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Investigation of the CO oxidation rate oscillations using electrochemical promotion of catalysis over sputtered-Pt films interfaced with YSZ

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ABSTRACT

The oscillatory behaviour of CO oxidation was studied at 250 °C and atmospheric pressure using an electrochemical catalyst composed of a thin (60 nm) sputtered-Pt film interfaced with an yttria-stabilized zirconia membrane. Oscillations of CO oxidation rate showed a perfect correlation with those of the electrochemical potential values. Electrochemical promotion of catalysis was used to initiate and stop the oscillatory behaviour. Small current application induced a permanent effect on the oscillatory behaviours. An extremely small negative current (−17 μA) led to a 4-fold increase of the catalytic activity and created oscillations that were stable even after current interruption. This permanent effect in the oscillatory behaviour of CO oxidation rate is observed for the first time using EPOC. This has been interpreted by the higher tendency of the nanometric-Pt particles to form PtO_x in thin sputtered films.

1. Introduction

The oxidation of carbon monoxide over platinum is one of the most studied catalytic reactions. Its importance in industrial and pollution control processes motivates both theoretical and experimental studies. Relevant reviews described the different aspects of CO combustion including rate oscillations [1,2]. Recent studies have focused on CO oxidation using FTIR [3,4]; X-ray absorption [4–6]; and scanning tunnelling microscopy [7], because there is still a need to further clarify the reaction mechanism under atmospheric pressure conditions.

The most plausible theoretical model to justify CO oxidation rate oscillations on Pt under atmospheric pressure is the oxide model [8,9], where the switching between two Langmuir–Hinshelwood kinetic branches is induced by a non-reactive platinum oxide (PtO_x) formation. In the high-reactivity branch, PtO_x is slowly formed by the high O coverage, gradually blocking the adsorption processes, and changing the system to the low-reactivity branch. CO slowly reacts with this oxide and when the surface is reduced, the reaction switches again to the high-reactivity branch [7].

The Electrochemical Promotion of Catalysis (EPOC) or Non-Faradaic Electrochemical Modification of Catalytic Activity (NEMCA) effect was discovered and developed by Vayenas and co-workers [10,11]. EPOC is an innovative concept that can be used to improve the catalytic activity. It is based on the modification of the work function due to the electrochemical migration of promoting species (O^{2-}) by an applied potential between a solid electrolyte (YSZ) and the surface of a porous catalyst (Pt) [11].

The CO oxidation and its oscillatory behaviour was one of the first systems studied with EPOC on Pt/YSZ [12,13]. However, these studies as well as the work of Tsampas et al. [14] were performed using Pt metalorganic paste films of 3–10 μm thickness and Pt particle sizes of ~1 μm. In the present work, CO oxidation was studied using a thin (60 nm) sputtered-Pt film interfaced with YSZ. This catalyst layer has a lower metal loading and a smaller Pt mean particle size (~50 nm) than conventional Pt-paste films.

The aim of this work is to investigate the impact of small current applications on the catalytic performance of sputtered-Pt electrochemical catalysts, which present a microstructure much closer to the conventional dispersed catalysts than the Pt-paste films. PtO_x formation is favoured in small Pt particles sizes [6,15]. This allows to compare the assumptions of the physicochemical origin of NEMCA effect proposed in the literature with the "oxide model".

2. Experimental

2.1. Catalyst preparation

Electrochemical catalysts were prepared with electrolyte dense pellets of 8% mol Y_2O_3-stabilized ZrO_2 (YSZ) (17 mm diameter, 1.5 mm thickness) [16].

The Pt polycrystalline film working electrode was obtained through deposition of pure Pt on one side of the YSZ pellets by DC-magnetron sputtering at low pressure [17]. The nanometric-Pt film presented

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~60 nm thickness and ~0.2 mg Pt total mass. SEM images of the Pt-sputtered films showed a 2-D porous Pt network structure and Pt grains of 50 nm mean size [18].

