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Preparation of noble metal supported carbon electrodes using photochemically reduced heteropolyanions in composite films

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Abstract

A novel reduction technique is developed for preparing a Pt/C system using organic–inorganic nanocomposite consisting of heteropolyanions. Transmission electron microscopic studies revealed the formation of anisotropic platinum nanocrystals. Cyclic voltammetry and electrochemical impedance spectroscopy were employed to evaluate the electrochemical methanol oxidation over the prepared Pt/C electrode. The effects of supporting electrolyte and temperature on the electrochemical oxidation of methanol were studied. The obtained Pt/C catalysts were found to exhibit higher activity and stability for methanol oxidation in perchloric acid than in sulphuric acid medium. The activation energy for methanol oxidation was found to be $41 \pm 3\,\mathrm{kJ\,mol^{-1}}$, being lower than the reported value. The lower activation energy for methanol oxidation on Pt/C could be attributed to the presence of anisotropic platinum nanoparticles. The described method is simple and elegant and can also be applied to the preparation of other noble metal supported catalysts.
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Keywords: Polyoxometalates; Methanol oxidation; Impedance spectroscopy; Anisotropic platinum nanoparticles; Organic–inorganic composite film

1. Introduction

Catalytic activity of supported systems essentially depends on the dispersion of the active component on the inert support. The effective utilization of supported active components, such as noble metals, can be achieved only if the active metals are dispersed on a nanometer scale with the required shape, size and geometry [1]. There have been various attempts in literature to generate these nanoparticles of active components on a variety of supports [2–5]. Many variations on the conventional methods of impregnating precursors of the active components to support and subsequent reduction of the precursors have been proposed in the literature. In a recent publication, Lizcano-Valbuena et al. have described one of these procedures for obtaining effective Pt-Ru catalysts supported on carbon using formic acid as a reducing agent [6]. Similar procedures have been employed for obtaining high dispersion of metal supported on carbon using a variety of reducing agents [7]. By using reducing agents in homogeneous medium, one could not effectively control the shape, size and preferential formation of certain crystallographic orientation of the active metal components on the supports, in spite of the fact that certain crystallographic planes of noble metals are effective in catalyzing the reactions [8,9]. In order to control, at least the size of the active particles formed on supports, novel synthetic strategies and reduction methods have been developed, such as the use of surfactant, protective agent [10,11], polymer sol–gel process [12], photoreduction technique [13] and sonochemical reduction of metal ions [14], in addition to the conventional reduction methods using a variety of chemical reducing agents.

Polyoxometalates (POMs) are well-defined metal–oxygen cluster anions [15–17]. The redox chemistry of POM is versatile and it undergoes stepwise reduction photochemically, electrochemically or by γ-radiolysis. Reduced polyoxometalates have been employed as reducing and stabilizing media for the preparation of various metal nanoparticles [18–20]. Recently, Keggin ions have been employed as UV-switchable

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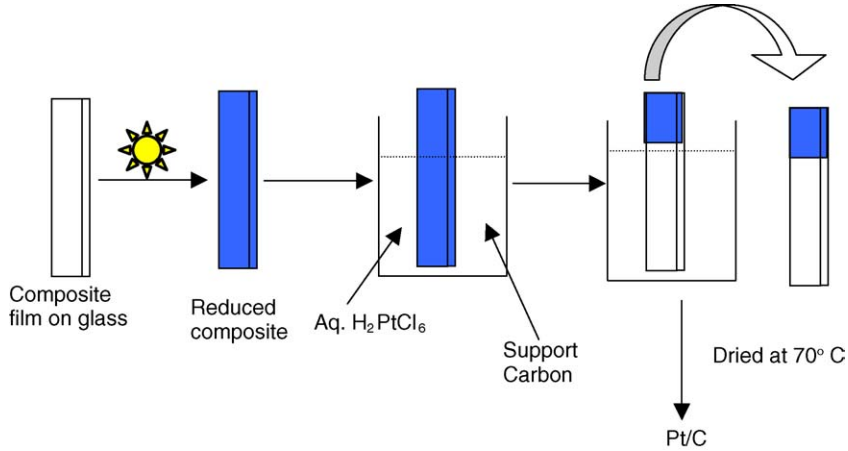

