Electrochemical promotion of catalysis

Constantinos G Vayenas¹,²*

¹Academy of Athens, Panepistimiou 28 Ave, 10679, Athens, Greece
²University of Patras, Caratheodory 1 St, GR-26504 Patras, Greece

The Electrochemical Promotion of Catalysis (EPOC) or Non-Faradaic Electrochemical Promotion of Catalysis (NEMCA effect) is a phenomenon observed as a reversible change in catalytic rate (i.e. no net charge transfer rate) of a chemical reaction occurring on a catalyst film (or supported dispersed catalyst) deposited on an ionically conducting or mixed electronically-ionically conducting solid electrolyte support upon the application of an electrical potential between the catalyst and a second conductive film deposited on the solid electrolyte support.

The EPOC or NEMCA phenomenon is closely related to the phenomenon of Metal-Support Interactions (MSI) in classical supported nano dispersed catalysts. The MSI phenomenon refers to the different catalytic performances observed when the same metal nanoparticles are dispersed on different supports. An example is given in Figure 1. In fact, in recent years it has become obvious that EPOC and MSI are operationally different but functionally identical phenomena and EPOC has been used to optimize the design and composition of commercial supported catalysts.

Figure 2 shows schematically the setup for EPOC studies of ethylene oxidation [1] while Figure 3 shows an SEM of an Ag-catalyst-electrode deposited on Yttria-stabilized-ZrO₂ (YSZ), an O²⁺ conducting solid electrolyte [1-4].

Figure 1: EPOC (inset) and MSI: Effect of \( p_{O_2} \) on the rate of \( C_2H_4 \) oxidation on Rh supported on five supports of increasing work function \( \Phi \). Catalyst loading 0.05wt%. Inset: Electrochemical promotion of an Rh catalyst film deposited on YSZ. Effect of potentiostatically imposed catalyst potential \( U_{WR} \) on the TOF dependence \( p_{O_2} \). Inset reprinted with permission.

Figure 2: Experimental setup used in NEMCA experiments.

Figure 3: Scanning electron micrographs of an Ag catalyst-electrode deposited on YSZ and used for NEMCA studies (a) Top view (b) Cross section of the Ag/YSZ interface. Reprinted with permission from Academic Press.

Two parameters are commonly used to describe the magnitude of the Electrochemical Promotion of Catalytic reactions (EPOC):

1. The Faradaic efficiency, \( \Lambda \), defined from

\[
\Lambda = \frac{\Delta r}{(1/2F)}
\]
Where $\Delta r$ is the induced change in catalytic reaction rate (in mol O/s) and $I$ denote the applied current. A catalytic reaction is said to exhibit Electrochemical Promotion (EPOC) when $\Lambda > 1$. Faradaic efficiency $\Lambda$ values up to $10^5$ has been measured [2,3].

2. The rate enhancement ratio, $\rho$, defined from

$$\rho = \frac{r_I + \Delta r}{r_0}$$

(2)

Where $r_0$ is the open-circuit catalytic rate, i.e. the rate before current application; $r_I$ is the rate before current application; $\Delta r$ is the induced change in catalytic reaction rate, $\rho$, value up to $10^5$ have been measured [1-8].

A catalytic reaction is termed electrophilic if $\Lambda > 0$, i.e. if the rate increases with positive applied current, i.e. with increasing catalyst potential, $V_{WR}$, with respect to a reference electrode, i.e. $\partial r / \partial V_{WR} > 0$. Examples are given in Figures 1,4. It is termed electrophilic when the opposite holds, i.e. $\Lambda < 0$, thus $\partial r / \partial V_{WR} < 0$. In electrophilic reactions, the electron acceptor reactant (e.g. O$_2$ or O$_2^-$) is more strongly adsorbed on the catalyst surface than the electron donor reactant, e.g. H or C$_2$H$_4$. The opposite holds for electrophilic reactions.

The EPOC phenomenon is closely related to classical (chemical) promotion and to the phenomenon of Metal-Support Interactions (MSI).

EPOC has been described in several books and review articles [7,8] by more than 20 catalytic groups [8] and for more than 200 catalytic reactions [8]. It is now well established that EPOC is due to an electrochemically controlled, via electrical potential application, reversible migration of promoting ionic species from the solid electrolyte support to the gas-exposed catalyst surface.

These promoting species (i.e. O$_2^-$ in the case of O$_2$- conduction supports such as YSZ, Na$^{+}$ in the case of Na$^+$ conducting supports) migrate on the gas-exposed, catalytically active catalyst surface and affect via lateral attractive or repulsive electrostatic interactions the coadsorbed reactants and products.

Figure 4 shows a typical galvanostatic (constant current) transient of C$_2$H$_4$ oxidation on Pt/YSZ.

Catalytic reactions were thus also soon directly grouped in four categories on the basis of the sign of the rate change observed upon positive potential application. Nucleophilic (or electrophobic), electrophilic, volcano-type, and inverted volcano type [6-8]. Simple analytical expressions were derived describing the rate vs work function dependence in excellent agreement with the experiment [6-8].

It was soon realized that the same rules also applied to classical ex-situ promotion and to the phenomenon of MSI and that therefore promotion, electrochemical promotion, and metal-support interactions are fundamentally identical phenomena and only operationally different.

Simple expressions were also derived for time constants of galvanostatic, i.e. fixed applied current, rate transients, and the first multichannel and multiplate EPOC units were designed and built. At the same time, aqueous NEMCA was demonstrated with Pt catalyst electrodes in aqueous alkaline solutions [5].

Current research efforts focus on two main directions: First, the design and testing of larger, simpler, and more efficient multiplate electropromoted units, and second Electrochemical Promotion of monodispersed catalysts.

The latter is more difficult since the particles of fully supported nano dispersed catalysts are already at least partially promoted via ion migration from the support to the surface of the nanoparticles. Such EPOC transients are often quite complex, exhibiting rate and potential spikes. The successful interpretation of such transients and concomitating electroproporation of such catalysts remains both challenging and promising and could lead to practical applications.

**References**


---

https://doi.org/10.29328/journal.aac.1001031

www.advancechemjournal.com


