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Propanol oxidation on the Pt/RuO_2 electrodes in alkaline solutions

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Abstract: The propanol oxidation has been studied on catalysts Pt/RuO_2. The electrocatalysts on titanium substrate was formed in the form of thin coating by thermal procedure. The catalytic activity has been revealed through the recording the cyclic voltammograms and polarization and chronocemperometric curves of the oxidation of 1- and 2-propanol in an alkaline anvironment. The rate of propanol oxidation on Pt/RuO_2 is strongly enhanced. A catalysts with a RuO_2 concentration from 40 mol% to 80 mol% RuO_2 were found to be the most active surface for propanol oxidation. Such systems form the so-colled bifunctional catalysts, where Pt facilitates fast adsorption and dehydrogenation. Ru forms oxigencontaing species at lower (0,5V) potentials than Pt. These species are effective in the oxidation of strongly adsorbed intermediaries. The activity of Pt/RuO_2 electrodes toward the electrooxidation of propanol is a balance of the primarily concentration-dependent rate of the dissociative chemisorption of propanol and the potential dependent oxidation rate of intermediaries accumulated on the surface during sustained propanol oxidation.

Key words: propanol, electrochemical oxidation, catalyst, electrode, platinum, catalytic activity.

Introduction

About 85 % of the world's energy today is obtained from fossil fuels. However, the reserves of these fuels are limited. During the process of the production of energy from fossil fuels in thermal power plants toxic substances polluting the human environment are released. The energy obtained by fission of heavy elements in nuclear reactors is relatively cheap, but accidents in nuclear power plants can have catastrophic consequences. The storage of nuclear wastes is also a big problem. Renewable hydroelectric resources are almost maximally used today. Rapid industry development imposes the need for new energy

sources. New renewable energy sources are the future of energetics. Solar energy and biomass are likely to become main energy sources in the near future. Owing to its vast potential, its being economical and to low pollution of the human environment during its exploitation, biomass is considered to be a major renewable energy source. By the year 2050 biomass will have covered 38% of energetic fuels requirements and about 17 % of electric energy needs. The usability of biomass and its place in the energetic system at today's level of scientific and technological development have drawn attention of scientists and energeticists throughout the world. Various solid, liquid and gaseous fuels can be obtained from biomass. Alcohols can be produced at relatively low cost from biomass by fermentation. Simple alcohols, thus produced, are potential fuels in fuel cells due to their being relatively cheap and easily stored (1-5).

Fuel cells are electrochemical reactors where a fuel's chemical energy is directly converted into electrical energy. The development of fuel cells is mostly conditioned by the development of a catalyst of high catalytic activity and corrosive stability.

The electrochemical oxidation of simple alcohols CH_3OH, C_2H_5OH and C_3H_7OH is mostly studied on a pure platinum electrode. The initial activity of Pt for oxidation is high, but it rapidly decreases over time. The mechanism of the electrochemical oxidation of simple alcohols is still not completely clear. The reaction begins with the adsorption of alcohol followed by its dehydrogenation and the formation of strongly adsorbed intermediates. The formed strongly adsorbed intermediates block the catalyst surface thus preventing adsorption and dehydrogenation of new molecules. The high initial catalytic activity of the electrode thus rapidly decreases. The strongly adsorbed species produced by the oxidation of CH_3OH, CH_2O and HCOOH is most likely CO_{ad} (6-9). The strongly bound intermediates are oxidized by oxy species formed on neighbouring Pt atoms. The reaction on pure platinum is slow because the coverage of Pt by oxy species is small in the potential range important for fuel cells.

The modification of Pt by Ru resulted in the obtainment of an alloy with better catalytic activity for the electrochemical oxidation of small organic molecules (10-16). The Pt and Ru alloy is a bifunctional catalyst. Rapid adsorption and dehydrogenation are performed on Pt atoms of the alloy. On Ru atoms oxy species are formed at more negative potentials than on Pt. These oxy species on Ru atoms at more negative potentials oxidize strongly bound intermediates on neighbouring Pt atoms causing a higher catalytic effect of the Pt/Ru alloy than pure Pt. Nevertheless, the advantage of the alloy over pure Pt quickly disappears because Ru is relatively easily extracted from the alloy. Metal is more slowly dissolved from many oxide structures than from pure metal. Dissolution of Ru from RuO_2 rutile is slower than from pure metal Ru.

