

# Catalytic Combustion of Methanol over Nano-Structured CeO<sub>2</sub>-Pt/Fecralloy Foam Catalysts

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## Abstract

Pt-based structured catalysts for the low-temperature combustion of methanol were prepared by pulsed electrodeposition, using Fe-Cr-Al alloy (Fecralloy) foam supports. Pt loading and surface area were measured by ICP-MS and cyclic voltammetry, respectively. Although the presence of a CeO<sub>2</sub> film decreased the Pt surface area accessible to electrolyte it enhanced the performance of the catalysts towards methanol combustion, without affecting the activation energy of the process, due to the formation of novel active sites along the Pt-CeO<sub>2</sub> interface of core-shell nanoparticles.

## Introduction

Methanol has been proposed as a valuable fuel for Pt-based catalytic burners integrated in fuel cells [1] or mobile thermoelectric power generators [2]. For those applications, catalytic burners are integrated into heat-exchanger reactors which inevitably require a shaping of the catalyst into a structured form [3]. Metallic foams represent a preferred choice to reduce the size of the reactor needed to reach high conversions [4] due to their outstanding heat- and mass-transfer properties. Among them, Fecralloy foams are optimal to design lightweight reactors with low thermal inertia and fast transient response during start-ups [4]. Nevertheless, the deposition of a firmly anchored, homogeneous catalytic active layer over the structured (foam) substrate is not a trivial matter.

In a recent paper, our group has reported on the low/medium-temperature catalytic combustion of methanol on Pt-modified Fecralloy foams prepared by electrodeposition [5]. This simple and straightforward method yielded structured catalysts with stable activity, very low CO emissions and complete selectivity to CO<sub>2</sub>. In this work we set out to further improve the performance of the methanol combustion catalysts, through the following actions: (i) diminishing the Pt loading, to enhance the dispersion of the noble metal and its mass activity; (ii) depositing a CeO<sub>2</sub> protecting shell above Pt nanoparticles to favour synergic catalytic effects.

## Experimental

Catalysts were prepared by depositing Pt, CeO<sub>2</sub> or both onto Fecralloy foams cylinders with 1.8 cm diameter and 2.3 cm<sup>3</sup> volume (Porvair, 50 pores per linear inch, 0.34 g cm<sup>-3</sup> apparent density, ca. 95% void volume). Electrodeposition of

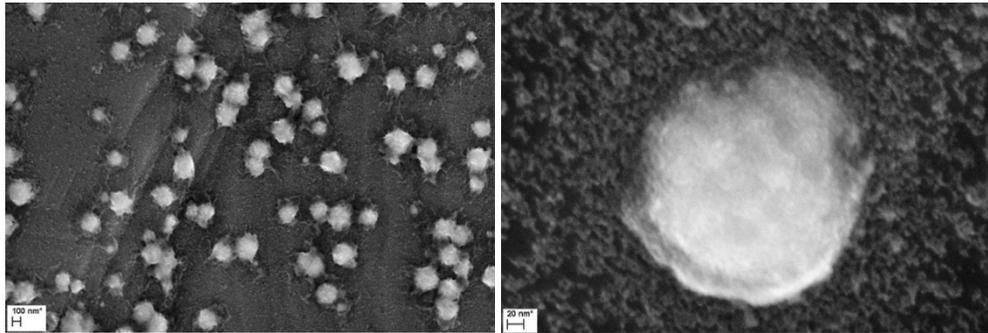
either CeO<sub>2</sub> or Pt was carried out in two-compartment cells. The Fecralloy-foam working electrode and a Pt wire counter electrode were placed in the main cell compartment, a Saturated Calomel Electrode (SCE) in the lateral compartment. Platinum was deposited from 0.002 M H<sub>2</sub>PtCl<sub>6</sub> solutions containing 1.0 M NaCl and HCl to yield pH 2.0. Electrolyses were performed by pulsing the working electrode potential between E<sub>1</sub>, in the range -0.6 to -1.2 V, inducing Pt electrodeposition, and E<sub>2</sub>, variable between 0.1 and -0.1 V. The number of cycles was varied to control the deposition charge and hence the Pt loading. Thereafter, CeO<sub>2</sub> was electrodeposited at constant potential from a 0.100 M Ce(NO<sub>3</sub>)<sub>3</sub> solution. Cyclic voltammograms aimed at assessing the exposed Pt surface area were recorded using either Pt-Fecralloy or CeO<sub>2</sub>-Pt-Fecralloy samples as working electrodes, a Pt wire as counter-electrode and an Hg/HgO/1 M KOH reference electrode using an Autolab PGSTAT 302N potentiostat. SEM images and EDS analyses were obtained with a Zeiss SIGMA instrument, equipped with a field-emission gun. Pt loading was determined by ICP-MS (Thermo Elemental X7-series) after microwave-assisted acid dissolution of samples.