Scheme 1. Preparation of Pt/C supported catalyst.

reducing agents for the synthesis of Au–Ag core–shell nanoparticles [21]. Supported metal systems are normally prepared by using metal ion precursors such as chloroplatinic acid (H_2PtCl_6) for Pt and $RuCl_3$ for Ru and after these ionic species are loaded on the support, the anchored or hooked up metal ions are reduced to the zero valent state by hydrogen at high temperatures or by using suitable reducing agents, such as formaldehyde, hydrazine and hydroxyl amine. Some of the limitations of the conventional methods are: (i) in the hydrogen reduction method, usually high temperatures have to be employed (around 400 °C), and hence it leads to agglomeration of the metal particles. If the particle sizes were in the range of 2–5 nm, metal dispersions can be high, and hence the activity of the resulting systems can be expected to be high. (ii) When formaldehyde is employed as a reducing agent, its lower equilibrium limitation restricts the extent of metal reduction. This means that all the metal ion precursors could not be reduced to the metallic state, and hence the effective utilization of the loaded noble metal will be hampered. The method proposed in this paper overcomes both these limitations, and also has other advantage of the easy removal of the reducing agent from the medium.

The aim of this paper is (i) to describe an alternative reduction technique for the preparation of noble metal supported carbon, (ii) to use it as an electrocatalyst for methanol oxidation and (iii) to study the effects of supporting electrolyte as well as temperature on the methanol oxidation.

2. Experimental

2.1. Composite synthesis

The organic–inorganic composite was prepared by the sol–gel method [22–24]. For a typical synthesis, 1.50 g of polyvinyl alcohol (72,000) was dissolved in 30 ml of distilled water and 2.50 ml of tetraethylorthosilicate (TEOS) was added to the above solution and the mixture was stirred for 10 min. A 0.50 g of silicotungstic acid was then added and refluxed at 70 °C for 6 h. The gel obtained was coated on a glass plate and exposed to sunlight for 10–30 min. This resulted in the formation of reduced heteropolyacid as evidenced by the color change from colorless to blue.

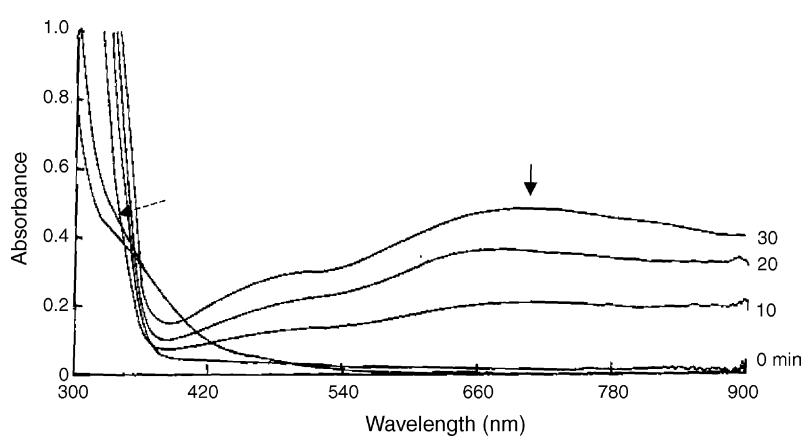

Fig. 1. UV–vis spectra of the reoxidation of reduced composite and the formation of platinum nanoparticles. A broken arrow indicates the formation of Pt colloids, solid arrow indicates reoxidation of $[SiW_{12}O_{40}]^{5-}$.

