EXTENDED ABSTRACT

The kinetics and mechanism of methanol oxidation on Pt and PtRu catalysts in alkaline and acid media*

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Abstract: The kinetic of methanol electrochemical oxidation for a series of platinum and platinum–ruthenium catalysts was investigated. A correlation between the beginning of OH_{ad} adsorption and methanol oxidation was demonstarated on Pt single crystals and Pt nanocatalyst. The activity of the nano-structured Pt catalyst was compared with single crystal platinum electrodes assuming the Kinoshita model of nanoparticles. The ruthenium-containing catalysts shifted the onset of methanol oxidation to more negative potentials. The effect was more pronounced in acid than in alkaline media. Based on the established diagnostic criteria, the reaction between CO_{ad} and OH_{ad} species according to the Langmuir–Hinshelwood mechanism was proposed as the rate determining step in alkaline and acid media on Pt and PtRu catalysts.

Keywords: methanol oxidation, role of anions, temperature effect, reaction mechanism.

Electrochemical oxidation of methanol is the topic of fundamental research representing the prototype of the oxidation of small organic molecules as well as being applicable to research in the scope of direct methanol fuel cells. The reaction of methanol electro-oxidation on Pt involves several adsorption steps, including the formation of chemisorbed species leading to a decrease in the catalytic activity of the electrode surface. Scientific discussions were focused on the nature of the intermediates and the reaction products[1–8] and on the modification of the platinum surface in order to improve its catalytic activity and sensitivity regarding poisoning species.[9–12] CO_{ad} species were detected as the adsorbed intermediates acting as poisoning species at lower potentials or reactive intermediates in the presence of OH_{ad} species, which were also proposed as participants in the oxidation reaction.[2,11,13,14] OH_{ad} species originate from the discharge of OH^- anions in alkaline solution or from the dissociation of H_2O mole-

cule in acid solution. Ru is mostly used as a promoter of Pt surfaces, in the form of Ru_{ad} on Pt or as PtRu alloys with different ratios of Ru to Pt. The effect of PtRu catalysts was described by the bifunctional mechanism,[9] when Ru promotes the oxidation of strongly bond CO_{ad} on Pt sites by supplying the oxygen source at lower potentials compared to pure Pt, or by the ligand effect,[12] when Ru changes the electronic properties of the surface and weakens the binding strength of CO_{ad}.

Methanol oxidation was investigated on Pt single crystals, polycrystalline Pt and supported platinum catalyst (Pt/C) and at two types of PtRu materials, *i.e.*, polycrystalline Pt modified with Ru adatoms in the process of electrochemical deposition (Pt/Ru) and a supported catalyst (PtRu/C). The reaction kinetics were investigated in alkaline and in acid media from the viewpoint of the influence of anion, pH and temperature. The reaction parameters were established and the rate determining step is suggested.

The quality of the electrode surfaces and the purity of the system were tested for Pt single crystal surfaces, polycrystalline Pt and a Pt/Ru electrode using cyclic voltammetry. In the case of the Pt/Ru electrode, this method enables the determination of the Ru surface coverage on polycrystalline Pt.[9] The nanocatalyst layer was also characterized by cyclic voltammetry in order to determine the reproducibility of the deposition and, in the case of the Pt/C catalyst, to define the real surface area and the particle diameter. The particle diameter was confirmed using physical methods (XRD and STM). The XRD measurements besides the average crystallite size, allow the phase composition to be determined, which for the Pt/C catalyst was one Pt phase and for PtRu/C two phases, *i.e.*, a solid solution of Ru in Pt and the hexagonal phase of Ru. The STM method was used for the determination of the topography of the electrodes. Analysis of STM images for the Pt/C and PtRu/C catalysts showed the almost spherical shape of the nanoparticles and their relatively uniform distribution on the carbon support. The obtained results are in accordance with TEM measurements.[15]

According to all the available results regarding methanol oxidation, the presence of OH_{ad} species at the electrode surface is necessary for this reaction. Linear extrapolation of the charging curve, which represents the dependence of the charge for the adsorption of oxygen containing species on potential, enables an estimation of the potential for the incipient formation of OH_{ad} species and the potential for oxide formation.[16] According to this method, which was applied for each Pt electrode, the adsorption of OH_{ad} species begins in the hydrogen region at the same potential in both the NaOH and $HClO_4$ solutions. In these solutions, oxide formation also commences at the same potential. These facts indicate that the ClO_4^- anions do not interfere with the adsorption of OH_{ad} species and oxide formation, while in H_2SO_4 solution the anions from the supporting electrolyte shift these processes to more positive potentials.

