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Electrochemical Promotion of Oxidative Coupling of Methane on Platinum/Polybenzimidazole Catalyst

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The electrochemical promotion of catalytic methane oxidation was studied using a (CH₄, O₂, Ar), Pt/polybenzimidazole (PBI)-H₃PO₄/Pt(H₂, Ar) fuel cell at 135°C. It has been found that CH₄, CO₂, and water are the main oxidation products. Without polarization the yield of CH₄ was 0.9% and the yield of CO₂ was 7.3%. This means that C₄ open-circuit selectivity was approximately 11%. Open-circuit voltage was around 0.6 V. It has been shown that the CH₄ → C₂H₂ catalytic reaction can be electrochemically promoted at negative polarization and exhibits a "volcano-type" promotion behavior, meaning that there was a maximum promotion effect at a polarization of −0.15 V, or 0.45 V catalyst potential vs. a hydrogen electrode (3.8% C₂H₂ yield). The catalytic rate enhancement ratio, \( r(C_2)/r_o(C_2) \), at this maximum was 4.2. There was no C₂H₂ production at polarization >0.1 and <−0.3 V. The yield of C₂H₂ decreased with decreasing temperature. Dependence of CO₂ yield on polarization also showed a "volcano-type" behavior with maximum yield of 8.3% at −0.15 V polarization. The catalytic rate enhancement ratio for CO₂ production, \( r(CO_2)/r_o(CO_2) \), at this maximum was 1.1, which means that this catalytic reaction is only slightly affected by the electrochemical polarization. This indicates that polarization especially affects the C₂ selectivity of the catalyst. The obtained data was explained by the electrochemical production of Pt-H active centers at the electrolyte-catalyst-gaseous reactant interface (\( \lambda \gg 1 \)). © 2002 The Electrochemical Society. [DOI: 10.1149/1.1504455] All rights reserved.

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\[ \eta = \Delta \Phi \]  

It was also suggested that this change in the work function is caused by spillover of the products of the charge transfer from the three-phase boundary to the catalyst-gas interface. The change in the work function was measured using the Kelvin probe technique.¹⁻⁶

However, it was found later⁹⁻¹¹ that the work function change of catalysts with different morphology, measured by the use of a Kelvin probe, may be only a part of the applied polarization⁹,¹⁰ or does not change at all.¹¹ Summarizing the results of Ref. 4-6 and 9-11, one can agree with the assumption of Metcalfe¹⁰ that

\[ \Delta \Phi = \xi \eta \]  

where \( \xi \) is a coefficient. Furthermore, one can also assume \( 0 \leq \xi \leq 1 \).

It is known that the electrochemical potential of an electron in a metal \( \mu_e \) (Fermi level) is a sum of the chemical potential of the electron in the metal \( \mu_e \) and \( \phi_e \), where \( \phi \) is the inner or Galvani potential. The Galvani potential is a sum of an outer (or Volta) potential \( \Psi \) and a surface potential \( \chi \). The work function of the electron, \( e \Delta \Phi \), is equal to the electrochemical potential of uncharged metal (\( \Psi = 0 \)), i.e.

\[ \Delta \Phi = \Delta \mu + \Delta \chi \]  

and \( \Delta \Psi \neq 0 \) is the reason for the difference between \( \Delta \Phi \) and \( \eta \) (Eq. 4).

Taking into account the considerations described and the published data on the electrochemical promotion,²⁻¹⁴ we can define three types of electrochemical promotion depending on values of the faradaic current (I) and \( \lambda \):

1. The electrochemical promotion effect is the charge-induced (electrostatic) change of the strength of chemisorptive bonds at the catalyst-reactant interface (CI-effect). The CI-effect is characterized by \( I = 0 \). Charging of the electric double layer at the catalyst-support interface is the only result of the polarization of the catalyst. \( \Delta \Psi \neq 0 \) and \( \Delta \Phi \neq \eta \).

2. The electrochemical promotion effect is induced by the electrochemical production of the catalyst promoters (EPP-effect). \( I \neq 0; \lambda \gg 1; \Delta \Psi \approx 0 \); and \( \Delta \Phi \approx \eta \).

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The case of electrocatalysis is when reactant (or reactants) of a catalytic reaction are oxidized or reduced electrochemically. $I \neq 0$, $\lambda = 1$.