The aim of this paper was therefore to thermally develop a thin catalytic film from metal Pt and RuO_2 crystals mixtures on titanium substrate and to examine its catalytic activity for the electrochemical oxidation of 1- and 2-propanol in an alkaline envrionment.

Experimental

Titanium substrate was activated for the electrochemical oxidation of propanol, by thermal formation of polycrystal film of metal Pt and RuO_2 (17-19). The solutions H_2PtCl_6 and $RuCl_3$ in 2-propanol at 10 mg cm^{-3} concentration based on the pure metals were spread over adequately prepared titanium plates their surface area being 2 cm^2. By adjusting the ratio H_2PtCl_6: $RuCl_3$ in the solution, the coatings of desired composition were obtained. Following evaporation of the solvent the electrodes were heated at 450°C in the airy atmosphere. The procedure was repeated five times until the coating depth of 15 gm^{-2} based on the pure metals was reached. After the spreading of the last layer, the electrodes were heated for 60 minutes at 500°C (17-19).

The electrochemical measurements were carried out with the usual electrical set-up consisting of a programmer with a potentiostat (RDE 3 POTENTIOSTAT Pine Instrument Co., Grove City, Pennsylvania), an x-y recorder (Hewlet Packard 7035B) and a digital voltmetre (Pro's Kit 039303C). The experiments were conducted in a standard electrochemical cell with a separate part for the reference electrode. The solutions were prepared by dissolving the reagent of the r.a. degree of purity in triply distilled water. Just prior to the electrochemical measurements, oxygen was removed from the solution by the introduction of nitrogen that was first purified by passing over molecular sieves and copper shavings.

Results and discussion

By a thermal procedure thin films of Pt and RuO_2 crystal mixture are formed on a titanium substrate. Adherent coatings with good mechanical properties are obtained. By an X-ray analysis it has been determined that the coatings consist of a mixture of fine crystals of metal platinum and RuO_2 the size of a crystal grain being 10-40 nm (17-19). The electrochemical behaviour of the formed coatings in an alkaline environment has been established by recording polarization, potentiodynamic and chronoamperometric curves.

Figure 1 presents cyclic voltammograms for electrodes of different composition recorded in 1.0 $moldm^{-3}$ KOH. Cyclic voltammogram for a thermally formed platinum coating on the titanium substrate (full line) corresponds to the voltammogram for massive platinum. The potentials of current maximums of hydrogen adsorption and desorption, the potential of current maximum of oxide reduction and potential of the onset of oxide formation have equal values for both massive platinum and thermally formed platinum coating on the titanium substrate. The facts mentioned indicate that the energetic condition of surface platinum atoms on the thermally formed platinum coating does not considerably differ from the energetic condition of the surface atoms of the massive platinum electrode. On a voltammogram for 100 mol% RuO_2 there are no clearly visible current peaks for hydrogen adsorption and formation of oxy species at potentials between the hydrogen and oxygen evolution potentials. With the increase of the RuO_2 concentration in Pt/RuO_2 coatings clearly differentiated peaks gradually disappear. Hydrogen adsorption on Ru atoms on the coatings