Based on the linear extrapolation method and on potentiodynamic measurements, a correlation between the beginning of the adsorption of OH_{ad} species and methanol oxidation was established for all the investigated Pt electrodes. The reaction commences at potentials close to the onset of OH adsorption, while the maximum of the methanol oxidation rate corresponds to the transition of oxygen species from the reversible to irreversible state. The activity of the investigated electrodes for the oxidation of methanol in alkaline solution was almost one order of magnitude larger than in acid solution. The significant effect of pH on the rate of methanol oxidation was explained by the pH dependent adsorption of OH_{ad} species.

The effect of anions on methanol oxidation was examined in $HClO_4$ and H_2SO_4 solutions. Although the sulfate anions from the H_2SO_4 supporting electrolyte suppress the rate of methanol oxidation, they do not influence the reaction path.

The investigation of methanol oxidation on single crystal platinum surfaces showed the structural dependence of the reaction. The difference in the activities of single crystal platinum electrodes can be explained by the different surface coverage with OH_{ad} species. The Pt/C catalyst is described by the Kinoshita model as cubooctahedral particles consisting of (111) and (110) oriented facets with low coordinated (110) edge and corner sites.[17] The obtained results showed that Pt/C catalyst closely obey the activities of (111) and (110) surfaces. In alkaline solution, the activity increase in the sequence (111) < (110) ≈ Pt/C < (332), while in acid solution the activity increase in the sequence (110) < Pt/C < (111).

Comparison of the activities of Pt and PtRu bimetallic electrodes shows a promoted methanol oxidation on the PtRu electrodes, since the Ru sites nucleate oxygen containing species at lower potentials, shifting the onset of the reaction to more negative potentials. The shift of the initial potential of the reaction between Pt and PtRu electrodes is larger in acid solutions. In alkaline solutions, Pt atoms adsorbed OH_{ad} species at as low potentials as does Ru, hence Ru atoms are not the only source of oxygen species. Consequently, the role of Ru as a donor of oxygen species in alkaline solutions is not as remarkable as in acid solutions. At higher potentials, the Ru sites influence the Pt atoms to form irreversible oxygen species, thus decreasing the activity of bimetallic electrodes.

The similarities in the structure of the Pt/Ru and PtRu/C catalysts results in the qualitatively same behavior of these catalysts regarding the initial potential of reaction and the Tafel slope.

Increasing the temperature shifted the onset of methanol oxidation to more negative potentials with the supported platinum and platinum ruthenium catalysts. The reaction rate was much higher at evaluated temperatures. According to the quasi–steady state measurements at three different temperatures in alkaline and acid solutions, the apparent activation energies for the methanol oxidation reaction were established for both supported catalysts.

On the basis of the determined diagnostics criteria, such as Tafel slope, transfer coefficient, reaction order with respect to methanol, OH^- ions in alkaline so-

lution and H$^+$ ions in acid solution, the reaction between CO$_{ad}$ and OH$_{ad}$ species according to the Langmuir–Hinshelwood mechanism was suggested as the rate determining step in the overall methanol oxidation reaction on supported Pt and PtRu catalysts.

И З В О Д

КИНЕТИКА И МЕХАНИЗАМ ОКСИДАЦИЈЕ МЕТАНОЛА НА Pt И PtRu КАТАЛИЗАТОРИМА У АЛКАЛНОЈ И КИСЕЛОЈ СРЕДИНИ

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Кинетика електрохемијске оксидације метанола је испитивана на низу катализатора од платине и платине−рутенијума. Показана је веза између почетка адсорпције OH$_{ad}$ честица и почетка оксидације метанола. Утврђено је да се наноструктурни Pt катализатор по активности може поредити са монокристалима платине, што је у складу са усвојеним моделом по коме се активност Pt нанокатализатора може повезати са уделима нискоиндексних равни на површини наночестице. Показано је да оксидација метанола почиње на негативнијим потенцијалима на катализаторима који садрже рутенијум, при чему је тај ефекат израженији у киселој него у алкалној средини. Испитиван је утицај pH, анјона и температуре, одређени су кинетички параметри, а за спори ступањ у оксидацији метанола предложена је реакција честица CO$_{ad}$ и OH$_{ad}$ према Ленгмир–Хиншелвудовом механизму.

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