2.2. Instrumentation

UV–vis spectra were obtained by a Perkin-Elmer Lamda 17 spectrophotometer. Transmission electron microscopy (TEM) images were taken using a Philips CM12/STEM equipment. TEM sampling grids were prepared by placing 2 μl of the solution on a carbon-coated grid and the solution was evaporated at room temperature. Cyclic voltammetric measurements were carried out by using a BAS Epsilon potentiostat with three electrodes system. All measurements were carried out with Ag/AgCl (satd KCl) as a reference electrode. Electrochemical impedance measurements were carried out by using a PARSTAT 2263 instrument and spectra were recorded in the frequency range of 100 kHz–100 mHz by using a sinusoidal excitation signal (single sine) with an excitation amplitude of 5 mV. A mixture containing 10 mg of Pt/C catalyst powder and 1 ml of distilled water was ultrasonicated for 20 min and 10 μl of dispersion was placed on glassy carbon, which was dried at 80 °C for 2 min, and then 5 μl of 5 wt% Nafion® solution was spread on the active layer and dried in air for 5 min. The cell was purged with nitrogen for 15 min prior to electrochemical measurements.

2.3. Preparation of metal supported catalyst

The reduced composite film was employed to reduce the metal precursors and after certain time, the composite was reoxidised (colorless) and the metal ions were reduced to the zero valent state. In a typical experiment, the composite film was placed in a medium containing 10 ml of 5 mM H_2PtCl_6 solution and 50 mg Vulcan XC 72 carbon for 30 min. Reduction of metal ions and reoxidation of polyoxometalates were monitored through UV–vis spectroscopy. Typical preparation of metal supported carbon is given in Scheme 1.

3. Results and discussion

3.1. Formation and characterization of platinum nanoparticles

The formation of platinum nanoparticles and reoxidation of active component in the composite can be seen from the UV–vis spectra (Fig. 1). The absorption band around 750 nm is due to reduced POM present in the composite [20]. When the reduced composite film is dipped into chloroplatinic acid solution, the band at 750 nm slowly disappeared with time and a new band appeared at 340 nm, due to the formation of platinum nanoparticles.

In order to assess the shape and size of the metallic particles, electron micrographs and electron diffraction patterns were recorded (Fig. 2). It is seen from the micrographs that the formation of platinum nanoparticles are facile in the initial stages and the individual particles aggregate into bigger clusters leading to anisotropic structures. Beck et al. have reported a controlled growth of palladium particles at the solid–liquid interface on silica [25]. The formation of anisotropic platinum nanocrystals at the solid–liquid interface indicates that the growth is highly localized, thus leading to considerable growth of the crystals away from the interface, forming nanoparticles of triangular, hexagonal, pentagonal, square, fused pentagonal and star like particles as evidenced from the TEM image (Fig. 2a). High crystallinity of platinum nanocrystals was confirmed by selected-area electron diffraction measurements (Fig. 2b). A hexagonal diffraction spot pattern indicates that the Pt nanocrystals are growing along the [1 1 1] crystal plane. The particles of different morpholo-