containing not only Pt but also RuO_2 takes place immediately following the oxy species reduction. Simultaneously with hydrogen desorption oxy species are formed on surface Ru atoms. The figure shows that on Ru atoms the oxy species are formed at potentials by about 0.50 V more negative than on platinum. The overlapping of hydrogen desorption current and oxy species formation current makes it difficult to determine the potential at which oxidation of Ru atoms begins. From the cyclic voltammograms it can be observed that with an increase of the RuO_2 concentration in the active coating the number of oxy species on the electrode surface formed at potentials by about 0.5 V more negative than on pure platinum is increased. This significantly affects the rate of the electrochemical oxidation of propanol. Figure 2 presents cyclic voltammograms for 100 mol% Pt and 20 mol% Pt, 80 mol% RuO_2 in alkaline solution containing 1-propanol. As seen from figure 2, oxidation of 1-propanol on 20mol% Pt and 80 mol% RuO_2 commences at more negative potentials than on pure Pt. This indicates that Pt/RuO_2 electrode has higher catalytic activity than pure Pt. Catalytic effect depends on the potential value and is more prominent at more negative potentials. Potentiodynamic curves for 2-propanol oxidation from alkaline solution 1.0 $moldm^{-3}$ KOH on Pt/RuO_2 electrodes of different composition show that the electrodes with RuO_2 concentrations ranging from 40 to 80 mol% have the highest catalytic activity. The potentiodynamic curves for the oxidation of 1- and 2-propanol on Pt/RuO_2 electrodes in alkaline environment show that 2-propanol is more easily electrochemically oxidized. Similar results are obtained from the polarized curves shown in figure 3. The curves were recorded after the electrode had spent 10 minutes at -0.8 V (v.s. SCE) and 3.0 minutes at a desired potential. During the ten-minute stay of the electrode at -0.8 V (v.s. SCE) balanced coverage with the adsorbed intermediaries is established and then during the three-minute stay of the electrode at the desired potential, steady-state is established. From figure 3 it can be noticed that the electrodes with the concentration of RuO_2 ranging from 40 to 80 mol% RuO_2 have a far higher catalytic activity for the propanol oxidation reaction than both thermally formed platinum and massive platinum. Based upon experimental data the cause of the catalytic effect of electrooxidation of 1- and 2-propanol on the Pt/RuO_2 electrodes can be assumed. Propanol adsorption and dehydrogenation, with the formation of strongly adsorbed intermediaries, is performed only on Pt atoms. These processes take place far more rapidly than intermediaries oxidation, which is confirmed by the experiment conducted as follows. The platinum electrode stays 30 seconds at potential E=0.0 V v.s. SCE. At this relatively positive potential all strongly bound particles are oxidized. Potential is then abruptly shifted to -0.4 V v.s. SCE (this potential is in the initial potential range of the polarized curves recording, figure 3). High initial current decreases over time and reaches stationary value after twenty minutes. During the propanol oxidation on pure platinum, current decreases more than one hundred times, which is conditioned by slow oxidation and accumulation of strongly bound species. The rate of propanol oxidation on pure platinum is determined by the oxidation of these species with coadsorbed oxygen containing species. The same experiments have been also conducted with Pt/RuO_2 electrodes. The experiments have shown that the decrease of the initial current to stationary value is reversely proportional

to RuO_2 concentrations in the coating. At RuO_2 concentrations in the coating higher than 60 % initial current is not considerably different from the steady one.

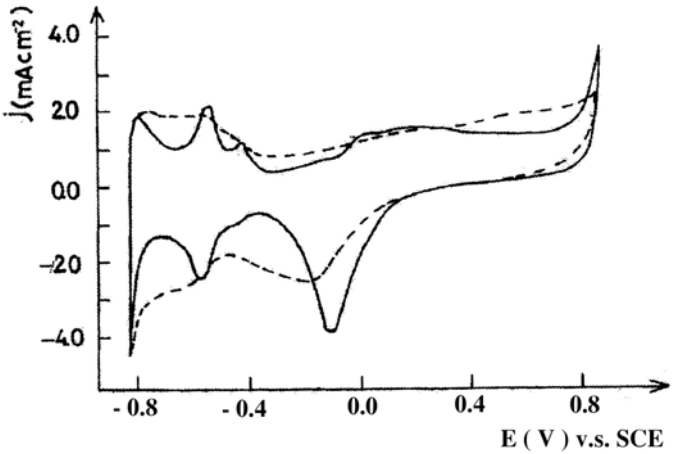

Figure 1. Cyclic voltammograms for the electrodes: (—)100 mol.% Pt, (---) 20 mol. % Pt, 80 mol. % Ru in 1.0 moldm^{-3} KOH. Sweep rate: 100 mVs^{-1}, t = 25 °C.