The CI-effect usually plays an important role in the electrochemical promotion of homogeneous catalytic reactions using non-catalytic electrodes. Most of the published cases of electrochemical catalytic reaction are oxidized or reduced electrochemically.

In the present research the electrochemical promotion of catalytic methane oxidation was studied using a new alternative to the $\text{CH}_4$-$\text{CO}_2$ route for the catalytic reaction through the electrochemical production of $\text{H}_2$-Pt active centers, i.e., using the EPP-effect.

The $\text{PBI-H}_3\text{PO}_4$ electrolyte was chosen because it is stable at temperatures higher than 100°C, at which CO poisoning of the Pt catalyst is of little importance.

**Experimental**

The setup for study of electrochemical promotion of the catalytic methane oxidation is given in Fig. 1. A carbon-supported Pt catalyst with Pt load around 0.5 mg/cm² was used in the present investigation. The morphology of the catalyst and the structure of the three-phase (Pt-electrolyte-gas) boundary are given in Fig. 2.

The $\text{PBI-H}_3\text{PO}_4$ electrolyte was chosen because it is stable at temperatures higher than 100°C, at which CO poisoning of the Pt catalyst is of little importance.

3. The aim of this study was to create electrochemically a new alternative to the $\text{CH}_4$-$\text{CO}_2$ route for the catalytic reaction through the electrochemical production of $\text{H}_2$-Pt active centers, i.e., using the EPP-effect.

The $\text{PBI-H}_3\text{PO}_4$ electrolyte was chosen because it is stable at temperatures higher than 100°C, at which CO poisoning of the Pt catalyst is of little importance.

**Results and Discussion**

The results of the investigation of the electrochemical promotion of the catalytic methane oxidation are given in Fig. 3-7.

It has been found that $\text{C}_2\text{H}_2$, $\text{CO}_2$, and water are the main oxidation products. Without polarization the yield of $\text{C}_2\text{H}_2$ was 0.9% (Fig. 3) and the yield of $\text{CO}_2$ was 7.3% (Fig. 4). This means that $\text{C}_2$ open-circuit selectivity was approximately 11%. The open-circuit voltage (OCV) was around 0.6 V. The reactions are assumed to be

\[
\text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} \quad [6]
\]

\[
2\text{CH}_4 + 3/2 \text{O}_2 \rightarrow \text{C}_2\text{H}_2 + 3\text{H}_2\text{O} \quad [7]
\]

The oxidative coupling of methane (OCM) is a relatively widely studied catalytic reaction. However, in most OCM cases the major products are $\text{C}_2\text{H}_4$, $\text{C}_2\text{H}_2$, and $\text{CO}_2$. It is also known that direct pyrolysis of methane to acetylene takes place at temperatures close to 2000°C with 30% methane conversion. An alternative route for direct conversion of methane into acetylene can be made through the activation in a two-stage burner by a hydrogen/oxygen flame. Thus, in an alumina reactor, acetylene can be produced from the preheated (700°C) $\text{CH}_4$/O$_2$/H$_2$ gaseous mixture with a yield of ~17%. It was found in a recent investigation that the plasma catalytic conversion of methane produces acetylene with high selectivity and yield under atmospheric pressure in the temperature range 70-500°C. The highest yield of $\text{C}_2$ hydrocarbons (about 20% $\text{C}_2$ yield and more than 85% selectivity toward acetylene) was obtained in the hydrogen-containing plasma. Lower temperature favors the formation of acetylene, while no acetylene is formed at higher temperatures (more than 300°C).
It can be concluded that the presence of hydrogen in the reactant mixture at low temperature increases the C₂H₂ yield of OCM. Therefore, the most probable explanation of the unusual CH₄ → C₂H₂ conversion in the present study is based on proton conductivity of the Pt catalyst support. It can be assumed that there is an H⁺ = H_ads equilibrium at the three-phase boundary of the catalyst, and this equilibrium is a source of the H_ads active centers for the CH₄ catalytic reaction.

