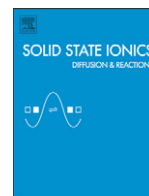




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Investigation of the Electrochemical Promotion of Catalysis origins on electrochemical catalysts with oxygen ion conductive supports: Isotopic labeling mechanistic studies

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ABSTRACT

The EPOC concept upon positive polarization of Pt/YSZ has been investigated with plethora of techniques. It is attributed to the presence of $O^{\delta-}$ species with the compensating charge in the metal catalyst. However, the origin of EPOC in the case of negative polarization is not yet well established. This study gives, for the first time, an insight of this mechanism. Isotopical labelling studies were conducted on a Pt/YSZ(O^{2-}) electrochemical catalyst for investigating the origins of Electrochemical Promotion of Catalysis (EPOC) using propane combustion as a model reaction.

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1. Introduction

Promoters play a key role in heterogeneous catalysis as they can significantly enhance catalyst activity, selectivity and useful lifetime [1–6]. Promoters are frequently divided into structural promoters and electronic promoters [1–6]. The former enhance and stabilize the dispersion of the active phase on the catalyst support. The latter enhance the catalytic properties of the catalytic phase itself by affecting the chemisorptive bond strength of adsorbed reactants and intermediates. Promoters can be added to the catalyst *ex situ*, during catalyst preparation (chemical promotion [1–6]) or *in situ* via electrical potential or current application when the active phase is in contact with an ionic or mixed ionic–electronic conducting support which can donate ionic species (e.g. partly ionized alkalis or anionic oxygen species [5,6]) to the catalyst/gas interface [6,7]. The latter case defines the field of Electrochemical Promotion of Catalysis (EPOC), also known as NEMCA (Non faradaic Electrochemical Modification of Catalytic Activity) effect.

EPOC utilizes electrochemical catalysts which are composed of catalytic films interfaced on solid electrolyte membranes. Ions contained in these electrolytes are electrochemically supplied (or removed) to (from) the catalyst surface and act as promoting agents to modify the catalyst electronic properties in order to achieve optimal catalytic performances. These promoting species profoundly affect the chemisorptive bond

strength of co-adsorbed reactants and reaction intermediates, thereby causing strong promotion of catalytic activity and selectivity.

In the case of electrochemical catalysts supported on O^{2-} ionically conducting ceramics, such as Yttria-Stabilized Zirconia (YSZ), the origin of EPOC upon positive polarizations is already established. Positive polarization leads to the electrochemical supply of O^{2-} species on a catalyst surface. When the catalytic surface is already covered with normally adsorbed oxygen (e.g. the well-known $O(2 \times 2)$ adlattice on Pt(111)), positive polarizations can generate a second more ionic and more strongly adsorbed species, denoted $O^{\delta-}-\delta^+$ (1), where δ is used to denote that these species are partly discharged. This latter is overall neutral, as the charge δ^- is compensated by the image charge, δ^+ , in the metal [7].



The spillover species $O^{\delta-}-\delta^+$ can act as promoters for catalytic oxidations due to their repulsive (or attractive) lateral interactions with normally coadsorbed oxygen $O(\text{ad})$ (or with coadsorbed electropositive adsorbates, e.g. carbonaceous species resulting from hydrocarbon adsorption). This mechanism is called “sacrificial promoter” model because the promoting ($O^{\delta-}-\delta^+$) species can also react with the oxidizable reactant, e.g. C_3H_8 , and thus has a finite mean residence time, τ_p , on the catalyst surface. The presence of oxygen ionic species has been evidenced in the EPOC literature by using many techniques such as Temperature-Programmed Desorption experiments [5–9]. In a recent study [10] we confirmed the “sacrificial promoter” model under

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positive polarizations by using isotopic oxygen labelling studies for propane combustion. Moreover significant production of $C^{16}O^{18}O$ was evidenced which was attributed to surface oxygen exchange, at triple phase boundaries. EPOC can also enhance the rate of this exchange.

Electropromotion of a reaction, when an oxygen ion conductor is utilized, can take place not only with anodic but also with cathodic polarizations. In the latter case, the mechanism is not clearly described in the literature. The aim of this study is to give, for the first time, an insight of the EPOC origin upon negative current applications of a Pt/YSZ electrochemical catalyst.

Isotopic labeling studies in a two compartment tubular Pt/YSZ electrochemical catalyst with three electrode (Pt) configurations (Fig. 1) were performed for distinguishing, the oxygen species coming (a) from the solid electrolyte, due to thermal migration, with (b) those from the gas phase during an electrochemically activated catalytic process (at atmospheric conditions). In this configuration, promoting ionic species (coming from YSZ) reaction with propane will form $C^{16}O_2$ while propane combustion with oxygen coming from the gas phase will lead to formation of $C^{18}O_2$. Therefore analysis of the reaction products can give an insight in mechanisms involved in electropromotion of propane combustion on Pt/YSZ upon negative polarizations.

