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The effect of catalyst film thickness on the electrochemical promotion of ethylene oxidation on Pt

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The effect of catalyst film thickness on the magnitude of the effect of electrochemical promotion of catalysis (EPOC or NEMCA effect) was investigated for the model catalytic reaction of C_2H_4 oxidation on porous Pt paste catalyst-electrodes deposited on YSZ. It was found that the catalytic rate enhancement ρ is up to 400 for thinner (0.2 μm) Pt films (40,000% rate enhancement) and gradually decreases to 50 for thicker (1 μm) films. The results are in good qualitative agreement with model predictions describing the diffusion and reaction of the backspillover O^{2-} species which causes electrochemical promotion.

KEY WORDS: electrochemical promotion; NEMCA effect; porous film thickness effect; ethylene oxidation; promotional rules.

1. Introduction

The electrochemical promotion of catalysis (non-Faradaic electrochemical modification of catalytic activity, NEMCA effect) has been already investigated for more than 70 catalytic reactions [1–17]. In electrochemical promotion studies the conductive catalyst is in contact with an ionic conductor and the catalyst is electrochemically promoted by applying a current or potential (± 2 V) between the catalyst film and a counter electrode [1–17].

As shown by numerous surface science and electrochemical techniques [16–21], including STM [19], electropromotion is due to electrochemically controlled migration (reversible backspillover or spillover) of promoting or poisoning ionic species (O^{2-} in the case of YSZ, TiO_2 and CeO_2, Na^+ in the case of β''-Al_2O_3, protons in the case of Nafion) between the ionic or mixed ionic-electronic conductor and the gas-exposed catalyst surface. The electropromoted catalytic rate can be up to 300 times larger than the unpromoted (open-circuit) catalytic rate [16,21] and up to $3 \cdot 10^5$ times larger than the rate I/nF of ion (charge n) backspillover from the ionic support to the catalyst surface [16,17].

The magnitude of electrochemical promotion is usually [15,16] described by two parameters, i.e.

(1) the rate enhancement ratio ρ defined from:

$$\rho = r/r_o \tag{1}$$

where r and r_o are the electropromoted and unpromoted catalytic rate.

(2) The Faradaic efficiency, Λ, defined from:

$$\Lambda = (r - r_o)/(I/2F) \tag{2}$$

2. Experimental

The apparatus used for atmospheric pressure kinetic studies utilizing online gas chromatography (Perkin–Elmer 300B), mass spectrometry (Balzers QMG 311), and IR spectroscopy (Beckman 864 CO_2 analyzer) has been described previously [15,16].

Reactants were Messer Griesheim-certified standards of C_2H_4 in He and O_2 in He. They could be further diluted in ultrapure (99.999%) He (L' Air Liquide).

The atmospheric pressure single-chamber quartz reactor has a volume of 30 cm^3 and has been also described previously [15,16].

The Pt catalyst electrode was deposited on one side of the YSZ disc (Zircoa Zycro 1373 for catalyst A, Ceraflex YSZ for catalyst B) by application of a thin coating of Engelhard Pt paste A-1121 followed by drying and calcination first (3 °C/min) to 450 °C for 1 h and then (2 °C/min) to 830 °C for 1 h. After investigating the catalytic and electropromotion behaviour of the Pt catalyst film, the catalyst deposition procedure was repeated on top of the preexisting Pt film, in order to examine the effect of catalyst film loading and thickness. Metal loadings were also converted to film thicknesses by assuming a 30% Pt film porosity, as inferred from previous SEM studies of similarly deposited films [16]. The Pt catalyst surface area (reactive oxygen uptake) was measured for all catalysts via the galvanostatic transient technique [16] using both the current application and current interruption rate transients.

It was found that the total Pt surface area (expressed in mol O, [16]) is nearly proportional to the film loading and thickness (it varies from 1.6×10^{-8} mol O to 10^{-7} mol O, as the metal loading increases from 0.42 to 1.9 mg/cm^2). This implies that the reaction surface area per unit volume remained nearly constant as the

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thickness was being increased, i.e. the porosity of the Pt film remained practically constant.

Gold counter and reference electrodes were deposited on the opposite side of the YSZ disc by using Engelhard Au paste and following the same calcination procedure as with the Pt catalyst. Constant current or potentials were applied using an AMEL 553 galvanostat–potentiostat.