Two gold films were deposited on the opposite side of the Pt film serving as counter and reference electrodes. Gold paste films were selected because of its negligible catalytic activity in CO oxidation. The catalyst potential, ΔE_{WR}, was measured between the working electrode (Pt) and the reference electrode (Au). The potential of the latter does not vary significantly with the gaseous mixture composition. The sputtered-Pt/YSZ electrochemical catalysts were pretreated for 10 h at 550 °C in the presence of 1% CO and 5% O_2 in helium to stabilize the Pt surface morphology. Platinum dispersion was 5%, one order of magnitude higher than for Pt-paste films [18].

2.2. Catalytic and electrochemical measurements

A continuous flow quartz reactor was used [16]. Catalytic measurements were performed at 250 °C. The overall flow rate, 4.5 L h^{-1}, was monitored with mass flow controllers (Brooks). The CO concentration (C_{CO}) was 1200 ppmv (Air Liquide, CO 1 ± 0.002% in He); oxygen concentrations (C_{O_2}) ranged from 3000 to 6000 ppmv (Air Liquide, O_2 99.95%), and helium was used as carrier gas. C_{CO} and C_{O_2} were analysed by an on-line micro gas-chromatograph (R3000 SRA Instruments). CO_2 was detected with a CO_2 IR analyzer (Horiba VA 3000). A potentiostat–galvanostat Voltalab PGP-201 was used.

Two parameters are used to quantify the magnitude of EPOC effect: the rate enhancement ratio, $\rho = r/r_0$, and the apparent Faradaic efficiency, $\Lambda = (r - r_0)/(I/nF)$, where r is the electropromoted catalytic rate, r_0 the open-circuit catalytic rate, I the applied current, and n the number of exchanged electrons during the electrode reaction, which in this case is equal to 2. A catalytic reaction exhibits NEMCA behaviour when $|\Lambda| > 1$ [11].

3. Results and discussion

Fig. 1 shows the effect of C_{O_2} in the gas feed on the CO conversion and ΔE_{WR} values on the electrochemical sputtered-Pt surface under open-circuit voltage (OCV) conditions. Initially, C_{O_2} was 3000 ppmv; and the CO conversion was 14%, equivalent to an oxidation catalytic rate of 0.85×10^{-8} mol CO_2 s^{-1}. At this low steady-state catalytic activity, the ΔE_{WR} value was constant at −270 mV, indicating high coverage of the surface with CO (electron-donor species), which poisoned the oxidation reaction [3]. The increase of C_{O_2} to 6000 ppmv in the feed caused an enhancement of the CO conversion, reaching 80% (4.95×10^{-8} mol CO_2 s^{-1}). Under this high C_{O_2}, ΔE_{WR} was close to +100 mV, probably due to a raise of oxygen (electron-acceptor species) coverage and a decrease of CO coverage. Both CO conversion and ΔE_{WR} values presented a slight oscillatory behaviour under this O_2/CO concentration ratio. CO oxidation achieved a bistable regime due to the presence of two different oxygen species on the Pt surface: the reactive chemisorbed oxygen; and the strongly adsorbed O as PtO_x, which blocks the active sites [2,8,13]. PtO_x formation is favoured at high O_2/CO ratio [5–7], while its slow reduction by CO is responsible for the oscillatory behaviour [2,4,8]. The decrease of C_{O_2} to its initial value in the feed (3000 ppmv) led to a new oscillatory state, changing frequency and amplitude during the first 250 min. Then, the CO conversion and ΔE_{WR} values reached a stable oscillatory behaviour, persistent for days. Oscillations presented a spiking "down" behaviour characteristic of a pre-reduced Pt surface at temperature lower than 400 °C [13]. Its conversion baseline was close to 70% (4.3×10^{-8} mol CO_2 s^{-1}), and ΔE_{WR} baseline was +65 mV.

