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Milestones and perspectives in electrochemically promoted catalysis

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ABSTRACT

Electrochemical promotion of catalysis is a unique tool for the *in situ* tuning of catalytic activity of electronically conductive metals or metal oxides in contact with solid electrolytes. The importance of electrochemical promotion to heterogeneous catalysis, surface science and electrochemistry research for the investigation of spillover phenomena and metal–support interactions is well recognized. The unlimited applications of the phenomenon, in terms of catalysts, solid electrolytes or catalytic reactions selection, has been proven through numerous laboratory investigations. Though the molecular origin of electrochemical promotion has been revealed, using a variety of experimental techniques and theoretical calculations, there is still a shortage on the practical level. However, in the last decade, spectacular progress has been made in the development of effective, low cost electropromoted catalysts and reactors. The major technological advances and milestones towards the practical utilization of electrochemical promotion are surveyed in view of electrocatalysts development and system/reactor engineering.

1. Introduction

Since the discovery [1] of the effect of non-Faradaic electrochemical modification of catalytic activity (NEMCA effect) or electrochemical promotion of catalysis (EPOC) [2–8] as a tool for controlling the catalytic activity of a catalyst interfaced with a solid electrolyte via electrical current or potential application, EPOC has been observed and investigated for more than 70 catalytic reactions. It is now well established that EPOC is not limited to any particular class of conductive catalysts, solid electrolytes or catalytic reactions [2–4]. Regarding the mechanism of the phenomenon, it is also well established through numerous electrochemical and spectroscopic techniques that EPOC is due to potential-controlled transport of ionic species (e.g. O^{2-}, H^+, Na^+) through the solid electrolyte support and migration of the discharged species to the catalytically active metal/gas interface [2–4,9]. The current understanding of the physicochemical origin of this phenomenon, its limits and obstacles for practical utilization have been reviewed recently [4].

The possibility of application of the NEMCA effect in conventional flow reactors has already been recognized since 1994 [10], as this would foster the ultimate direct utilization of electrochemical promotion in commercial reactors, as those used in the chemical industry and in automotive exhaust catalysis. The latter depends on several technical and economical factors [11] which are intimately related to specific technical considerations and problems, among which two stand out:

1. Moving from low surface area, high materials cost, thick film catalyst structures (state-of-the-art in current laboratory experiments) to electrochemically promotable, nano-scale structures that are sufficiently active, robust and inexpensive so as to be deployed in practical reactors.
2. Devising configurations for thin film or nanoscopically patterned catalyst–electrode structures with efficient current collection and compact design.

These anticipated technical challenges have been the subject of sedulous research in this decade and the latest progress in modeling, materials development and reaction engineering has been impressive pointing out that the main obstacles for practical utilization can be overcome. At the same time, there is also a strong industrial interest and involvement aiming to EPOC commercialization.

The present review discusses a series of critical technological developments in electrochemical promotion studies towards its direct utilization in two areas:

(i) Electrocatalysts development.
(ii) System/reactor engineering.

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2. Results and discussion

2.1. Electrocatalysts development

2.1.1. Electrochemical promotion of classically promoted and commercial catalysts

Most electrochemical promotion studies employ model catalysts, usually noble metals, with low dispersion. Thus, although electropromotion in low activity catalysts is well established there was a concern whether an already active or even classically promoted catalyst could be further promoted electrochemically. In this direction the electropromotion of a "classically" promoted catalyst and of a commercial catalyst were explored.

In the former case, a Rh catalyst film deposited on YSZ electrolyte was classically promoted by depositing on its surface a NaOH solution followed by drying and thorough H_2O evaporation in a classical "dry impregnation" process [12]. The resulting promoted Rh film exhibited a dramatic enhancement in its catalytic performance, compared to the same unpromoted Rh/YSZ film for the reduction of NO by CO in presence of O_2 (Fig. 1). The promoting effect of sodium was an expected result evident from previous electrochemical promotion investigations on Rh films deposited on β''-Al_2O_3, an Na^+ conductor. The main reason is that Na further enhances NO dissociation. The question that arises now is: can one further enhance the performance of this "classically" promoted Rh catalysts by using electrochemical promotion? For that reason, the effect of application of external voltage and the concomitant supply (+1 V) or removal (−1 V) of O^{2-} to or from the promoted Rh surface was examined. The results showed an enhancement in catalytic performance (the light-off temperature is further decreased and the selectivity is further enhanced) under positive potentials and negligible effect under negative polarization (Fig. 1). So, the answer to the question is clear: *one can electrochemically promote an already classically promoted catalyst*. The fact that negative potentials fail to further enhance catalysts performance is not surprising since the effect of negative potentials is equivalent to alkali supply on the catalyst surface, in terms of decrease of catalysts work function. The Rh catalyst was already promoted by the alkali species (Na) and thus already having a low work function can only be marginally affected by negative potential application.

