Electrochemical catalysts for hydrocarbon combustion

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Two series of electrochemical catalysts were prepared from sputtered Pt thin films onto two kinds of electrolyte membranes, 8 mol\% $Y_2O_3$-stabilized $ZrO_2$ (YSZ), an $O^{2-}$ conducting oxide and $Na_3Zr_2Si_2PO_12$ (NASICON), a $Na^+$ one; respectively. The thickness of the Pt films varied from 8 to 120 nm. Therefore, the Pt loading was extremely low. The catalytic activity of Pt/YSZ and Pt/NASICON systems has been investigated between 200 and 500 °C for propane and propene, respectively. In spite of the low Pt loading, the Pt/YSZ electrochemical catalysts exhibited high activity for propane combustion. Furthermore, the catalytic activity can be in-situ controlled by applying electrical polarisation with high Faradaic efficiency ($10^3$). The catalytic rate of propene deep oxidation on Pt/NASICON electrochemical catalyst was found to be limited by the number of active sites, which is low on very thin Pt films. Moreover, initial anodic polarisation indicate that $Na^+$ ions are already present on the top surface of Pt, probably proceeding from the preliminary stabilisation treatment of Pt in the reactive mixture. Nevertheless, polarisation allows the tuning of the catalytic activity of the electrochemical catalysts for propene oxidation. Finally, for both kinds of electrochemical catalysts, our results have evidenced that the measurement of the open-circuit voltage during catalytic process can be an indicator of the hydrocarbon conversion.

\textbf{KEY WORDS:} Platinum; Yttria Stabilised Zirconia (YSZ); NASICON; magnetron sputtering; electrochemical catalysts; NEMCA; hydrocarbon combustion.

1. Introduction

Catalytic combustion of hydrocarbons is a non-polluting means of heat generation. The most effective catalysts for the catalytic combustion of light hydrocarbons such as methane, propane or propene are supported noble metals. However, this kind of catalyst is very expensive and then requires stages of recovery and recycling. The goal of this study is to evaluate the catalytic activity of electrochemical catalysts composed of a thin sputter-deposited film of Pt interfaced with a solid electrolyte. Electrochemical catalysts can implement the concept of electrochemical promotion of catalysis (EPOC). This former process, also named Non-Faradaic Electrochemical Modification of Catalytic Activity (NEMCA) effect, discovered and developed by Vayenas et al. [1,2], is an innovative concept which can be used to improve the catalytic activity. EPOC is based on the control, by an applied potential, of the work function due to electrochemical pumping of ions between a solid electrolyte and the surface of a porous catalyst. In the case of $O^{2-}$ conductors, these former ionic species act as sacrificial promoters. Compared to classical promotion, the coverage of the promoting species on the electrochemical catalysts can be \textit{in situ} controlled by the polarisation. The electrochemical promotion of $CH_4$ [3], $C_2H_4$ [4,5], $C_2H_6$ [6], $C_3H_6$ [7,8] and $C_3H_8$ [7,9,10] combustion has been investigated on the Pt/YSZ system between 300 and 500 °C and for different hydrocarbon/oxygen ratios. All these studies have been performed with Pt films made from commercial paste, typically 1–10 $\mu$m thick and containing about 1 mg cm$^{-2}$. In our study, thin films of Pt were sputter-deposited by magnetron sputtering of a Pt target on two different solid electrolytes: 8 mol\% $Y_2O_3$-stabilized $ZrO_2$ (YSZ), an $O^{2-}$ ionic conductor and $Na_3Zr_2Si_2PO_12$ (NASICON), a $Na^+$ one. We have shown in previous studies [11,12] that magnetron sputtering is a suitable technique for synthesis of catalyst coatings. The development of electrochemical catalysts composed of a very thin layer of sputtered catalyst onto a solid electrolyte can considerably reduced the Pt loading. We have selected propene and propane as hydrocarbon models because several studies have shown than both propane and propene oxidation rates can be significantly controlled via voltage application, in a reversible manner, on Pt/YSZ [7–10] and Pt/NASICON [13] systems. Concerning propane deep oxidation, both studies of Kokkofitis et al. [9] and Kotsionopoulos and Bebelis [10] have found that, for oxygen to propane ratios lower than the stoichiometric ratio, the rate of this reaction could be reversibly enhanced by application of both positive and negative overpotentials (“inverted volcano” behaviour). We did not find the same results since we observed [7] that the propane conversion increased at positive potentials but decreased at negative ones. However, our experiments were carried out under excess of oxygen and at lower temperatures.
Propane and propene exhibit different reactivity, propene combustion occurring at lower temperature than propane one. Taking into account that NASICON presents a much higher ionic conductivity than YSZ, propene combustion has been performed on Pt/NASICON electrochemical catalysts whereas propane deep oxidation occurred on Pt/YSZ systems.

Catalytic activity investigation of Pt/YSZ and Pt/NASICON electrochemical catalysts has been carried out between 200 and 500 °C for propane and propene combustion, respectively. The influence of the Pt film thickness has been investigated as well as the effect of the polarisation.

