. Studies of methane CC using the spinel cobalt oxide (II,III), Co_3O_4 , demonstrated good reactivity of the metal compound with low alkanes and, for that reason, Co_3O_4 has been recurrently chosen as the catalyst for many studies of CC [21,28,15,29,16].

Traditional methods for catalyst deposition on metallic reactors require a washcoat layer on the reactor inner walls to support the catalyst. The washcoat layer not only increases the manufacturing complexity but also hampers the heat transfer from inside the reactor to its wall, causing the development of hot spots that deteriorate the catalyst layer. Electrodeposition, a technique used to deposit thin layers of a metal or metal compound with highly complex and porous nanostructures [30,31] directly over metallic substrates, eliminates the need of the washcoat layer. Consequently, there is less heat resistance between the catalysts film and the reactor walls, improving the heat management of the reactor. This technique has been extensively applied in the industry of metallic coatings and electrode manufacturing given its simplicity and low-cost. Electrodeposition of Co_3O_4 on metallic substrates has been reported extensively in the literature, describing different crystalline nanostructured surface morphologies such as nano-sheets, nano-blocks and nano-flowers [31–34]. With this in mind, electrodeposition not only provides a simple and inexpensive method for the application of catalytic films on catalytic micro-channel reactors, but also presents benefits to their performance.

This work investigates the catalytic activity of electrodeposited cobalt oxide films on the combustion of ultra-lean methane mixtures (equivalence ratio lower than 0.2) inside two parallel micro-channels. Herein, the main goal is to demonstrate exclusively the catalytic activity of cobalt-based coatings electrodeposited on metallic alloys. Heat transfer considerations are out of the scope of this work and will be addressed in the future on a numerical study of the same setup presented here. The fabrication of the films by electrodeposition will be described and the detailed characterization of the film with Raman spectroscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM) will follow. Cobalt-based coatings with different thicknesses will be tested to investigate the loading effect of the film on the catalytic activity. In order to benchmark the performance of the films, a comparison with other catalytic reactors, coated with cobalt-based films by different manufacturing processes, will be presented. Finally, the influence of reactants concentration on the catalytic activity of the films will be assessed. With the catalytic reaction rates measured at different reactant concentrations and temperatures, an extrinsic reaction model will be devised.

2. Experimental setup

2.1. Preparation of the catalyst

The Co_3O_4 catalytic films were prepared by cathodic electrodeposition of $\text{Co}(\text{HO})_2$ onto Fecralloy® plates, followed by a thermal treatment. The electrolyte consisted of a 0.05 M cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$, Sigma Aldrich) aqueous solution. The electrodeposition experiments were carried out at room temperature in a three-electrode electrochemical cell controlled by a Voltalab PGZ 100 potentiostat. On this setup, the working electrode were 0.5 mm thick Fecralloy® plates, two graphite plates, connected in parallel, were used as counter electrodes and a saturated calomel electrode (SCE) as reference electrode. $\text{Co}(\text{HO})_2$ was deposited on both faces of the Fecralloy® plates. The galvanostatic mode was chosen for the cathodic

electrodeposition with applied current densities of -0.6 , -1.2 and -2.4 mA/cm^2 , during a fixed duration of 500 s, corresponding to samples A, B and C, respectively. Before electrodeposition, the Fecralloy® plates were cleaned on hydrochloric acid 50% for 3 min, rinsed in distilled water and washed in alcohol on an ultrasound bath for 10 min. The samples were kept on an ahacoll bath until electrodeposition, before being dried with compressed air and weighted. After electrodeposition, the samples were annealed in a laboratory oven (Mettler) at $250 \text{ }^\circ\text{C}$ for 3 h.

2.2. Surface characterization

The crystal structures of the Co_3O_4 films were investigated using X-ray diffraction (XRD). Diffractograms were recorded at room temperature by Bruker AXS-D8 Advance powder diffractometer with a Bragg–Brentano geometry [Cu $K\alpha$ radiation source ($\lambda = 0.150619 \text{ nm}$)] and the diffraction patterns collected over a 2θ range from 10° to 90° . Raman spectroscopy was also used to analyze structures of the Co_3O_4 films. For that purpose a radiation source with a solid-state laser operating at 532 nm with an output power of 20 mW was applied. A spectrograph with a 600 lines/mm grating was used and a 50 times objective lens focused the laser beam on the cobalt films. Spectra were obtained with acquisition time of 15 s and 15 accumulations. Both XRD and Raman spectra were compared with those of database and literature. The morphological characterization of Co_3O_4 films was performed by using scanning electron microscopy (FEG-SEM, JEOL-JSM7001F).

2.3. Catalytic activity tests

Three reactors (R1, R2 and R3) were built to evaluate the combustion of a methane-oxygen mixture and the effect of film thickness on the combustion. The reactors consisted of three parallel plates coated with the cobalt film in a two-channel configuration. The two channels with an opening of 0.5 mm constitute the reaction zone of the reactors. The three plates on each reactor correspond to samples A, B or C as follows: reactor R1 contains three plates of sample A, reactor R2 contains three plates of sample B and reactor R3 contains three plates of sample C. A fourth reactor without catalyst was built and tested as reference. In Fig. 1 is a schematic of the micro-channel reactor. The total inner volume of the reactor channels was 1400 mm^3 and the total coated area was 56 cm^2 . The tests were carried out on a vertical plug-flow quartz tube with an inner diameter of 40 mm and a length of 450 mm and installed inside a programmable tube furnace. The three plates were hold in place inside the quartz tube with a Fecralloy®

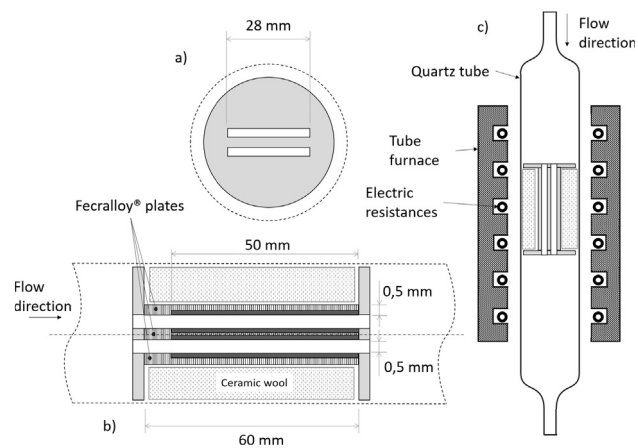


Fig. 1. Catalytic micro-channel reactor inside the quartz tube. The darkest bands inside the channels illustrate the cobalt films deposited on the Fecralloy® plates: top view of the reactor (a), cross-sectional view with the details of the coated samples inside (b) and reactor installed inside the quartz tube (c).

Download English Version:

<https://daneshyari.com/en/article/6630502>

Download Persian Version:

<https://daneshyari.com/article/6630502>

[Daneshyari.com](https://daneshyari.com)