Dependence of the C₂H₂ yield on polarization is given in Fig. 3. It can be seen that the CH₄ → C₂H₂ catalytic reaction can be electrochemically promoted at negative polarization and exhibits a clear “volcano-type” promotion behavior. This means that there is a maximum promotion effect at a polarization of ~0.15 V, or 0.45 V catalyst potential vs. the hydrogen electrode (3.8% C₂H₂ yield). The catalytic rate enhancement ratio, r(C₂)/r₀(C₂) (Ref. 4), at this maximum is 4.2. It can also be seen from Fig. 3 that there is no C₂H₂ production at polarizations ≥0.1 V and ≤~0.3 V. The yield of C₂H₂ decreases with decreasing temperature. The value of λ calculated for the case of maximum promotion effect was 7.9 × 10³, i.e., λ ≫ 1. This means that the electrochemical promotion for the CH₄-C₂H₂ route has an EPP nature.

Dependence of CO₂ yield on polarization is given in Fig. 4. This dependence also shows a volcano-type behavior with maximum yield of 8.3% at ~0.15 V, i.e., at the same potential as for C₂H₂ production. The catalytic rate enhancement ratio for CO₂ production, r(CO₂)/r₀(CO₂), at this maximum is 1.1, which means that this catalytic reaction is only slightly affected by the electrochemical polarization. This also means that the polarization affects the C₂ selectivity more than the CO₂ selectivity. Figure 5 shows the “volcanic” nature of the dependence of the ratio between r(C₂) and r(CO₂) + r(CO₂) with a maximum at ~0.2 V. Similar to the C₂H₂ path, CO₂ production is inhibited at very positive and very negative polarizations and decreases with a temperature decrease from 135 to 100°C (Fig. 4). The value of λ calculated for the case of maximum promotion effect was 2.7 × 10³, i.e., λ ≫ 1, meaning that the electrochemical promotion for the CH₄-CO₂ route (as in the case of the CH₂-C₂H₂ route) has an EPP nature.

The same potential of maximum promotion for both C₂H₂ and CO₂ paths shows that polarization probably has the same effect on the rate-determining stages of these paths. It would therefore be useful to review the published data on electrochemical conversion of methane. Since the 1960s there have been many publications on the electrocatalytic oxidation of methane in connection with the development of phosphoric acid fuel cells. This reaction was mainly studied on platinum and platinum group metal catalysts. In most of the studied cases there was a complete electrocatalytic oxidation of methane to CO₂. It has been shown that the rate-determining step of this reaction is dissociative chemisorption of methane at the catalyst-electrolyte interface. Moreover, it has been found that on a Pt-black catalyst in 4.3 M HClO₃ at 65°C the maximum amount of methane is adsorbed at 0.3 V vs. the standard hydrogen electrode (SHE).

The only studied electrochemical system that provided the oxidative coupling of methane was a high-temperature fuel cell with zirconia-based solid electrolytes. The effect of polarization on the oxidative methane coupling in the CH₄-O₂/Ag/YSZ/Pt/O₂ fuel cell at 800°C was studied by Seinanides and Stoukides. They have shown that “oxygen pumping” at positive polarization promotes methane conversion to CO₂ and that negative polarization slightly promotes the OCM to C₂H₂ and C₂H₆, therefore promoting C₂ selectivity.

In order to explain similarities and differences in the electrochemical promotion of methane conversion in CH₄-O₂/Pt/PBI-H₃PO₄/Pt, H₂ and CH₄-O₂/Ag/YSZ/Pt/O₂ fuel cell systems we should compare the open-circuit potentials of the Pt and Ag catalysts in these systems. In the present study for the Pt catalyst it was 0.6 V vs. the hydrogen electrode and in Ref. 24 it was...
0.45 V vs. the oxygen electrode, i.e., approximately 0.6-0.8 V against the hydrogen electrode. Considering the value of the potential of the maximum CH₄ adsorption, i.e., 0.3 V vs. SHE, the catalyst potentials in both fuel cells should be moved in the negative direction in order to achieve this maximum. The data obtained in this work on OCM and C₂ selectivity is in agreement with this assumption. Moreover, the much stronger promotion effect in the CH₄, O₂/Pt/PBI-H₃PO₄/Pt, H₂ system can be explained on the basis of the difference in the current carriers in this system and the CH₄, O₂/Ag/YSZ/Pt/O₂ fuel cell, protons and oxide ions, respectively.

