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Research Article

Comparative Study of Preparation, Phase formation and Application of Ti/TiO_2 electrode prepared by thermal decomposition of $TiCl_3$ with HNO_3/H_2O_2

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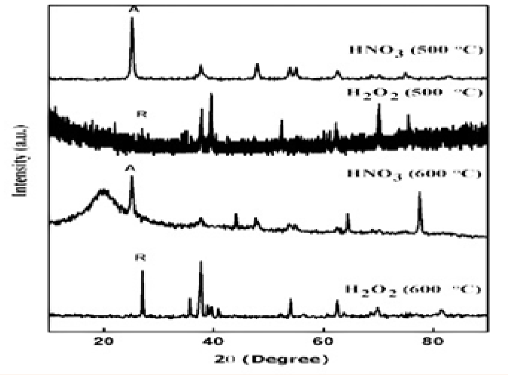
Abstract

Ti/TiO_2 electrodes were prepared on metallic titanium substrate by the thermal decomposition of $TiCl_3$ with HNO_3/H_2O_2 at different temperatures. Comparative study of Ti/TiO_2 electrodes in terms of phase formation of TiO_2, electrocatalytic activity and the yield of succinic acid obtained by the electroreduction of fumaric acid were carried out. Crystalline structures of TiO_2 film were studied by X-ray Diffraction (XRD). The electrocatalytic activity of the electrodes was studied by cyclic voltammetric studies.

Keywords: Ti/TiO_2 electrode; Phase; Electrocatalytic activity; Organic Synthesis.



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Introduction

TiO_2 films were prepared by a variety of deposition techniques such as sol-gel process [1,2], sputtering techniques [3,4], thermal plasma [5] and electron beam evaporation [6,7].The preparation of titania is very much interesting since titania exhibits polymorphism (anatase, rutile and brookite) and the phase formation is highly dependent on the preparation conditions. In fact, anatase has higher photocatalytic activity than rutile because of a difference in Fermi energy [8] and the charge carrier in anatase thin film has a higher mobility than that of rutile [9]. Earlier Beck and coworkers developed a TiO_2 electrode by this method using titanyl acetyl acetonate as a source material. The electrode was used as a cathode and behaves as a stable redox electron carrier [10]. TiO_2 were used as an electrocatalyst in the reduction of nitro compounds [11, 12]. Titanyl acetyl acetonate being a costly material, in this work an attempt was made to prepare TiO_2 electrode using $TiCl_3$ as a source material. The preparation variables affecting the nature of TiO_2 on titanium substrate and its electrocatalytic properties are also not well studied The aim of the present work is to investigate the structural and electrochemical properties of Ti/TiO_2 electrodes prepared from $TiCl_3$ using thermal decomposition method with two different oxidizing agents HNO_3 , H_2O_2. The anatase and rutile phases are the focuses of this investigation.

Experimental

Materials and Reagents

In general the experimental procedure recommended by Beck and Co- workers [13] was adopted. The Ti/TiO_2 electrode was prepared by the following procedure. $TiCl_3$ solution were prepared in 0.15N using $TiCl_3$, HNO_3 (5.0%v/v) and isopropyl alcohol (Merck). In this solution the concentration of HNO_3, H_2O_2 and isopropyl alcohol were kept constant. A stable clear yellow solution is obtained. This solution was sprayed over pretreated titanium substrate strips. And the adherent film was dried in an oven at 100-110^{0}C. The metal strip was placed in a muffle furnace for 25 minutes at 500^{0}C. This procedure was repeated at least six times to get a good coating of TiO_2 on titanium metal. Same way the experiment was repeated at 600^{0}C. These electrodes were essentially prepared in two different standard sizes viz. 1x5cm and 9x12cm for cyclic voltammetric and preparative scale experiments respectively.

Results and Discussion

Microstructure analysis of Ti/TiO_2 by X-Ray diffraction

The XRD pattern of the electrodes prepared by the thermal decomposition method using $TiCl_3$ with HNO_3/H_2O_2 at two different temperatures show is given in **Figure 1**.