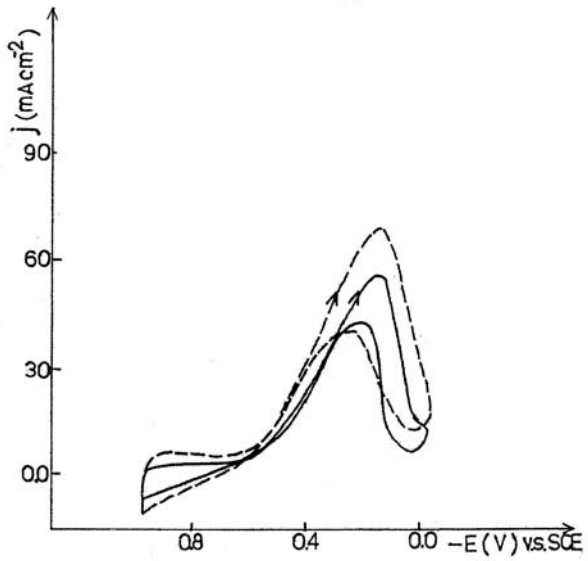

Figure 2. Cyclic voltammograms for the electrodes: (—)100 mol.% Pt, (---) 20 mol. % Pt, 80 mol. % Ru in 1.0 moldm^{-3} KOH, 1.0 moldm^{-3} 1-propanol. Sweep rate: 100 mVs^{-1}, t = 25 °C.

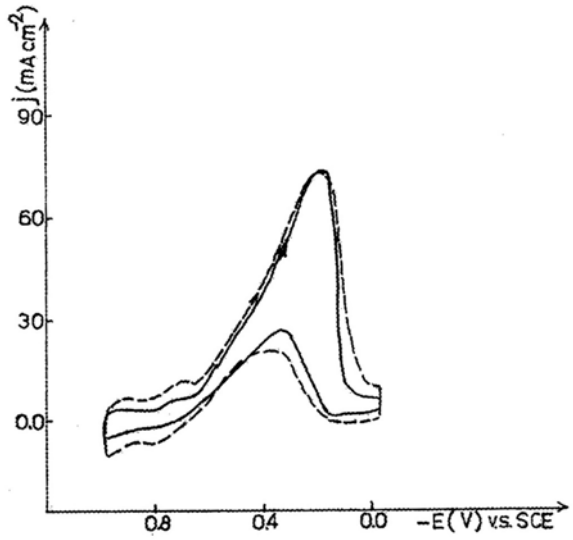

Figure 3. Cyclic voltammograms for the electrodes: (—)100 mol.% Pt, (---) 20 mol. % Pt, 80 mol. % Ru in 1.0 moldm^{-3} KOH, 1.0 moldm^{-3} 2- propanol. Sweep rate: 100 mVs^{-1}, t = 25 °C.

The oxy species are formed at more negative potentials on Ru than on pure platinum. The oxy species formed at more negative potentials than those formed on Pt react with the strongly bound intermediaries on Pt. By facilitating the reaction of oxidation of these intermediaries the surface of Pt is released for the adsorption and dehydrogenation of new propanol molecules. At Ru concentrations higher than optimal there are enough oxy particles for an immediately oxidation of all the strongly bound intermediaries formed. Therefore, at concentrations of Ru higher than optimal, the rate of propanol oxidation is determined by dehydrogenation. With an increase of Ru concentrations, at concentrations of Ru higher than optimal, the share of Pt atoms in the active film and the number of available propanol adsorption and dehydrogenation sites are decreased. This results in the decrease of the total propanol oxidation current. Maximum catalytic effect is reached at Ru concentrations providing the equality of propanol dehydrogenation and strongly adsorbed intermediaries oxidation rates. In order to determine the accuracy of the explanation of the catalytic effect of propanol oxidation on Pt/RuO_2 electrodes, the dependence of the degree of electrode coverage by strongly bound intermediaries on the coating composition is experimentally examined. The experiment has been conducted as follows. The electrodes stay for 20 minutes at potential -0.8 V v.s. SCE in the solution of 1.0 moldm^{-3} KOH + 1.0 moldm^{-3} propanol. Within the 20 minutes balanced coverage by adsorbed organic intermediaries is established. The solution containing propanol is then replaced by the basic electrolyte (1.0 moldm^{-3} KOH), following which potentiodynamic curves are recorded. On cyclic voltammogram, as regards pure Pt, current peak in the potential range of -0.55 to -0.2 V is observed. The peak is caused by the

