Catalytic combustion of methanol over Pt-CeO$_2$ on Fecralloy foam catalysts prepared by electrodeposition.

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Highlights

- Pt and CeO$_2$ were deposited, in this order, onto Fecralloy foams.
- Pulsed deposition yielded Pt nanoparticles which were coated with CeO$_2$ thin films.
- CeO$_2$-Pt-Fecralloy was superior to Pt- Fecralloy in catalytic combustion of methanol.
- Active catalytic sites were located at Pt-Fecralloy and Pt-CeO$_2$ interfaces.

1. Introduction

Lightweight catalytic burners are often realized using metal foams, due to their outstanding properties in terms of heat and mass transfer coupled with low pressure-drops and thermal resistance. Among the foam materials, Fe-Cr-Al alloy (Fecralloy) have outstanding resistance to high temperatures [1,2]. The procedures for depositing firmly anchored, homogeneous catalytic layers onto the foam substrates are often cumbersome and involve many steps. Therefore, there is interest for innovative preparation methods which take advantage of the metallic nature of the foam support, such as electrodeposition [2,3]. In this work, we have investigated the cathodic deposition of Pt nanoparticles onto 3D Fecralloy foams followed by that of discontinuous CeO$_2$ promoting layers for the preparation of active structured catalysts for low-temperature catalytic combustion of methanol. The pulsed deposition of Pt enabled us to control size and surface distribution of nanoparticles. The CeO$_2$ deposit thickness and porosity were controlled through the deposition charge, in order to maintain a significant part of the Pt surface accessible to electrolyte or gaseous reactants.

2. Methods

Structured catalysts were prepared starting from commercial Fecralloy foam samples (Porvair, 50 pores per linear inch, 0.34 g cm$^{-3}$ apparent density, ca. 95% void volume, and approximate diameters of struts and pores 1.0 x 10$^{-2}$ cm and 5.5 x 10$^{-2}$ cm) which were cut in the form of cylinders (d=1.8 cm, h= 0.9 cm). Pulsed electrodeposition of Pt nanoparticles from an H$_2$PtCl$_6$ solution, followed by cathodic electrodeposition of CeO$_2$ thin films from a nitrate bath was the most successful preparation strategy. In particular, the reduction of nitrates induced a local pH increase at the foam/electrolyte interface and caused the precipitation of mixtures of Ce(OH)$_3$ and CeO$_2$, which were converted to CeO$_2$ by heating in air (2h at 600 °C). The Pt loading in the catalysts was measured by ICP-MS and the noble metal surface area by cyclic voltammetry, through the H desorption charge. SEM images and EDS analyses were obtained with a Zeiss SIGMA instrument, equipped with a field-emission gun. XRD spectra were obtained by using a Philips X-PERT PW3710 diffractometer.

The catalytic combustion of methanol over foam catalysts was investigated under dry lean feed conditions (0.5 – 2.0 % vol. in air) using a lab scale test rig [2]. The reactor was operated at nearly atmospheric pressure, under pseudo-isothermal conditions, by ramping up the temperature with an electric furnace, starting from 50°C, at ca. 3°C min$^{-1}$. The CO$_2$ production rate was estimated from low conversion data assuming differential conditions, isothermal plug flow reactor, and constant molar flow.

3. Results and discussion

SEM analysis revealed that the pulsed electrodeposition of Pt onto Fecralloy foams effectively deposited the noble metal on the struts of their outer and inner cells, with similar surface densities of Pt nuclei, consisting
of clusters of quasi-cubical nano-particles. As a general trend, their characteristic dimensions were lower for more negative $E_1$ potential, and increased with the number of pulses. Pt particles were stable under CeO$_2$ deposition conditions and were not removed from the Fecralloy substrate. Fig. 1a shows that a ca. 20 nm thick, probably discontinuous, CeO$_2$ skin formed on the Pt particles, producing a sort of core-shell system. A discontinuous CeO$_2$ layer was visible on the Fecralloy substrate too.

Although the presence of a CeO$_2$ film decreased (by ca. 70%) the exposed Pt surface area accessible to electrolyte it enhanced the performance of the catalysts towards methanol combustion. Fig 1b shows that CeO$_2$-Pt-Fecralloy catalysts were superior to Pt-Fecralloy counterparts with the same noble metal loading, without affecting the apparent activation energy of the process (ca. 70 kJ/mol). Methanol combustion to yield CO$_2$ (with negligible CO formation), started around 100°C and reached an asymptotic value, limited by external diffusion mass transfer, around 250°C. Conversion to CO$_2$ attained 100% when the contact time was sufficiently long. The catalysts were stable and their performance was constant during successive cycles involving temperatures up to 600°C. The enhanced catalytic performance was ascribed to the formation of additional active sites along the interface between CeO$_2$ and Pt that remained easily accessible in the nanoparticles with a quasi-core-shell configuration. Experimental evidence was found that active sites for methanol catalytic combustion represent only a small fraction of the total exposed Pt surface, thus highlighting the fundamental role of those atoms, located at the Pt-Fecralloy and Pt-CeO$_2$ interfaces, which were accessible to methanol.

![Figure 1](image)

**Figure 1.** a) SEM image of CeO$_2$-Pt-Fecralloy sample. b) Methanol yield to CO$_2$ as a function of temperature over Pt-Fecralloy, CeO$_2$-Pt-Fecralloy, CeO$_2$-Fecralloy catalysts and a bare Fecralloy foam. Feed conditions: 40 Sdm$^{-3}$ h$^{-1}$, CH$_3$OH 0.5 - 1.0 % in air

### 4. Conclusions

In this work, we have demonstrated how the cathodic deposition of noble metal nanoparticles followed by that of discontinuous oxide layers may be an original and effective way to use electrochemistry for the preparation of active structured catalysts for low-temperature catalytic combustion processes.

### References


**Keywords**

Structured catalytic reactors; Core-shell nanoparticles; Electrodeposition.