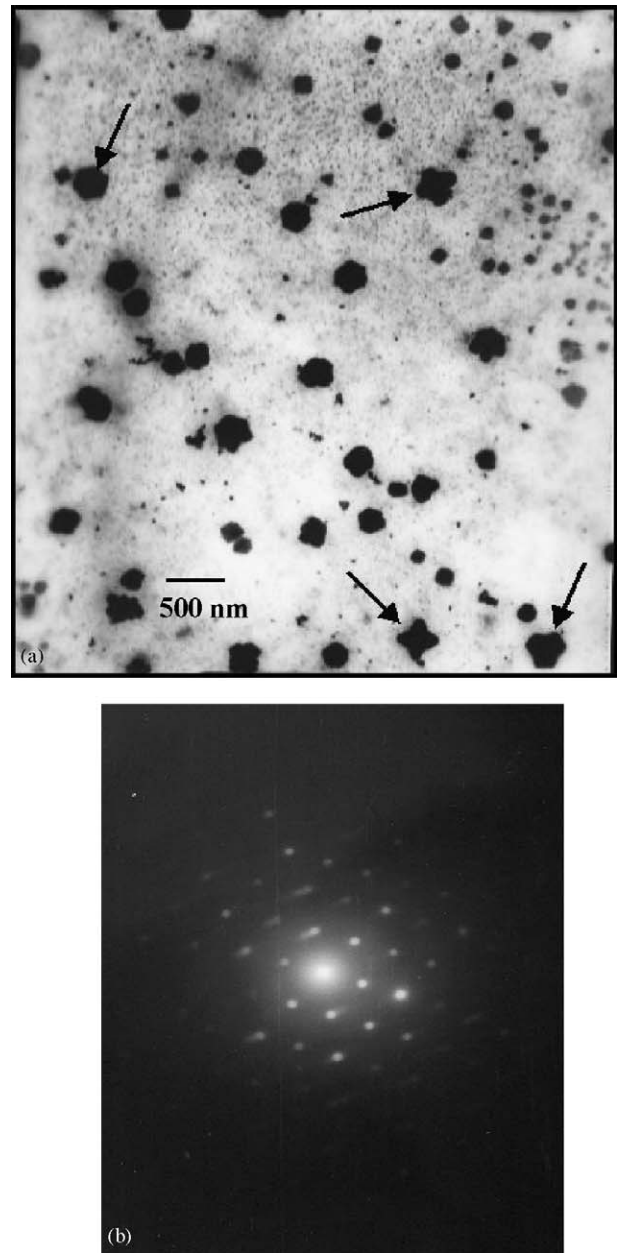

Fig. 2. (a) Transmission electron micrograph of Pt sol prepared by composite reduction method; arrows indicate the formation of anisotropic Pt nanocrystals. (b) Electron diffraction pattern of Pt nanocrystals.

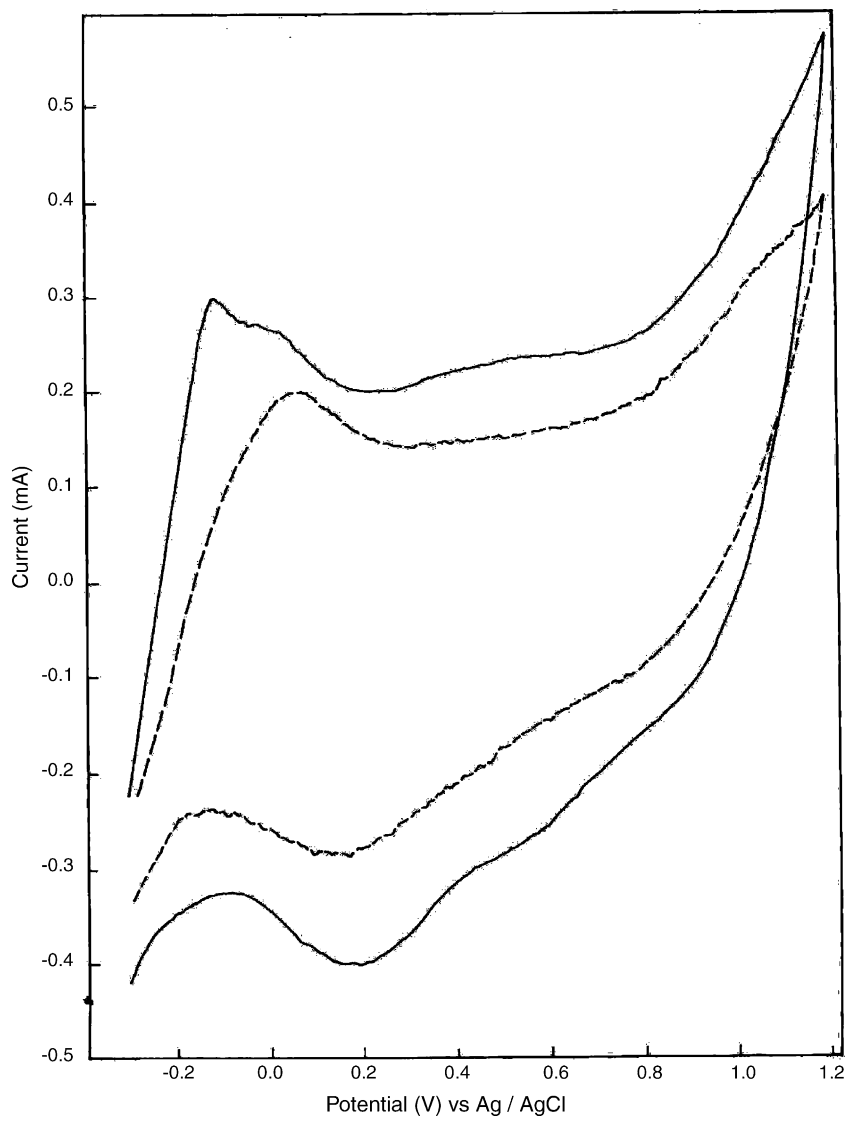

Fig. 3. Cyclic voltammograms of Pt/C in 0.5 M $HClO_4$ (—) and 1 M H_2SO_4 (- - -), scan rate: 25 mV s^{-1}; Pt loading: 28 μg cm^{-2}.

