Electrochemical Promotion of Propylene Combustion on Ag Catalytic Coatings

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Abstract: Catalytic and electrocatalytic measurements have been carried out in a solid oxide cell for propylene combustion using Ag catalytic films deposited on yttria-stabilized zirconia. Competitive adsorption between oxygen and propylene has been observed while catalytic performances can be tailored by current application in a non-Faradaic manner. The predominant impact of current applications is to modify the reactivity of oxygen present on the Ag surface. Positive current applications enhance the propylene conversion by producing more reactive oxygen species. This beneficial effect is more pronounced under lean-burn conditions where the oxygen coverage on Ag is high.

Keywords: Electrochemical Promotion of Catalysis (EPOC), Propylene Combustion, Ag catalytic films.

1. Introduction

Catalytic combustion as a process used for removal of hydrocarbons from automotive gas exhausts or for energy production has been widely implemented on supported PGM (Platinum Group Metals) based catalysts[1]. Since PGMs are very costly and rare, there is a strong need for an equally effective and less expensive catalyst. The electrochemical promotion of catalysis (EPOC), is a promising concept to *in-operando* boost catalytic processes in a reversible and controlled manner[2].

The two parameters that are commonly used to quantify the magnitude of EPOC are the rate enhancement ratio, ρ, defined by Eq. (1) and the apparent Faradaic efficiency, Λ, given by Eq. (2):

$$\rho = r/r_0 \qquad (1)$$

$$\Lambda = \Delta r_{catalytic}/(I/2F) \qquad (2)$$

where: r denotes the electropromoted catalytic rate, r_0 is the unpromoted rate (i.e. the open-circuit catalytic rate), $\Delta r_{catalytic}$ is the current- or potential-induced observed change in catalytic rate (in mol O/s), and I is the applied current.

The aim of this study was to develop Ag-based electrochemical catalysts for low temperature propylene deep oxidation. EPOC of propylene combustion has been carried out in the literature but mainly on Pt catalytic films[1,3], while this phenomenon was attributed to the modification in the propylene chemisorption[3].

2. Experimental

Nanostructured electrochemical catalysts were prepared by screen-printing and reactive Physical Vapor Deposition (PVD) method. Screen-printing technique is a flexible tool to prepare few μm thick porous films at low cost whereas extremely thin coatings of Ag can be produced by PVD. Thickness and porosity of Ag coatings were modified by changing the deposition parameters (duration and pressure for PVD, nature of the ink and calcination temperature for screen-printing) to optimize the catalytic properties.

Catalytic and electrocatalytic tests have been carried out in a specific quartz reactor[1] which operated under continuous flowing conditions at atmospheric pressure. The catalytic activity was monitored in a temperature range of 100 to 400 °C under lean-burn conditions, as encountered in Diesel exhausts. The most active Ag films were also evaluated under closed circuit conditions (± 2V) in order to measure the impact of polarization between the silver working electrode and a Au reference electrode. Both electrodes were exposed to the same atmosphere in a single chamber configuration[4].

3. Results and discussion

Figure 1 shows an SEM image (cross-view) of "fresh" Ag/YSZ sample prepared via the screen printing method. The thickness of Ag layers prepared by this method is in the range of 10-25 μm. Figure 2 shows catalytic activity measurements under current application for a Ag/YSZ sample under lean-burn conditions, at 300 °C. Values of Faradaic efficiencies in the range of 300 were obtained while the conversion could be tailored from 14 to 21%. Negative current applications lead to the decrease of the CO_2 production while positive current application corresponds to a pronounced increase of the catalytic performance. Upon positive current applications, the rate enhancement ratio increases with the intensity of the current. This indicates that the coverage of promoting ionic species ($O^{\delta-}$) increases with the current, then producing more weakly bonded oxygen species coming from the gas phase.

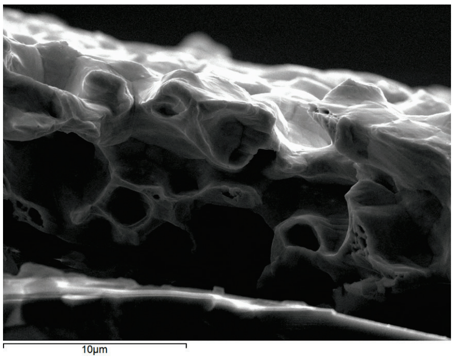

Figure 1. SEM image (cross-view) of a "fresh" Ag coating interfaced on YSZ (calcined at 600 °C)

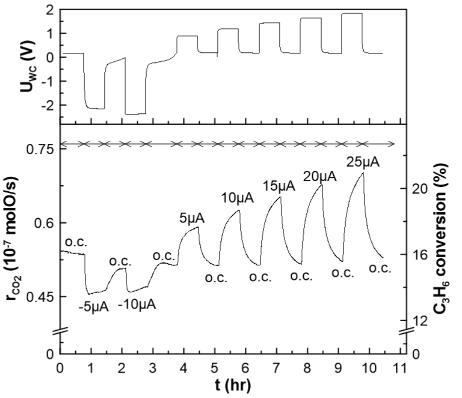

Figure 2. Transient effect of applied currents on U_{WC} as well as on the catalytic rate of CO_2 production and on C_3H_6 conversion.

4. Conclusions

This study reports, for the first time, that the catalytic activity for propylene of Ag coatings deposited onto YSZ can be tailored by current applications in a non-Faradaic manner. The predominant impact of current applications is to modify the reactivity of oxygen present on the Ag surface. Positive current applications increase the propylene conversion by producing more reactive oxygen species. This beneficial effect is more pronounced in an oxidizing atmosphere, where the oxygen coverage on Ag is high. This demonstrates that EPOC can enhance catalytic properties of Ag coatings for the abatement of propylene in air.

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References

1. P. Vernoux, F. Gaillard, L. Bultel, E. Siebert, M. Primet, J. Catal., 208 (2002) 412-421.
2. C.G. Vayenas, Electrochemical Activation of Catalysis: Promotion, Electrochemical Promotion, and Metal-Support Interactions, Springer, 2001.
3. A. Kaloyannis, C.G. Vayenas, J. Catal., 182 (1999) 37-47.
4. I. Kalaitzidou, T. Cavoue, A. Boreave, L. Burel, F. Gaillard, L. Retailleau-Mevel, E.A. Baranova, M. Rieu, J.P. Viricelle, D. Horwat, P. Vernoux, Cat. Com., 104 (2018) 28-31.