3. Results and discussion

3.1. Transient electrochemical promotion behaviour

Figure 1 shows transient electropromotion experiments with all five catalysts of series A at 375 °C upon imposing an anodic potential $U_{WR} = 2$ V. (W stands for the catalyst (working electrode) and R for the reference electrode.) The maximum rate enhancement ratio ρ (at near steady-state) is very high, up to 300, for the thinner film, and gradually decreases to 130 for the thicker film. On the other hand, as shown in the Figure caption, the corresponding Λ values increase at steady state from 116 to 289 as the film thickness is increased.

As shown in figure 2 the catalytic rate is enhanced both with positive and negative potentials for all film loadings, i.e. the reaction exhibits inverted volcano behaviour [16]. This is in agreement with the promotional rules of catalysis [16,22–25] which predict inverted volcano behaviour when the rate is positive order in both reactants, as in the present case.

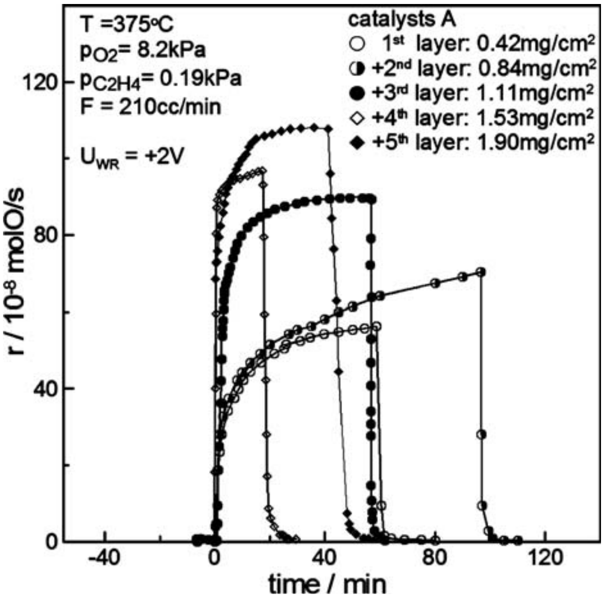

Figure 1. Transient effect of imposed catalyst potential $U_{WR} = 2$ V at $T = 375$ °C on the rate of C_2H_4 oxidation for five catalysts of series A. The steady state current and Λ values for the five catalysts are (I = 928, 921, 834, 758, 714 μA), (Λ = 116, 147, 206, 244, 289), respectively from 1st to 5th layer.

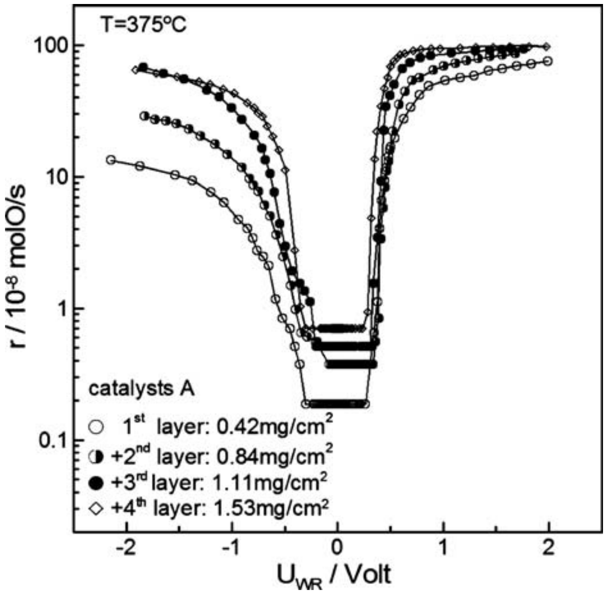

Figure 2. Steady state effect of catalyst potential and metal loading on the rate of C_2H_4 oxidation at $T = 375$ °C for the five catalysts of series A. The corresponding current and Λ values for the maximum high U_{WR} rates are (I = 1.1, 1.1, 0.9, 0.9 mA, Λ = 133, 151, 202, 209), respectively and for the maximum low U_{WR} rates are (I = −0.5, −0.5, −0.6, −0.6 mA, Λ = −51, −111, −217, −207), respectively from 1st to 4th layer.