2. Experimental

Electrochemical catalysts have been prepared from a polycrystalline Pt film deposited on two different solid electrolytes, i.e. 8 mol% Y₂O₃-stabilized ZrO₂ (YSZ), an O²⁻ ions conductor, and Na₃Zr₂Si₂PO₈ (NASICON), a Na⁺ one. Thin Pt films were deposited onto solid electrolyte pellets by DC-magnetron sputtering at low pressure (0.3 Pa) in order to get low porosities. YSZ membranes were prepared from YSZ powder (TOSOH, 99.99%, average grain size: 0.3 μm) sintered at 1350 °C for 2 h (densification higher than 98%). NASICON powder was prepared by the sol–gel method as described elsewhere [14] and samples of high density were obtained for 2 h (densification higher than 98%). NASICON pellets were 17 mm in diameter and 1 mm or 2 mm thick, for YSZ and NASICON, respectively. The experimental device, described elsewhere in detail [15], is a 40-l sputtering chamber pumped down via a secondary oil diffusion pumping system allowing a base vacuum of about 10⁻⁴ Pa before refilling with argon to reach the convenient pressure of 0.3 Pa. The substrates are positioned at 30 mm from the target axis (D_M), at a draw distance (D_T-s) of 100 mm. The target is mounted on an unbalanced magnetron and is powered by a 1.5 kW Advanced Energy DC supply. In all the experiments, the discharge current is maintained at a constant value of 0.2 A, for a duration lying from 15 s to 2 min. The argon flow rate is controlled with MKS flowmeters and the total pressure is measured using a MKS Baratron gauge. The thickness of the coatings is determined either by the step method using tactile profilometry, or by optical transmission spectroscopy in the visible range, using a fitting software developed by PVDc0 s.a.r.l. [16]. Gold counter and reference electrodes were deposited onto the opposite side of the electrolyte disc. Gold was selected because it does not exhibit any significant activity in both propane and propene combustion under our operating conditions. The reference electrode was deposited close to the counter-electrode, but at a distance (about 3 mm) sufficient to avoid any electrical perturbation. The three electrodes, W (catalyst electrode or working electrode), R (Reference) and CE (Counter-Electrode) were connected to a potentiostat–galvanostat Voltalab 80 (Radiometer Analytical). Voltage or current was applied and measured according to the procedure generally used in conventional three-electrode electrochemical cells. The catalyst potential V_WR was measured between the working electrode (Pt) and the reference electrode (Au) which may be considered as a pseudoreference since we have checked that its potential does not vary significantly with the composition of the gaseous mixture. The overpotential ΔV_WR was defined as the difference between V_WR and the open-circuit voltage (OCV). The polarisation effect on the catalytic reaction is characterized by the rate enhancement ratio (ρ) defined as ρ = r/r₀, where r₀, in mol O/s, is the catalytic rate at OCV, and r the catalytic rate under polarisation. The enhancement factor or Faradaic efficiency, Λ, was defined by:

\[ Λ = (r - r₀)/(I/nF) = Δr/(I/nF), \]  

where n is the number of exchanged electrons during the electrode reaction (n = 2 with an O²⁻ conductor) and Δr is the catalytic reaction rate change induced by a current I. A catalytic reaction exhibits the NEMCA effect when \(| Λ | > 1\). A reaction which is accelerated by a negative current or overpotential (oxygen removed from the catalyst surface) exhibits an electrophilic NEMCA behaviour and corresponds to a value of Λ lower than –1. In parallel, when the catalytic reaction is promoted by a positive current or overpotential (oxygen supplied to the catalyst surface), its NEMCA behaviour is called electrophobic (Λ > 1). Catalytic properties of these electrochemical catalysts according to their Pt layer thickness (from 8 to 120 nm) have been carried out for the propane and propene combustion, on Pt/YSZ and Pt/NASICON, respectively. The overall flow rate was 10 L h⁻¹ and the reactive mixture was composed of HC/O₂: 2000 ppm/1% with HC=C 3H₆ or C 3H₈. The catalytic properties of the Pt film were evaluated in a specific quartz reactor described in a previous study [6] at atmospheric pressure. The reaction gases were C₃H₈ (Air Products, 8000 ± 80 ppm C₃H₈ in He), C₃H₆ (Air Liquide, 8000 ± 240 ppm) and O₂ (Air Liquide, 99.95%). Before analysis, the water produced by the catalytic reactions was trapped by an electro-gas cooler (M&C Products, ECP1000-G). For propane combustion, the products of reaction were analysed by an online micro gas-chromatograph (VARIAN CP2003). The micro-chromatograph was made of two modules, each one equipped with its own thermal conductivity micro-detector. The first module enabled the separation of CO₂, C₂H₆ and C₂H₅ by using a Poraplot U column (10 m length and 0.32 mm in internal diameter) heated at 60 °C. The second one was equipped with a molecular sieve heated at 90 °C (10 m length and 0.32 mm in internal diameter) preceded by a back flush column. This module analysed O₂, N₂ and CO. The overall