2. Experimental

A tubular Pt/YSZ electrochemical catalyst with two compartments and three electrodes is depicted in Fig. 1. The electrodes were porous Pt films deposited on YSZ (8% mol Y_2O_3 -stabilized ZrO_2 , TOSOH) tube by using a platinum paste (Engelhard-Clal 6926). The deposited paste was annealed at 800 °C for 6 h in air and the platinum loading was 2.5 mg/cm². The electrochemical catalyst (Pt/YSZ) or working electrode (W) had a geometrical area of 35 cm² and was placed at the outer, while

counter and reference electrodes were at the inner surface of the YSZ tube.

The catalytic performances of the Pt electrode-catalyst for the propane deep oxidation were investigated at 350 °C in oxygen – excess conditions: C_3H_8/O_2 : 1000 ppm/2.5% and with an overall flow rate of 2.4 L/h. The reaction gases were mixtures of C_3H_8 (Air Liquide, 8000 ± 80 ppm), $^{18}O_2$ (Eurisotop®, 97.95% $^{18}O_2$) and He (Air Liquide, 99.999%) as the vector gas. The gas composition was controlled by mass flow controllers (Brooks), with accuracy of 1%.

An Inficon CIS Transceptor-2 quadrupole mass spectrometer was used for the analysis of the different isotopic combustion products in the gas stream. Signals at m/z 29, 32, 34, 36, 44, 46, and 48 amu were recorded in order to determine the amount of C_3H_8 , $^{16}O_2$, $^{16}O^{18}O$, $^{18}O_2$, $C^{16}O_2$, $C^{16}O^{18}O$ and $C^{18}O_2$. EPOC experiments were performed under constant polarizations which were applied using a VoltLab galvanostat–potentiostat (VOLTALAB 80) between the Pt working electrode exposed to the reactive mixture and the counter-electrode in air. In order to quantify the magnitude of EPOC, two parameters are commonly used. First, the rate enhancement ratio, ρ :

$$\rho = r/r_o \quad (2)$$

and second, the apparent Faradaic efficiency, Λ :

$$\Lambda = (r - r_o)/(I/nF) \quad (3)$$

where r is the electropromoted catalytic rate, r_o the open-circuit catalytic rate, I the applied current, and n the number of exchanged electrons during the electrode reaction, ($n = 2$ in this case) and F is the Faraday's constant. The Faradaic efficiency, Λ , has been estimated for the 3 different CO_2 products ($\Lambda_{C^{16}O_2}$, $\Lambda_{C^{16}O^{18}O}$, $\Lambda_{C^{18}O_2}$) and the overall Faradaic efficiency value, Λ_{tot} , was defined as the sum of these three contributions.

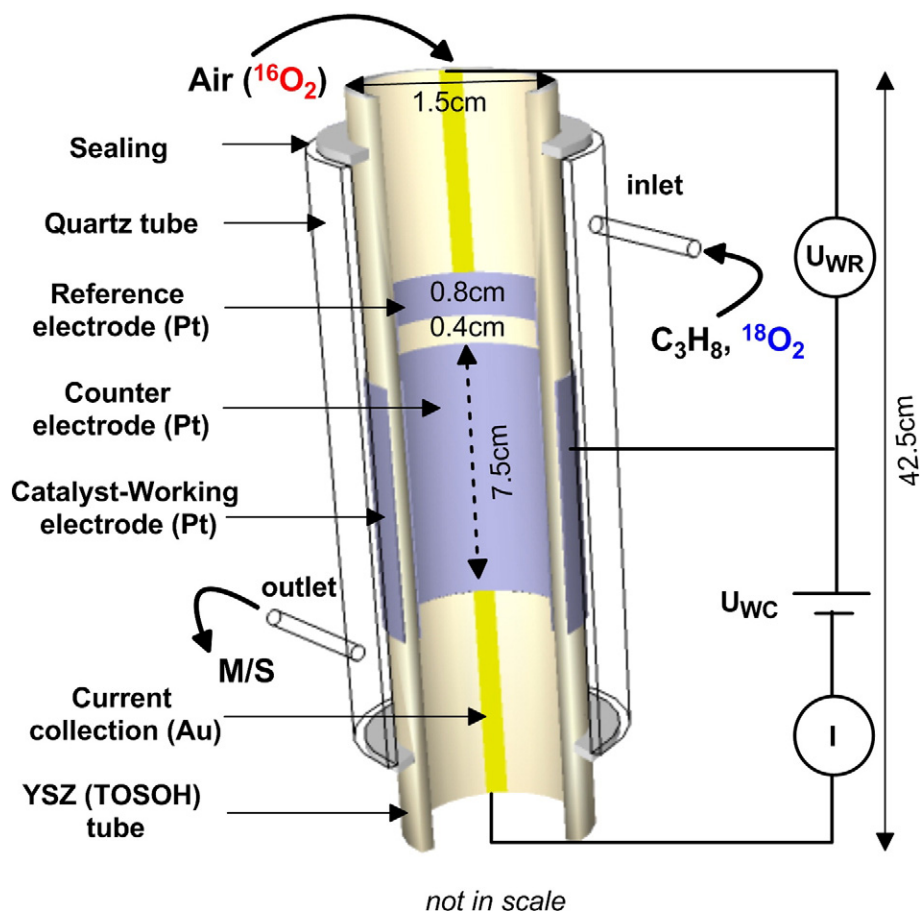


Fig. 1. Schematic representation of the two compartment and three electrode configuration reactor [10].

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