

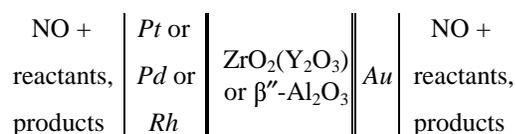
## Electrochemical Promotion of the NO<sub>x</sub> Reduction over Pt, Pd and Rh Catalysts

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During the last fifteen years it has been extensively shown that solid electrolytes can be used to promote the performance of metal or metal-oxide catalysts for a wide variety of catalytic processes, using various combinations of different catalysts, solid electrolytes and catalytic reactions (1). This phenomenon is termed in the literature *Electrochemical Promotion* or *NEMCA effect* (*Non-Faradaic Electrochemical Modification of Catalytic Activity*).

In this communication we summarize the most interesting Electrochemical Promotion studies on NO<sub>x</sub> reduction processes, catalyzed by Rh, Pt or Pd (Table I). These catalytic reactions are very important for the effective removal of nitrogen oxides in the three-way catalytic converters of internal combustion engines, operating under stoichiometric or lean-burn conditions. The catalytic properties can be significantly altered by means of externally applied potentials (or currents) between the catalyst – working electrode and the reference (or counter) electrode, in galvanic cells of the type:



The magnitude of Electrochemical Promotion is given by the Faradaic efficiency,  $\Lambda$ , and the rate enhancement ratio,  $\rho$ , defined from (1,2):

$$\Lambda = \Delta r / (I/2F) \quad ; \quad \rho = r / r^0 \quad [1]$$

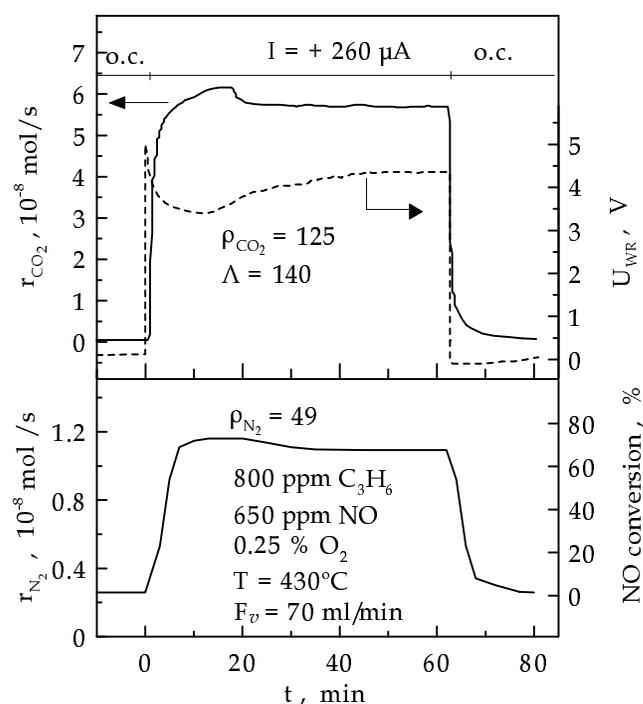
where,  $r$  and  $r^0$  are the electrochemically promoted and the open-circuit (unpromoted) catalytic rate values respectively,  $\Delta r = r - r^0$ , is the electrochemically induced change in catalytic rate,  $I$ , is the applied current and  $F$  is the Faraday constant. In most cases, it was observed that under polarization conditions both the catalytic activity and the product selectivity could be modified in a dramatic way. For instance,  $\Lambda$  and  $\rho$  values as high as  $10^3$  and 150 (or even infinite) have been observed, respectively (3,4). A typical NEMCA experiment is shown in Figure 1 for the case of NO reduction by propene in the presence of oxygen. As shown in this figure an external application of a positive current ( $I=260\mu\text{A}$ ) establishes a new steady-state (within 20 min) on the surface of the Rh catalyst-electrode, corresponding to 12500% and 4900% increases of the catalytic rates of CO<sub>2</sub> and N<sub>2</sub> production, respectively. Similar behavior has been recorded for the majority of the NEMCA studies of the NO<sub>x</sub> reduction reactions. The results presented in this paper show that solid electrolytes act as active catalyst supports, which via the effect of Electrochemical Promotion cause dramatic activity and selectivity enhancement of NO<sub>x</sub> reduction catalysts.

## REFERENCES

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**Table I:** NO<sub>x</sub> reduction processes that have been shown to exhibit the NEMCA effect.

Reactants	Catalyst	Solid electrolyte	$\rho_{\text{max}}$	$\Lambda_{\text{max}}$
C <sub>2</sub> H <sub>4</sub> , NO	Pt	ZrO <sub>2</sub> (Y <sub>2</sub> O <sub>3</sub> )	7	-50
C <sub>2</sub> H <sub>4</sub> , NO	Pt	$\beta''$ -Al <sub>2</sub> O <sub>3</sub>	$\infty$	-
C <sub>3</sub> H <sub>6</sub> , NO	Pt	$\beta''$ -Al <sub>2</sub> O <sub>3</sub>	10	-
CO, NO	Pt	$\beta''$ -Al <sub>2</sub> O <sub>3</sub>	13	-
H <sub>2</sub> , NO	Pt	$\beta''$ -Al <sub>2</sub> O <sub>3</sub>	30	-
C <sub>3</sub> H <sub>6</sub> , NO, O <sub>2</sub>	Rh	ZrO <sub>2</sub> (Y <sub>2</sub> O <sub>3</sub> )	150	1000
CO, NO, O <sub>2</sub>	Rh	ZrO <sub>2</sub> (Y <sub>2</sub> O <sub>3</sub> )	20	20
CO, NO	Pd	ZrO <sub>2</sub> (Y <sub>2</sub> O <sub>3</sub> )	3	-700
CO, N <sub>2</sub> O	Pd	ZrO <sub>2</sub> (Y <sub>2</sub> O <sub>3</sub> )	2	-20



**Figure 1.** C<sub>3</sub>H<sub>6</sub>/NO/O<sub>2</sub> reaction on Rh catalyst-electrodes: Transient effect of the applied current on the catalytic rates of CO<sub>2</sub> and N<sub>2</sub> production, on the NO conversion and on the catalyst potential.