Methanol catalytic combustion tests were performed in a lab scale quartz reactor (d<sub>inner</sub>=20 mm), operated at nearly atmospheric pressure, by ramping up the temperature with an electric furnace from 50°C to 600°C at 3°C/min. Inlet and outlet temperatures were measured by two K-type thermocouples. A lean methanol in air feed (0.5–2.0 % vol., total flow-rate 40 Sdm<sup>3</sup> h<sup>-1</sup>) was prepared by mixing two air streams, regulated by independent MFCs, and one of these passed through a methanol saturator. The effluent gas was dried and continuously analyzed with an ABB Advance Optima2020 and a GEIT FLUE GAS, equipped with ND-IR detectors for CO, CO<sub>2</sub>, CH<sub>4</sub> and an electro-chemical cell for O<sub>2</sub>. In fact the CH<sub>4</sub> detector gave a linear response to methanol, thus it was used to measure its concentration in the feed stream after a specific calibration.

Methanol conversion to CO<sub>2</sub> (yield) was simply defined as the molar ratio between CO<sub>2</sub> formed (outlet) and methanol in the feed. The CO<sub>2</sub> production rate was estimated from low conversion data assuming differential conditions, isothermal plug flow reactor, and constant molar flow.

## Results and Discussion

Pt nano-particles formed directly onto Fecralloy foams and consisted of clusters of quasi-cubical particles, deposited with similar surface densities on the struts of outer and inner cells. The number of Pt nuclei per unit surface became larger as E<sub>1</sub> was made more negative, up to reach an asymptotic value around E<sub>1</sub> ≤ -1.0 V, and was essentially independent of the number of pulses. The particles dimensions were narrowly distributed, were lower for more negative E<sub>1</sub> potential, and increased with the number of pulses. The Pt loadings (Table 1) were well-below those of catalysts described in [5], and remained unchanged after CeO<sub>2</sub> addition, confirming that Pt nanoparticles were stable under those deposition conditions.



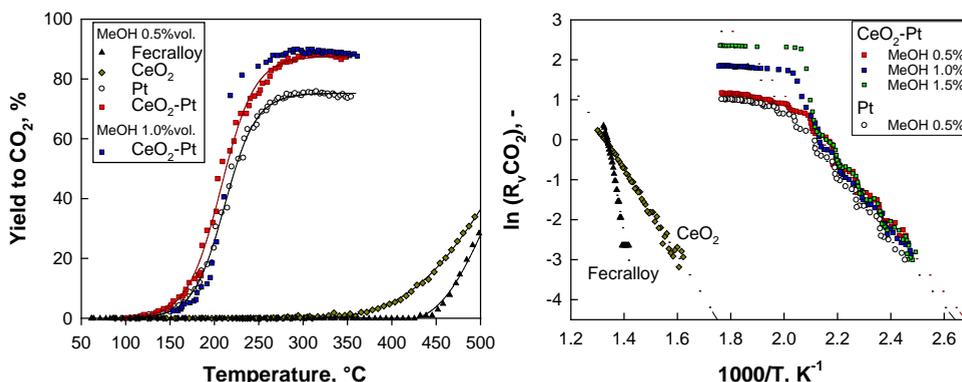
**Figure 1.** SEM images of CeO<sub>2</sub>-Pt-Fecralloy foam catalyst. Pt was deposited from 0.002 M H<sub>2</sub>PtCl<sub>6</sub> with E<sub>1</sub> = -0.7 V and 800 pulses. CeO<sub>2</sub> was deposited in 0.100 M Ce(NO<sub>3</sub>)<sub>3</sub> at -1.2 V with 13 C cm<sup>-3</sup> deposition charge.

Figure 1 shows SEM images of nano structured CeO<sub>2</sub>-Pt-Fecralloy foam catalysts. The formation of Ce-containing deposit, assessed through EDS analyses, occurred both on the Pt particles and on the Fecralloy substrate. The b image, obtained with 500k x magnification, shows that a ca. 20 nm thick, probably discontinuous, oxide skin formed on the Pt particles, producing a sort of core-shell system. A discontinuous CeO<sub>2</sub> layer was visible on the Fecralloy substrate too. Accordingly, the Pt surface area calculated from the H desorption charge (S<sub>w,EC</sub><sup>Pt</sup>, Table 1), progressively decreased upon deposition of increasing quantities of CeO<sub>2</sub>. In fact, CeO<sub>2</sub>-Pt-Fecralloy catalyst used in methanol combustion preserved a residual Pt surface area equal to 30% of the initial one.