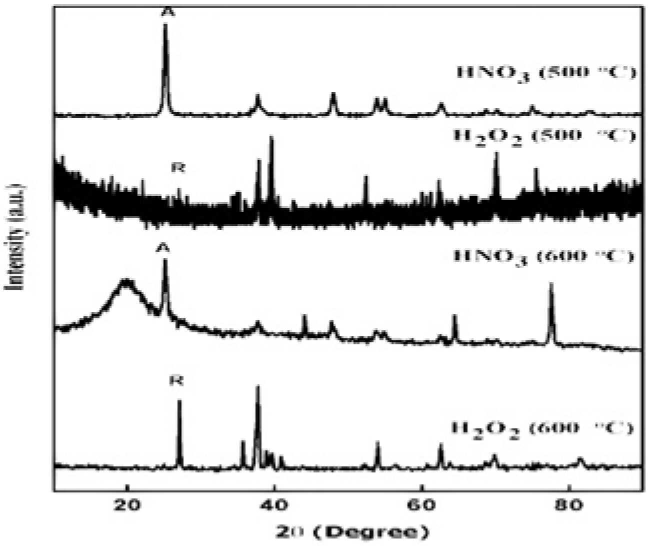


Figure 1 Microstructure of Ti/TiO_2 from $TiCl_3$ with HNO_3/H_2O_2 at 500 & 600^{0}C
(A-Anatase, R-Rutile)

XRD pattern of Ti/TiO_2 prepared by the thermal decomposition of $TiCl_3$ with HNO_3 at 500 and 600^{0}C show anatase phase with (110) peak. The anatase (110) occurred at 2θ = 52.90 and 25.82.The anatase crystallite size of the film TiO_2 decreases as the calcination temperature increase. It can be seen in the electrodes treated at 600^{0}C that, together with an increase in the intensity of the anatase which points to further crystallization of the amorphous component of the dioxide, there appear low-intensity peak related to anatase. The total rate of a transformation from amorphous to anatase is dependent upon both nucleation and growth rates. And since HNO_3 was added which gave high acidic pH, this attributes to the formation of anatase phase in the electrodes prepared both at 500 and 600^{0}C [14]. Generally the high temperature calcination at 600^{0}C not only changed the structure of the film and also passivated the film catalysts. Thus HNO_3 activated the film catalysts and had comparative strong oxidation effects on the film, which could activate the TiO_2 film effectively while disposing the impurities on the film surface. Therefore the addition of HNO_3 brought out amorphous to anatase crystalline phase and thus contributing towards better electrocatalytic activity of the electrode Ti/TiO_2. At 600^{0}C the characteristic peak corresponding to anatase (2θ=25.6) was formed as the high intensity peak which confirms the TiO_2 predominantly formed as anatase. The various phases of the specimen were identified by matching each characteristics of XRD peak with those in JCPDS files.

When H_2O_2 was used, TiO_2 formed at 500^0C from the XRD pattern it has been inferred that having more of rutile phase and two peaks alone corresponding to the anatase phase 2θ values are 68.0, 25.0. During the thermal treatment, the changes of the composition of the film catalysts were related to the phase transition and the oxidation of the substrate. These two aspects played important roles at two different temperatures. When the film was calcined at 500^0C, the amorphous TiO_2 was easily turned into few anatase and rutile forms. Meanwhile by increasing the temperature at 600^0C oxidation on the substrate generally led to the formation of more of rutile TiO_2.