It is worth noting in figure 2 that the rate versus catalyst potential behaviour is at negative potentials different from that at positive potentials, i.e. larger potential differences (overpotentials) are required to reach the maximum value rates, particularly for lower metal loadings. This may be due to the easier and thus enhanced thermal backspillover of $O^{\delta-}$ (from YSZ to the Pt catalyst) as the film thickness is decreased and the concomitant need of larger overpotentials for electrochemical O^{2-} removal (spillover from Pt into the YSZ support [16]).

It can also be seen from figure 2 that the open-circuit catalytic rates relate linearly to the Pt loading. This shows, that the open-circuit catalytic rates are not subject to external or intra-catalyst (internal) diffusion limitations. In contrast, the NEMCA activated rates, particularly at positive potentials, approach asymptotic values which increase but do not scale linearly with film loading, a strong indication for the onset of intra-catalyst transport limitations.

Figure 3 shows the effect of metal loading and corresponding film thickness on the rate enhancement ratio ρ and Faradaic efficiency Λ. As expected from the O^{2-} reaction-diffusion sacrificial promoter model of electrochemical promotion [26], ρ decreases significantly with film thickness, since the surface concentration of O^{2-} near the gas-exposed top of the porous film decrease significantly due to the reaction with C_2H_4 [16,26]. As also shown in figure 3, the Faradaic efficiency Λ increases moderately with metal loading and film thickness,

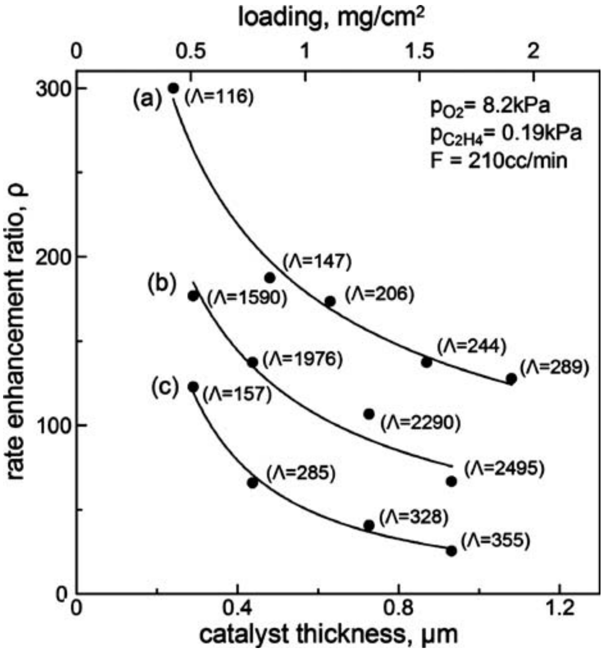

Figure 3. Effect of Pt catalyst loading and corresponding film thickness on the rate enhancement ratio ρ (a) catalysts A, T = 375 °C, U_{WR} = 2 V; (b) catalysts B, T = 280 °C, I = 50 μA; (c) catalysts B, T = 375 °C, I = 350 μA.

which is also in agreement with a key aspect of the theory of electrochemical promotion, i.e. the prediction:

$$\Lambda \approx 2Fr_o/I_0 \tag{3}$$

where r_o is the unpromoted rate and I_0 is the exchange current of the catalyst-support interface [16]. Due to the linear increase in r_o with film thickness and the much weaker dependence of the three-phase boundary length and thus of I_0 on film thickness, one expects a weak increase in Λ with film thickness as observed experimentally (figure 3).

4. Discussion

The present results illustrate the effect of catalyst film thickness on the electrochemical promotion of catalytic oxidation reactions and, also in view of the very good agreement with the theoretical predictions of the promoting sacrificial backspillover O^{2-} reaction-diffusion model, provide a solid confirmation of the sacrificial promoter model of electrochemical promotion [15,16,26].

According to this model [16,26] for first-order catalytic reactions (which is the case here for C_2H_4 oxidation under fuel-lean conditions), the promotional effectiveness factor, η_p, defined from

$$\eta_p = \frac{C_i}{C_{i,\max}} \tag{4}$$

where C_i is the surface concentration of the promoter (O^{2-} in the present case) and $C_{i,\max}$ is its maximum value, is given by:

$$1/\eta_p = 1/J + \Phi_p/\tanh\Phi_p \tag{5}$$

where Φ_p is the promotional Thiele modulus defined as:

$$\Phi_p = L\sqrt{k/D_s} \tag{6}$$

where L is the film thickness, k is the first order kinetic constant of consumption of the promoting species (desorption or reaction with C_2H_4), D_s is the surface diffusivity of O^{2-} and J is a dimensionless current defined by:

$$J = I/(2FkC_{i,\max}L\ell_{tpb}) \tag{7}$$

where ℓ_{tpb} is the three phase-boundary length [16,26].