A steady-state voltammetric curve obtained at the Pt catalyst (curve 1) and C₂H₂ yield vs. polarization dependence (curve 2) are given in Fig. 6. It can be seen that the polarization range of the C₂H₂ production (0.3-0.6 V vs. the hydrogen electrode) is the potential range of the reduction wave Red₁ of this wave has a limiting current density of the maximum CH₄ adsorption, against the hydrogen electrode. Considering the value of the potential of the maximum CH₄ adsorption, i.e., 0.3 V vs. SHE, the catalyst potentials in both fuel cells should be moved in the negative direction in order to achieve this maximum. The data obtained in this work on OCM and C₂ selectivity is in agreement with this assumption. Moreover, the much stronger promotion effect in the CH₄, O₂/Pt/PBI-H₃PO₄/Pt, H₂ system can be explained on the basis of the difference in the current carriers in this system and the CH₄, O₂/Ag/YSZ/Pt/O₂ fuel cell, protons and oxide ions, respectively.

The combination of the maximum CH₄ adsorption and electrochemical production of Pt-H active sites in the Pt-H active sites (in the same potential region), which stabilize C₂ products, can provide a strong promotion effect at the CH₄, O₂/Pt/PBI-H₃PO₄ boundary. In the case of the CH₄, O₂/Ag/YSZ/Pt/O₂ fuel cell, this effect is much weaker because of the absence of the proton current carriers in the solid electrolyte.

It was found that electrochemical conversion of CH₄ into CO₂ proceeds through the formation of the so-called O-type products of the dissociative adsorption of methane, i.e., ≡COH, ≡CHO. This means that in this case parameters of the oxygen adsorption should play an important role in the kinetics of the methane conversion. Positive polarization of the Ag catalyst probably provides the optimum potential for the oxygen adsorption at the catalyst-gas interface.

The experimental data is in good agreement with our assumption about the EPP nature of the electrochemical promotion in the CH₄, O₂/Pt/PBI-H₃PO₄/Pt, H₂ system. It is also in agreement with the assumption that through the reversible electrochemical production of Pt-H sites we can create a new OCM route for catalytic CH₄ oxidation.

The experimental data given in Fig. 7 are also in agreement with the assumption about the EPP nature of the production of C₂H₂. Reversibility of the H⁺ ⇌ H_ads electrochemical reaction means that this reaction proceeds under diffusion control. Therefore, by changing the H⁺ concentration gradient across the PBI electrolyte, we should affect the H⁺ diffusion rate and in this way the electrochemical H⁺ reduction rate and the rate of OCM. As can be seen from Fig. 7, the zero hydrogen pressure at the counter electrode, which should provide a lower H⁺ concentration gradient across the electrolyte, also provides a weaker promotion effect on the methane conversion into C₂H₂.

**Conclusions**

The possibility of creation of a new OCV route for catalytic CH₄ oxidation by the electrochemical production of Pt-H centers at the Pt-PBI(H₃PO₄)-gas boundary has been demonstrated.

It was shown that Pt catalyst activity and selectivity toward the CH₄ → C₂H₂ reaction can be electrochemically promoted with the maximum promotion effect at ~0.15 V.

The nature of electrochemical promotion was discussed. The conclusion was made that there are three different types of electrochemical promotion depending on values of faradaic current (I) and λ.

1. The electrochemical promotion effect is the charge-induced (electrostatic) change of the strength of chemisorption bonds at the catalyst-reactant interface (CI-effect). The CI-effect is characterized by I = 0. Charging of the electric double layer at the catalyst-support interface is the only result of the polarization of the catalyst. ∆Ψ ≠ 0 and ∆ΔΨ ≠ η.

2. The electrochemical promotion effect is induced by the electrochemical production of the catalyst promoters (EPP-effect). I ≠ 0; λ ≈ 1; ∆Ψ ≈ 0, and ∆ΔΨ ≈ η.

3. The case of electrocatalysis is when reactant (or reactants) of a catalytic reaction is oxidized or reduced electrochemically. I ≠ 0, λ ≈ 1.

The EPP nature of the electrochemical promotion of the CH₄ → C₂H₂ catalytic reaction was demonstrated (λ ≈ 1).
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