gies formed initially aggregate to give particles of specific shapes. The mechanism and growth process of metallic particles revealed by the reduction technique adopted in this study appear to give rise to specific morphology, which can exhibit interesting surface properties.

3.2. Electrochemical studies

3.2.1. Cyclic voltammetric studies

The cyclic voltammograms of 2 wt% Pt/C observed in 1 M sulphuric acid and 0.5 M perchloric acid are shown in Fig. 3. It is evident from the cyclic voltammograms that the hydrogen adsorption and desorption currents are higher in perchloric acid than in sulphuric acid. And also, double layer charging current (potential range 0.2–0.5 V) is higher in perchloric acid than in sulphuric acid. This may be due to strong adsorption of SO_4^{2-} ions on the platinum surface sites. This feature has been interpreted as due to adsorption of OH^- ions from H_2O [26,27].

The cyclic voltammograms of 1 M methanol in 1 M sulphuric acid and 0.5 M perchloric acid are shown in Fig. 4. The methanol oxidation onset potential of ∼0.06 V is lower in perchloric acid than in sulphuric acid solution. The anodic and cathodic peak potentials, in perchloric acid medium, are found to be 0.84 and 0.52 V, respectively, whereas the same take place at 0.84 and 0.45 V in H_2SO_4 medium. It is evident from Fig. 4 that the methanol oxidation activity is higher in perchloric acid than in sulphuric acid. The influence of the nature of the supporting electrolyte was rationalized in terms of an inhibiting effect caused by the specific adsorption of anions [28–30].

It has been reported that methanol undergoes dissociative adsorption during oxidation leading to the formation of a series of adsorbed carboxyl intermediates, such as $(CH_xO)_{ad}$

