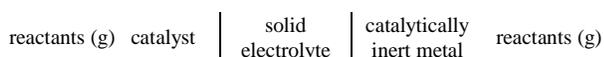


Electrochemical Promotion of IrO₂ Catalyst for the Gas-Phase Combustion of Ethylene

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The catalytic activity of thin porous metal or metal oxide films towards gas-phase reactions can be modified in a controlled manner in an electrochemical cell of type



via polarization of the catalyst/solid electrolyte interface. The effect, first reported in the late 1980s [1], is called electrochemical promotion (EP). Since the increase in catalytic rate may exceed the maximal electrochemical (Faradaic) rate by several orders of magnitude, the phenomenon is also called non-Faradaic electrochemical modification of catalytic activity (NEMCA effect). The current theory of EP [2] attributes the effect to promoting species generated electrochemically at the solid electrolyte/catalyst/gas three-phase boundary (tpb) then spreading out over the gas-exposed catalyst surface. Specific *in situ* techniques allowing identification and inspection of particular promoting species being hardly available, so the mechanism of promotion has mainly been investigated by phenomenological techniques like catalytic rate measurements, cyclic voltammetry and work function measurements, providing overall parameters of the complex phenomenon [3,4]. The aim of this work is to contribute to better understanding of the mechanism of EP via investigation of polarization and relaxation transients by means of such phenomenological techniques.

The catalytic combustion of ethylene over IrO₂ catalyst at $T=375^{\circ}\text{C}$ was studied. The porous catalyst film deposited onto yttria-stabilized zirconia (YSZ) solid electrolyte by thermal decomposition technique served as working electrode, the counter-electrode was made of gold. The reaction rate was determined by monitoring CO₂ production. *In situ* cyclic voltammetry provided evidences that (i) not only the proximity of the tpb but the whole gas-exposed catalyst surface was charged during polarization, and (ii) the reaction rate was closely related to the charge stored at the surface of the polarized catalyst. This suggests that the observed increase in the reaction rate during polarization reflects the accumulation of charged promoting species at the gas-exposed surface.

The galvanostatic transient behavior of the reaction rate during both polarization and relaxation was investigated as a function of the applied current. Fig. 1 shows a typical transient exhibiting a well-established steady-state rate under polarization and also full reversibility of the polarization cycle. A possible irreversible contribution ("permanent promotion"), known with IrO₂ catalysts [3] and attributed to current-assisted chemical surface modification, was avoided by low concentrations of reactants in the feed. At any polarizing current, the kinetics of polarization was faster than that of relaxation. Both polarization and relaxation transients showed a very fast, if not prompt, initial step followed by a much slower step with a time constant of the order of

about 15-30min. This was in a good agreement with cyclic voltammetric evidence of the existence of differently accessible regions for surface charging. In the slow steps, the polarization time constant decreased with increasing polarizing current, whereas the relaxation time constant was independent of the applied current. The increase in reaction rate from its open-circuit value, r_o , to the steady-state rate under polarization, r_{st} , was an increasing function of the applied current tending to an apparent saturation as illustrated in Fig. 2. For the interpretation of these results, a tentative model of electrochemical promotion, including current-generated formation of charged promoting species as well as their consumption in a chemical reaction, will be presented.

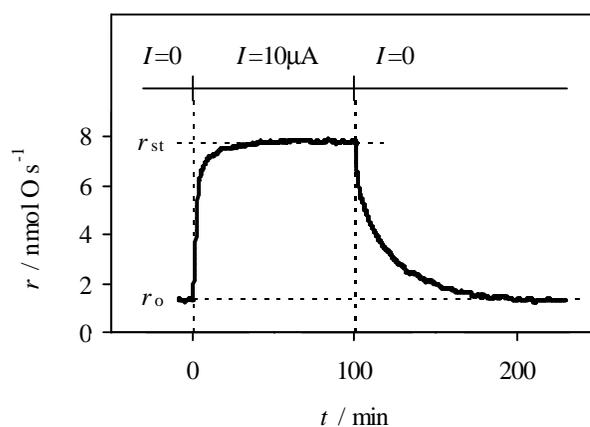


Fig. 1. Typical polarization and relaxation transients of the reaction rate of ethylene oxidation, r , on IrO₂/YSZ catalyst. Galvanostatic anodic polarization with $I=10\mu\text{A}$ during 100min. Catalyst loading: 77 μg IrO₂. Feed composition at $p_{\text{tot}}=100\text{kPa}$: $p_{\text{C}_2\text{H}_4}=12.5\text{Pa}$, $p_{\text{O}_2}=1.25\text{kPa}$, balance Helium. $\dot{v}=200\text{mLmin}^{-1}$ STP, $T=375^{\circ}\text{C}$.

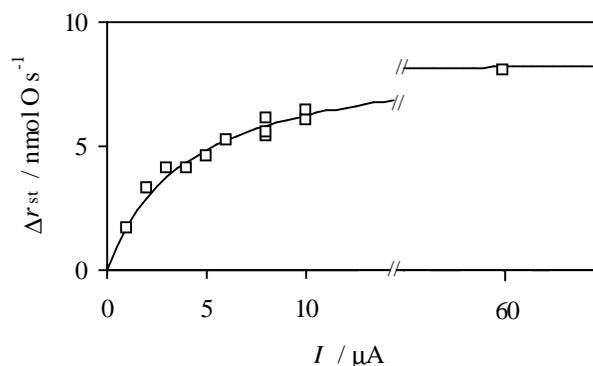


Fig. 2. Plot of the steady-state reaction rate increase, Δr_{st} ($=r_{st}-r_o$), against the anodic polarizing current, I . Experimental conditions as in Fig. 1.

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