A step forward for the electropromotion of promoted catalysts was realized by Yiokari et al. [13] who attempted to electropromote a commercial catalyst for the NH_3 synthesis. The catalytic synthesis of ammonia from its elements via the Haber–Bosch process is of major industrial importance and the high pressure synthesis is catalyzed by Fe promoted with K_2O, CaO and Al_2O_3. In that study, a commercial fully promoted Fe-based catalyst (supplied by BASF) was used, deposited on $CaZr_{0.9}In_{0.1}O_{3-\alpha}$, a proton conducting solid electrolyte. The catalyst was milled and deposited via a slurry. Since the commercial Fe-based catalyst is electronically conducting, as it is not supported on an insulating support (e.g. SiO_2, Al_2O_3), it was found that this catalyst film deposited on the H^+ conductor had sufficient conductivity to also act as an electrode of the solid electrolyte cell. The reaction was carried out in a high pressure (50 atm) reactor incorporating 24 $CaZr_{0.9}In_{0.1}O_{3-\alpha}$ cell-pellets, electrically connected in parallel (Fig. 2) [13].

The rate of ammonia production was enhanced by more than 1100% in the nitrogen rich regime (Fig. 3), upon potential application of −1 V between the working electrode and the Ag reference electrode. The extent of the NEMCA effect depends strongly on the kinetic regime of the reaction. Very pronounced non-Faradaic behavior is observed in the regime $0.33 \leq H_2/N_2 \leq 0.67$ where ρ values of 12 or more were obtained. The enhancement in the catalytic activity is due to the electrochemical supply of H^+ to the catalyst which decreases the catalyst work function and thus strengthens the chemisorptive bond of electron acceptor N while at the same time weakening the bonds of electron donor H and NH_3. Thus, it was once again confirmed that a promoted, already active, catalyst can be further enhanced by electrochemical promotion.

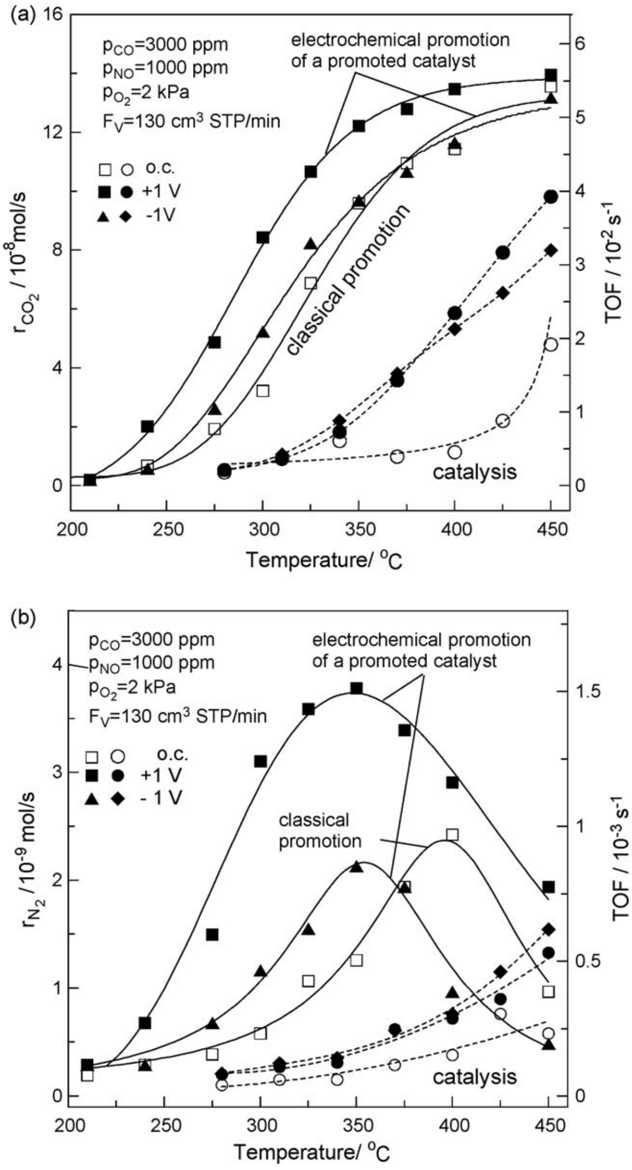

Fig. 1. Catalysis (○), classical promotion (□), electrochemical promotion (●, ◆) and electrochemical promotion of a classically promoted (sodium doped) (■, ▲) Rh catalyst deposited on YSZ during NO reduction by CO in presence of gaseous O_2 [12]. The figure shows the temperature dependence of the catalytic rates and turnover frequencies of CO_2 (a) and N_2 (b) formation under open-circuit (o.c.) conditions and upon application (via a potentiostat) of catalyst potential values, U_{WR}, of +1 and −1 V [12].

2.1.2. Electrochemical promotion with highly dispersed catalysts and sputtered films

A major drawback of typical electrochemical promotion catalysts was the use of thick catalyst films (0.1–5 μm thick) mostly made via paste deposition, leading to poor material utilization (metal dispersion below 0.01%). Practical applications would require the use of thin (on the order of few nm thick) catalyst electrodes or dispersed catalysts.