**Table 1.** . Pt loading and Pt surface area and catalytic activity data for the foam catalysys tested for methanol combustion.

System	Pt Load mg cm <sup>-3</sup>	S <sub>w,EC</sub> <sup>Pt</sup> m <sup>2</sup> g <sup>-1</sup>	E <sub>a</sub> kJ mol <sup>-1</sup>	R <sub>w</sub> CO <sub>2</sub> @150°C mmol g <sub>Pt</sub> <sup>-1</sup> h <sup>-1</sup>	S <sub>w</sub> <sup>Pt</sup> m <sup>2</sup> g <sup>-1</sup>
Fecralloy	-	-	310	-	
CeO <sub>2</sub> -Fecralloy	-	-	88.5	-	
Pt-Fecralloy	0.37	16.6	70.4	296	0.12
CeO <sub>2</sub> -Pt-Fecralloy	0.37	5.0	70.4	415	0.19
Pt-Fecralloy [ref.5]	5 - 13	12 - 13	69.0	100 - 300	-

Figure 2a presents the results of the lean methanol combustion tests with foam catalysts in terms of the yield to CO<sub>2</sub> as a function of the reaction temperature. Preliminary tests were run with a bare Fecralloy foam and indicated that, under the investigated experimental conditions, the oxidation of methanol started above 375°C with the initial production of CO, followed by the formation of CO<sub>2</sub> only above ca 430 °C.



**Figure 2.** a) Methanol yield to CO<sub>2</sub> as a function of the reaction temperature over Pt-Fecralloy, CeO<sub>2</sub>-Pt-Fecralloy, CeO<sub>2</sub>-Fecralloy catalysts and a bare Fecralloy foam. b) Corresponding Arrhenius plots for the specific CO<sub>2</sub> production rate per unit volume of foam during methanol combustion. Feed conditions: 40 Sdm<sup>3</sup> h<sup>-1</sup>, CH<sub>3</sub>OH = 0.5 - 1.5 % in air.

The deposition of CeO<sub>2</sub> on the Fecralloy foam induced a limited improvement in the overall methanol oxidation activity of the system, showing some CO<sub>2</sub> formation from ca. 350 °C (Fig. 2a), always accompanied by the production of comparable amounts of CO. In contrast, the Pt-based catalysts displayed a significant activity for methanol total oxidation, despite their rather low noble metal content. CO<sub>2</sub> formation became measurable starting from slightly above 100°C and its yield increased steeply along with the reaction temperature, and eventually reached an asymptotic value above 250 °C. This corresponded to the presence of some unconverted methanol in the exhaust gas leaving the catalyst, whereas no other products were detected.

CeO<sub>2</sub>-Pt-Fecralloy catalyst outperformed its Pt-Fecralloy counterpart with identical noble metal loading, both in terms of catalytic activity before light-off as well as in the final CO<sub>2</sub> yield at high temperatures (87.7 % vs. 75.3 %). Moreover, CO formation was never detected in the exhaust gas from the CeO<sub>2</sub>-Pt-Fecralloy sample, and remained below 20 ppmv with Pt-Fecralloy system, in good agreement with our previous results on similar foam catalysts with higher Pt-loadings [5]. Reactivity measurements were repeated after having exposed the catalysts to reaction conditions at 600°C (2h), and gave substantially identical results, indicating a good stability of the catalytic activity of Pt-based foams.

As shown in Figure 2a for the case of CeO<sub>2</sub>-Pt-Fecralloy, when the inlet concentration of methanol was increased, the CO<sub>2</sub> yield plots shifted slightly towards higher temperatures, indicating a less than linear dependency of the catalytic combustion rate on fuel concentration at low temperature. Analogous results were also found over the Pt-Fecralloy catalyst. Figure 2b presents the Arrhenius plots for the specific CO<sub>2</sub> formation rate over the foam catalysts. Data sets obtained with CeO<sub>2</sub>-Pt-Fecralloy in the low temperature region (under kinetic