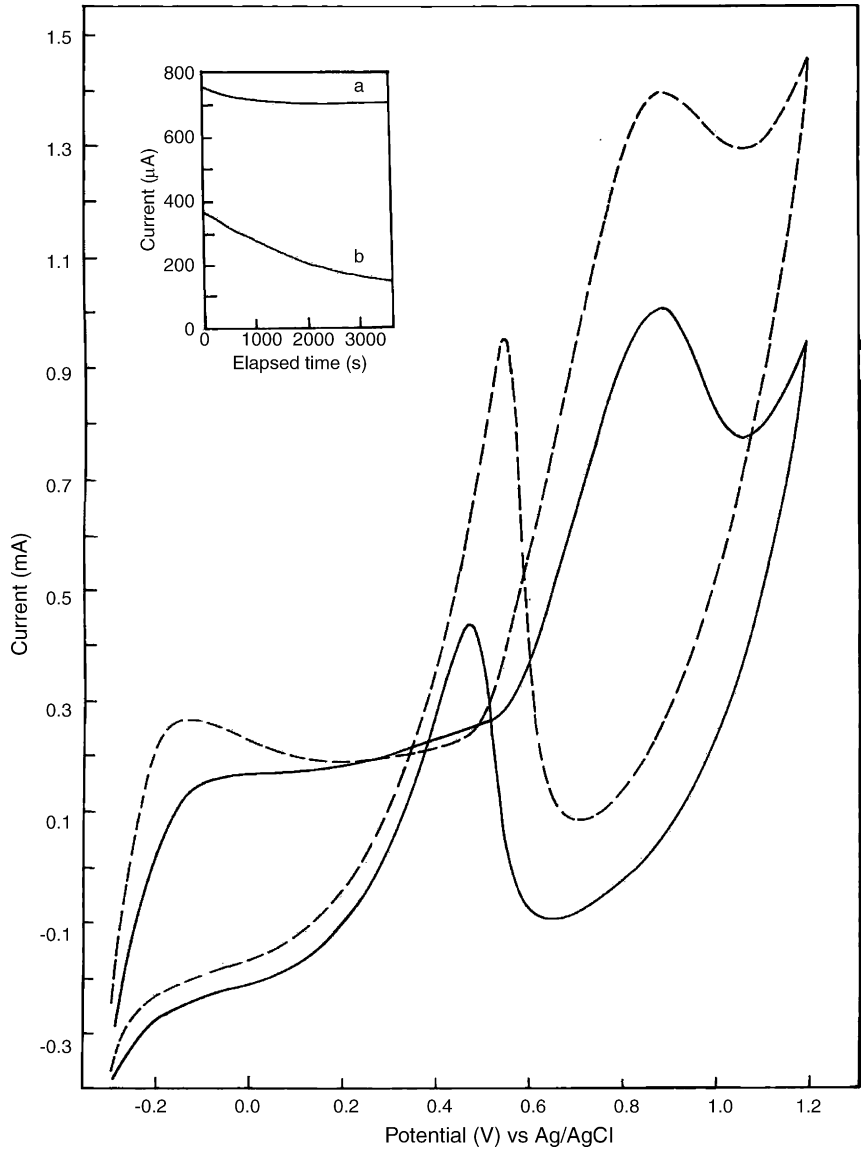

Fig. 4. Cyclic voltammograms for methanol oxidation in 0.5 M $HClO_4$ (- - -) and 1 M H_2SO_4 (—); 1 M, methanol, scan rate: 25 mV s^{-1}; inset chronoamperometric response of Pt/C in different electrolytes: (a) 0.5 M $HClO_4$ and (b) 1 M H_2SO_4; polarization potential: 0.6 V; Pt loading: 28 μg cm^{-2}.

($x = 1$–3), together with the formation of strongly bound adsorbed CO species. The lower methanol oxidation activity in sulphuric acid can be attributed to the competing adsorption of SO_4^{2-} ions in addition to methanol adsorption. The decrease in the current in the presence of adsorbed SO_4^{2-} ions is due to the strong adsorption of SO_4^{2-}, which inhibits the adsorption of methanol [28].

Methanol is adsorbed on the platinum surface followed by the dehydrogenation of the adsorbed species at lower potentials. As evidenced from Fig. 4 the onset of methanol oxidation shifts negatively by 0.06 V for perchloric acid. This suggests that the dehydrogenation of the adsorbed species is facile, as it is taking place at lower potential, and this catalytic reaction leads to the rapid removal of the adsorbed hydrogen atoms from the platinum surface. Inset of Fig. 4 shows the chronoamperometric response of methanol oxidation over Pt/C prepared by the composite reduction method in different supporting electrolytes. It is clear from the inset, the current decay rate is higher in sulphuric acid, suggesting that the poisoning of the electrode might have occurred due to the adsorption of sulphate ions on the platinum surface sites, thus blocking the adsorption of methanol as well as the dehydrogenation of adsorbed species. On the other hand, in perchloric acid, there is a gradual decay in current and the decrease in the catalytic activity is found to be around 6.6% at the end of 1 h compared to 55.5% in sulphuric acid. This demonstrates the effect of electrolyte on the activity and the stability of the electrode. Another interesting observation is that though the initial activity in $HClO_4$ is found to be only two times higher than in sulphuric acid, the activity at the end of 1 h is found to be nearly four times higher.