In this case increasing the temperature results in the increase of rutile content in TiO_2 at the pH (4.4) may be due to the severe oxidation on the substrate and the remarkable phase transition from anatase TiO_2 to rutile TiO_2 [15]. In the $TiCl_3/H_2O_2$ solution, not only hydrolysis of $TiCl_3$ but also some other reactions proceed, because the solution was in orangish brown in color suggested [16] that the formation of the complex $[TiO\ (H_2O_2)]^{2+}$ was responsible for the color. Then equation (1) may explain the hydrolysis of $TiCl_3$.

$$TiCl_3 + H_2O + H_2O_2 \rightarrow TiO_2\ (ppt) + [TiO(H_2O_2)]^{2+} + 2H^+ + Cl^- \qquad \text{Eq.(1)}$$

Thus, both acidity and complex formation in the solution retard the precipitation of titania, according to the equilibrium equation (1). In contrast, Tengvall et al [17] proposed dissolution of titania under the presence of H_2O_2 to yield some hydrated complexes in the preparation of TiO_2 powder:

$$Ti\ (IV)\ oxide + nH_2O \rightarrow [Ti\ (IV)\ (OH)_n\ (^{(4-n)+}] + nH^+ \qquad \text{Eq. (2)}$$

Thus acidity favor's the precipitation of titania according to equation (2), while decomposition of those complexes in either in Eq. (1) or (2) leads to titania formation. Direct corrosive reaction of titanium with hydrogen peroxide might also be taken into consideration for larger H_2O_2 concentrations [18, 19].

$$Ti + H_2O_2 \rightarrow TiO_2 + H_2\ (aq) \qquad \text{Eq. (3)}$$

Those issues add complexity to the titania deposition reactions. Since the hydrolysis rate was slow, rutile phase of TiO_2 formed on the titanium substrate. But as the temperature increased from 500 to 600^0C low intensity anatase peaks disappeared and the characteristic peaks corresponding to rutile phase appeared 2θ = 27.5. Thus phase formation TiO_2 film can be controlled by temperature, pH, and the oxidizing reagent used for the deposition of the film. The electrode prepared at 600^0C shows more of anatase phase and this electrode is taken for cyclic voltammetric studies and galvanostatic reduction of fumaric acid.

Cyclic voltammetric analysis of Ti/TiO_2 in H_2SO_4

Cyclic voltammograms were recorded for Ti/TiO_2 electrode prepared from a solution of $TiCl_3$ with HNO_3/H_2O_2 (at 600°C) and presented in Figure 2. The electrolyte was 1.0 M H_2SO_4. The cyclic voltammogram has a reduction peak of Ti^{4+} to Ti^{3+}, coupled with H_2 evolution. The peak potential is around -560mv/SCE. At -480mv/SCE a well defined peak was observed in the reverse. This peak is due to the surface oxidation of Ti^{3+} formed to Ti^{4+} at the electrode surface. Thus this redox cycle is consistently maintained throughout the process.

From this cyclic voltammogram the redox electrocatalytic activity of Ti/TiO_2 electrode was well established. The difference in the cathodic and anodic peaks potential showed the process is a quasi reversible process. The Ti/TiO_2

electrodes prepared by thermal decomposition of $TiCl_3$ and HNO_3 are mainly having anatase type TiO_2, which exhibits well defined redox electrocatalytic activity. But in the case of Ti/TiO_2 electrode from $TiCl_3$ and H_2O_2, the XRD pattern clearly reveals that the crystalline structure is rutile type TiO_2 (Figure 2. b). This might be the cause for the absence or very poor redox behavior of the electrode.