oxidation of strongly adsorbed intermediaries remaining on platinum electrode after the replacement of the solution. With an increase of Ru concentration in the coating the peak is decreased and shifted to more negative potentials. At Ru concentrations higher than 60 mol% the peak disappears. This indicates that on electrodes rich in Ru (the concentration of Ru being higher than 60 mol %) strongly adsorbed intermediaries do not develop. The results obtained confirm the accuracy of the suggested catalytic effect mechanism.

Conclusion

By thermal procedure active coatings of metal Pt and RuO_2 mixtures have been formed on a titanium substrate. The obtained catalyst has higher catalytic activity than pure Pt for the propanol oxidation reaction in an alkaline environment. The highest catalytic activity is observed in the coatings with the RuO_2 concentrations varying from 40 to 80 mol%. The catalytic effect is explained by bifunctional properties of the catalyst. Rapid adsorption and deydrogenation of propanol is performed on Pt atoms with the formation of strongly bound intermediaries. The oxidation of these intermediaries with oxy species on Pt atoms is a slow stage in the reaction mechanism of the electrochemical oxidation of propanol on pure Pt. However, on Ru atoms the oxy species are formed at about 0.5 V more negative potentials than on Pt. The oxy species on Ru atoms oxidize the strongly bound intermediaries on neighboring Pt atoms thus releasing Pt surface for the adsorption and dehydrogenation of successive propanol molecules. Maximum catalytic effect is reached at the concentrations of Ru providing the equality of propanol hydrogenation rate and the rate of strongly bound intermediaries oxidation.

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OKSIDACIJA PROPANOLA NA Pt/RuO_2 ELEKTRODAMA U ALKALNOJ SREDINI

- originalni naučni rad -

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Rezime

Termičkim postupkom na podesno pripremljenoj titanskoj osnovi formiran je tanak film od fine smeše kristala, veličine od 10 do 40 nm, metalne platine i dioksida rutenijuma. Dobijeni katalizator ima veći katalitiččki efekat od čiste Pt za reakciju oksidacije propanola u alkalnoj sredini. Najveću katalitičku aktivnost imaju prevlake koje sadrže od 40 do 80 mol % RuO_2. Katalitički efekat se objašnjava bifunkcionalnim svojstvom katalizatora. Na Pt atomima se odvija brza adsorpcija i dehidrogenizacija propanola uz formiranje čvrsto adsorbovanih intermedijera. Oksidacija ovih intermedijera sa oksi-česticama na Pt atomima je spori stupanj umehanizmu oksidacije propanola na čistoj Pt. Međutim na modifikovanom Pt/RuO_2 katalizatoru, oksi čestice se na Ru atomima formiraju na 0,5 V negativnijim potencijalima nego na Pt atomima. Ove oksi čestice na Ru atomima oksiduju čvrsto vezane intermedijere adsorbovane na susednim Pt atomima i tako oslobađaju površinu Pt za adsorpciju i dehidrogenizaciju sledećih molekula propanola. Maksimalni katalitički efekat imaju elektrode sa takvim sadržajem RuO_2 koji obezbeđuje izjednačenu brzinu dehidrogenizacije propanola sa brzinom oksidacije čvrsto vezanih intermedijera.