

## ELECTROCHEMICAL PROMOTION AND METAL-SUPPORT INTERACTIONS

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The origin of the effect of electrochemical promotion (Non-Faradaic electrochemical Modification of Catalytic Activity, NEMCA effect (1)) is discussed in light of recent surface spectroscopic (XPS, UPS, TPD, STM) and electrochemical (AC impedance spectroscopy, cyclic voltammetric) investigations.

It is shown that electrochemical promotion is due to an electrochemical (Faradaic) introduction of promoting ions ( $O^{2-}$ ,  $Na^+$ ,  $H^+$ ) at the catalyst/gas interface where these ions form an effective electrochemical double layer (Fig. 1). Thus it is shown that electrochemical promotion is catalysis in presence of a potential- or current- controlled electrochemical double layer.

It is then shown that the same type of double layer is formed at the metal/gas interface of dispersed nanoparticle catalysts supported on  $ZrO_2$ -,  $CeO_2$ - and  $TiO_2$ - based commercial supports (Fig. 2). The conclusion (based both on kinetic and surface spectroscopic investigations) is that the mechanism of metal-support interactions on these supports is identical to the mechanism of electrochemical promotion, i.e. continuous migration (backspillover) of promoting  $O^{2-}$  ions from the support to the metal/gas interface (2).

### References

1. C.G. Vayenas, M.M. Jaksic, S. Bebelis, and S.G. Neophytides, "The Electrochemical Activation of Catalysis, in *Modern Aspects of Electrochemistry*", J.O.M. Bockris, B.E. Conway, and R.E. White, eds., Kluwer Academic/Plenum Publishers, New York (1996), pp. 57-202.
2. C.G. Vayenas, S. Bebelis, C. Pliangos, S. Brosda, and D. Tsipalakes, "*Electrochemical Activation of Catalysis: Promotion, Electrochemical Promotion and Metal-Support Interactions*", Kluwer/Plenum Press, New York (2002).

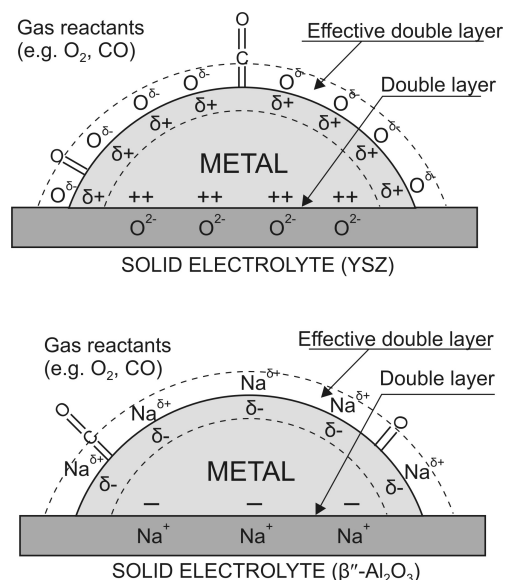


Fig. 1. Schematic representation of a metal electrode deposited on a  $O^{2-}$ -conducting (left) and on a  $Na^+$ -conducting (right) solid electrolyte, showing the location of the metal-electrolyte double layer and of the effective double layer created at the metal/gas interface due to potential-controlled ion migration (backspillover).

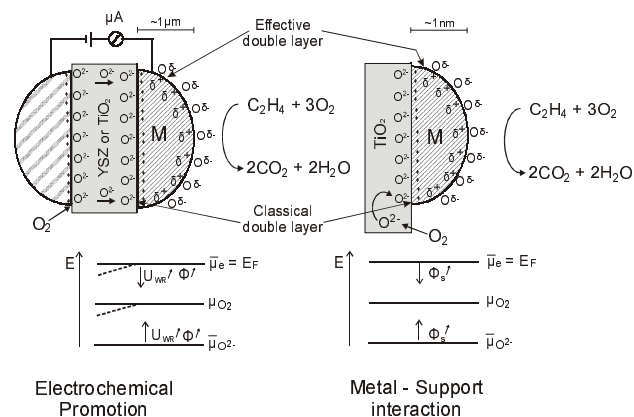


Fig. 2. Schematic of a metal grain ( $\sim\mu\text{m}$ ) in a metal catalyst film deposited on  $YSZ$  or  $TiO_2$  under electrochemical promotion conditions (left) and of a metal nanoparticle ( $\sim\text{nm}$ ) deposited on a porous  $TiO_2$  support showing the locations the classical double layers formed at the metal/support interface and of the effective double layers formed at the metal/gas interface.