control) at various inlet methanol concentrations merged into a single line within experimental accuracy, and departed from it above the light-off temperature. The apparent activation energy ( $E_a$ , Table 1) was estimated equal to ca 70 kJ mol<sup>-1</sup>, and it was hardly affected by the addition of CeO<sub>2</sub> as a promoter for Pt or by the noble metal content. Methanol combustion mechanism on Pt-Fecralloy appeared qualitatively insensitive to the addition of CeO<sub>2</sub>. On the other hand, the methanol combustion rate ( $R_w$ , Table 1) at 150°C increased by a factor as large as 1.4, due to the formation of some additional active sites most probably located at the interface between the Pt and CeO<sub>2</sub>. As a consequence, the utilization factor of the costly noble metal was significantly enhanced with respect to our previous results with Pt-Fecralloy foams (Table 1).

The asymptotic behaviour of methanol conversion (which is equal to the CO<sub>2</sub> yield) upon light-off suggests the onset of full external mass-transfer control. Indeed, the asymptotic methanol conversion (CO<sub>2</sub> yield) level attained with each foam catalyst was independent of methanol feed concentration. On the other hand, methanol conversion increased to almost 100 % (not shown) when the tests were repeated doubling the contact time at fixed gas velocity, i.e. using two identical catalytic foams in series. Under the assumption of isothermal plug flow behaviour and irreversible reaction, the steady-state mass balance for methanol in the reactor becomes:

$$-\ln(1-x) = \frac{S_v V_{foam} k_m}{Q} \quad (1)$$

where  $x$  represents methanol conversion,  $S_v$  is the specific area of the active sites per unit volume of the foam [cm<sup>2</sup> cm<sup>-3</sup>],  $V_{foam}$  is the foam volume [cm<sup>3</sup>],  $k_m$  is the mass transfer coefficient [cm h<sup>-1</sup>], and  $Q$  is the volumetric flow [cm<sup>3</sup> h<sup>-1</sup>]. The value of  $k_m$  was estimated equal to 30 cm/s at 350 °C with the correlation given by Giani et al. [4], by considering that the approximate diameters of struts ( $d_s$ ) and pores ( $d_p$ ) in the Fecralloy foams were respectively 1.0 x 10<sup>-2</sup> cm and 5.5 x 10<sup>-2</sup> cm, and the geometric void fraction was 92.2%.

Assuming that  $k_m$  was not affected by the addition of the thin CeO<sub>2</sub> overlayer on Pt particles, it was possible to calculate for both catalysts the specific area  $S_v$  of those Pt sites that were active after light-off (Table 1). Noteworthy, CeO<sub>2</sub> addition increased the surface area of active sites by as much as 50%, in good agreement with the already reported activity increase before light-off.

Since CeO<sub>2</sub> was added at the final step of preparation after Pt-deposition so that neither metal loading nor its morphology were significantly affected, it can be argued that the increase in the number of available catalytic active sites in CeO<sub>2</sub>-Pt-Fecralloy was associated to the formation of novel CeO<sub>2</sub>-Pt interface sites that were easily accessible in the nanoparticles with a quasi-core-shell configuration.

Comparing the values of the specific surface area of active Pt sites per gram of metal to the corresponding figures estimated by voltammetric experiments, i.e. comparing  $S_{w,EC}^{Pt}$  with  $S_w^{Pt}$  (Table 1), it is evident that the active sites for methanol catalytic combustion at 350°C were only a small fraction of the total exposed Pt

surface, respectively 0.7% and 3.8% for Pt-Fecralloy and CeO<sub>2</sub>-Pt-Fecralloy foams. SEM inspection of used CeO<sub>2</sub>-Pt-Fecralloy catalysts showed that there was no Pt particles loss, and that the shape and size of the particles remained unchanged. A change in the morphology of the CeO<sub>2</sub> deposit on Fecralloy, presumably due to crystallization, was detected. These results agree with the observed stable catalytic activity of the samples when they were used in successive methanol combustion tests.

### 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 catalysts for low-temperature catalytic combustion processes. Platinum and CeO<sub>2</sub> were deposited, in this order, onto Fecralloy foams to obtain structured catalysts for methanol combustion. The CeO<sub>2</sub>-Pt-Fecralloy catalysts were superior to Pt-Fecralloy catalysts with the same noble metal loading. The catalysts were stable and their performance was constant during successive cycles involving temperatures up to 600°C.

The increase in the number of available catalytic active sites in CeO<sub>2</sub>-Pt-Fecralloy was associated to the formation of novel CeO<sub>2</sub>-Pt interface sites that remained easily accessible in the nanoparticles with a quasi-core-shell configuration.

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