The rate enhancement ρ value is given by:

$$\rho = \exp(\Pi\eta_p) \tag{8}$$

where [16,26]:

$$\Pi = \frac{\alpha e N_m P_i}{\varepsilon_o k_b T} = \frac{\Delta\Phi}{k_b T} = \frac{e\Delta U_{WR}}{k_b T} \tag{9}$$

is a dimensionless catalyst work function change at fall promoter coverage (N_m is the surface atom concentration, P_i is the promoter dipole moment and ϵ_o is the permeativity of vacuum).

For large Φ_p and J values it follows from equation (5) that:

$$\eta = 1/\Phi_p \tag{10}$$

so that:

$$\rho = \exp(\Pi/\Phi_p) = \exp\left(\Pi\sqrt{\frac{D_s}{k}}/L\right) \tag{11}$$

This equation, i.e.:

$$\ln\rho = \Pi\sqrt{\frac{D_s}{k}}/L \tag{12}$$

is in very good agreement with experiment as shown in figure 4, which is based on the results of figure 3.

The slopes of the semilogarithmic plots vary between 1 and 0.25 μm (figure 4). Since Π at maximum ρ is typically of the order of 10, it follows from equation (11) that

$$\sqrt{\frac{D_s}{k}} \approx 0.059 \text{ to } 0.025\,\mu\text{m}$$

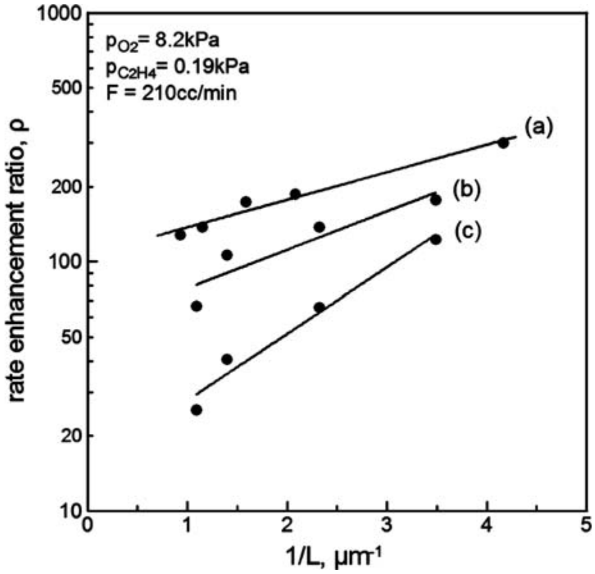

Figure 4. Effect of $1/L$ on the rate enhancement ratio ρ for catalysts A at 375 °C and $U_{WR} = 2$ V (a) and for catalysts B at 280 °C and $I = 50$ μA (b) and at 375 °C and $I = 350$ μA (c).

thus

$$\sqrt{\frac{k}{D_s}} \approx 17 \text{ to } 40\,\mu\text{m}^{-1}$$

Since L varies between 0.3 and 0.9 μm (figure 3) it follows that Φ_p (equation (6)) is between 5 and 44, i.e. always larger than 3, which justifies the approximation made in equation (10).

The experimentally observed linear variation of ln ρ with L^{-1} according to equation (12) provides additional strong support for the above $O^{\delta-}$ promoter reaction-diffusion model and for the sacrificial promoter mechanism of electrochemical promotion.

5. Conclusions

Increasing the thickness of porous catalyst films used in electrochemical promotion studies causes a decrease in the rate enhancement ratio ρ due to the gradual axial decrease from the three-phase-boundaries to the top of the film of the surface concentration of the promoting backspillover O^{2-} species which diffuse and react on the porous catalyst surface. The ρ behaviour is in good agreement with analytical model prediction [16,26] and provides additional support for the sacrificial promoter model of electrochemical promotion.

Acknowledgments

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