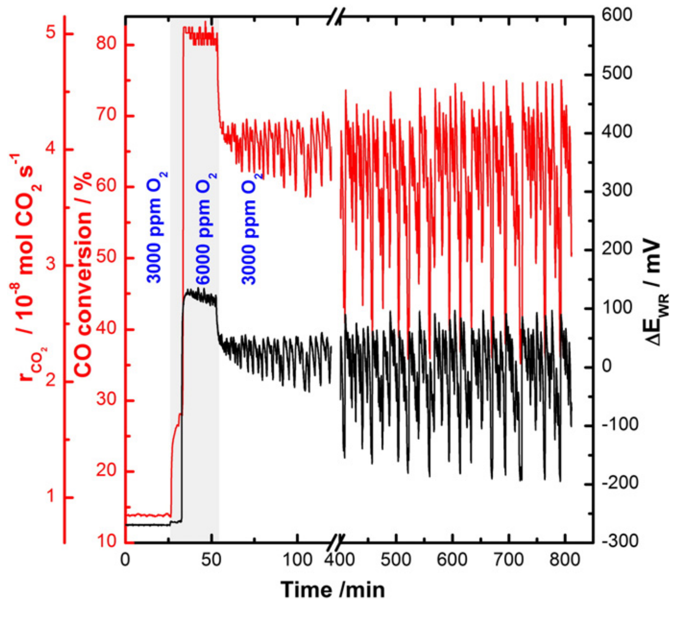

Fig. 1. Effect of O_2 concentration on CO conversion, CO_2 formation rate and ΔE_{WR} values at T = 250 °C, OCV conditions, and C_{CO} = 1200 ppmv.

The oscillatory profiles of the CO oxidation rate and ΔE_{WR} values were directly correlated as shown in Fig. 2a and b, being the latter a zoom of Fig. 2a. The increase of ΔE_{WR} indicates a raise in oxygen activity on the surface, producing an increase of CO conversion. As predicted by the Langmuir–Hinshelwood mechanism, the surface oxygen activity, linked to the oxygen coverage on Pt, influenced the CO oxidation rate. Consequently, our electrochemical catalyst can be used as a CO combustion rate sensor.

Fig. 2a shows two types of spikes in the oscillations according to their amplitude. In spikes with higher amplitude and an 18 min period, CO conversion oscillated between 70 and 30%; and ΔE_{WR} oscillated between +65 and −200 mV. In spikes with lower amplitude, observed between oscillations with higher amplitude, CO conversion and ΔE_{WR} values oscillated from 70 to 60% and from +65 to −73 mV, respectively. The presence of mixed-mode oscillations (more than one type of spikes) in CO oxidation at atmospheric pressure can be attributed to the fact that the catalytic surface can be considered as a set of internal completely coupled areas. These elementary oscillators display relaxation oscillations with different autonomous frequencies [19,20].

The application of a small positive current of +15 μA (migration of O^{2-} ions onto the Pt surface) during oscillations, decreased the conversion from 70% (4.3×10^{-8} mol CO_2 s^{-1}) to 13% (0.8×10^{-8} mol CO_2 s^{-1}); and also stopped both CO oxidation rate and ΔE_{WR} oscillations (Fig. 3a). Λ value was −450. After the positive current interruption, CO conversion and ΔE_{WR} did not return to their oscillatory behaviours, but CO conversion slightly increased from 13 to 14%, and the OCV stabilized at −230 mV. These values were similar to those achieved at OCV conditions in the first step of Fig. 1 at C_{O_2} = 3000 ppmv, suggesting that the surface was poisoned by CO.

According to NEMCA effect origin and theory [11], positive polarization causes an increase of the Pt work function by the presence of the electronegative promoting species on the catalyst surface. Therefore, a small positive polarization strengthened the Pt–CO interaction and weakened the Pt–O interaction since CO is an electron-donor and oxygen is an electron-acceptor. This led to an enhanced CO coverage on the catalytic surface, and to PtO_x decomposition, not allowing oscillations.

The application of a negative current was also evaluated (Fig. 3b). Before current application to a reactive mixture of C_{CO} = 1200 ppmv and C_{O_2} = 6000 ppmv at 250 °C, in absence of oscillations, CO conversion and ΔE_{WR} were 19.5% (1.2×10^{-8} mol CO_2 s^{-1}) and −210 mV, respectively. When a current of −17 μA was applied for 1 h, the conversion and ΔE_{WR} profiles presented two steps. During the first 20 min, the catalytic activity increased similarly to a typical EPOC experiment [11] from 19.5% to 31% (1.8×10^{-8} mol CO_2 s^{-1}). After