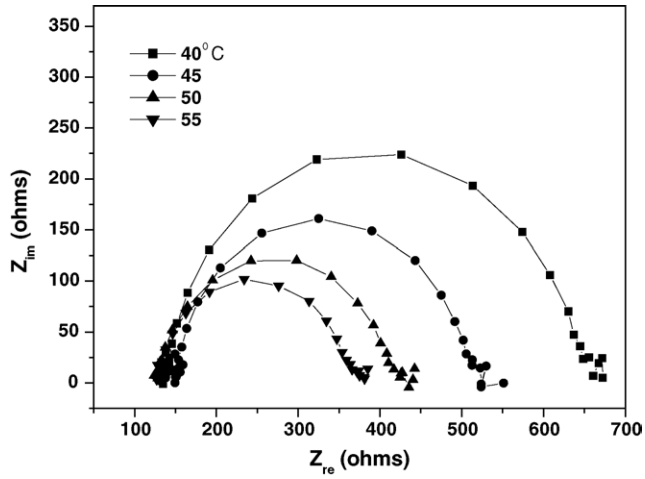

Fig. 5. Nyquist plots for methanol oxidation on Pt/C at different temperatures, Methanol concentration 1 M; 1 M H_2SO_4; polarization potential: 0.6 V; frequency: 100 kHz–100 mHz; Pt loading: 28 $\mu g\,cm^{-2}$.

3.2.2. Electrochemical impedance studies of methanol oxidation

The impedance spectra of Pt/C shows a semicircle with ohmic resistance of the analyte solution and charge transfer resistance at the low frequency end along with the ohmic resistance. The charge transfer resistance was obtained from the Nyquist plot by taking the diameter of the semicircle. The temperature dependence of methanol oxidation was measured at an applied potential of 0.6 V at different temperatures (40, 45, 50 and 55 °C) by means of impedance spectroscopy and the obtained results are shown in Fig. 5. As the temperature is increased, the charge transfer resistance is decreased but there is no appreciable change in the ohmic resistance. The decrease in the charge transfer resistance with increase in temperature can be attributed to the higher methanol oxidation activity. As the temperature increases, the double layer capacitance increases. This may be due to higher dehydrogenation of intermediates, which are formed on platinum and also due to the formation of more facile adsorption sites. Fig. 6 represents the Arrhenius plot for methanol oxidation over Pt/C prepared by composite reduction. The activation energy derived from the plot was found to be $41 \pm 3\,kJ\,mol^{-1}$. The obtained activation energy is lower than the reported values $51 \pm 3\,kJ\,mol^{-1}$ [31] and $46 \pm 3\,kJ\,mol^{-1}$ [32]. This may be due to the presence of anisotropic platinum nanoparticles.

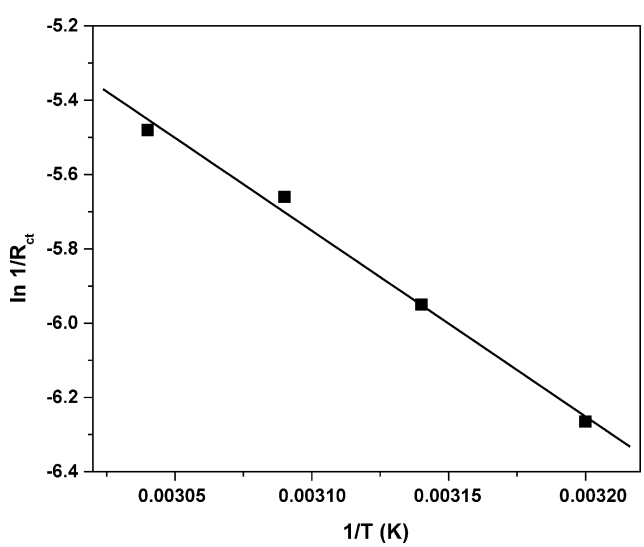

Fig. 6. Arrhenius plot for methanol oxidation on Pt/C, charge transfer resistance was extracted from Fig 5.

4. Conclusions

The results presented in this article demonstrate a method for the preparation of supported metallic catalyst system with specific morphology. These systems show enhanced surface activity due to the presence of anisotropic platinum nanocrystals. The prepared catalyst showed higher methanol oxidation activity in perchloric acid than in sulphuric acid medium. Superior stability of the Pt/C was observed in perchloric acid than in sulphuric acid. Activity for methanol oxidation was found to be higher at higher temperatures. The activation energy for methanol oxidation over Pt/C was found to be $41 \pm 3\,kJ\,mol^{-1}$. The described method is simple and elegant for the preparation of noble metal supported catalysts.

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