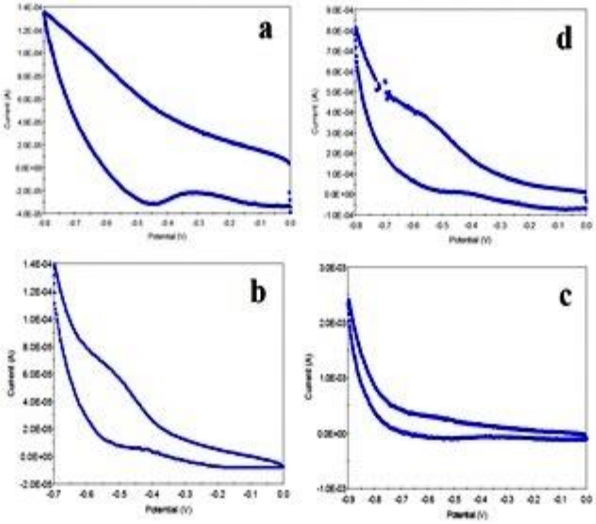


Figure 2 Cyclic voltammogram of Ti/TiO_2 electrode in 1.0 M H_2SO_4;
a. with HNO_3; **b.** with H_2O_2; **c.** with 0.2mM fumaric acid at 50mV (electrode using HNO_3); **d.** using H_2O_2

Cyclic voltammetric analysis of Ti/TiO_2 in H_2SO_4 with fumaric acid

Organic compounds are found to be adsorbed on electrode surfaces when their electrochemical behaviors are investigated in aqueous solutions. These adsorbed species give rise to the so called adsorption currents. Such adsorbed monolayer redox species can catalyze a number of other electrochemical reactions. As a group monolayer redox processes are one of the simplest ones to treat at the phenomenological level, these processes are well described by charge transfer, adsorption effects, and chemical reactions. Since the total charge transfer involved is rather small at the monolayer level, mass transfer effects need not be considered at all.

The monolayer formation process may be represented as

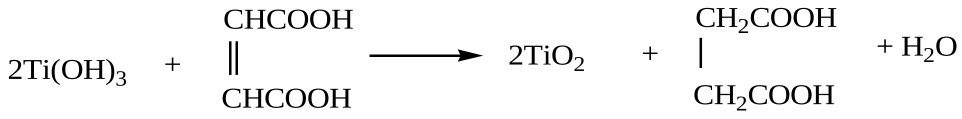
$$M - O_x + n\,e^- \rightleftharpoons M - R$$

The surface redox process to be treated here is quite similar in form. However, both the oxidized and the reduced species are now attached to the electrode surface.

$$M - O_x + n\,e^- \rightleftharpoons M - R$$

The cyclic voltammograms of Ti/TiO_2 prepared from$TiCl_3$ with HNO_3 at 600°C with 0.2mM fumaric acid is presented in Figure 2. c. As discussed earlier when the organic species comes near to the cathode surface it is readily reduced by the presence of Ti^{3+}, a strong reducing agent, present in the electrode surface. As the Ti^{3+} reduces the organic species, it oxidizes itself to Ti^{4+} on the electrode surface. Hence there should not be any anodic peak or peak with reduced current should be there in the reverse sweep. Figure 2.c clearly shows this behavior. In the forward sweep peak current also increases due to the reduction of organic species as well as there is no peak in the reverse sweep, which clearly explains the surface redox process as well as fumaric acid reduction in the forward sweep.

But in the case of Ti/TiO_2 electrode from $TiCl_3$ and H_2O_2, the XRD pattern clearly reveals that the crystalline structure is rutile type TiO_2. This might be the cause for the absence or very poor redox behavior of the electrode. Cyclic voltammograms obtained with fumaric acid are presented in Figure 2.d as there was no redox activity at the base electrode, addition of fumaric acid does not change the cyclic voltammetric pattern appreciably. The above point was well established with the results of preparative scale electrolysis. The yield efficiency is low with this electrode. Yield of succinic acid from fumaric acid from the preparative electrolysis for both the electrodes are given in Table 1. The reduction of fumaric acid to succinic acid at the Ti/TiO_2 electrode is given as follows.



$$\mathrm{2Ti(OH)_3} + \begin{array}{c}\mathrm{CHCOOH} \\ \| \\ \mathrm{CHCOOH}\end{array} \longrightarrow \mathrm{2TiO_2} + \begin{array}{c}\mathrm{CH_2COOH} \\ | \\ \mathrm{CH_2COOH}\end{array} + \mathrm{H_2O}$$

Preparative electrolysis and Product analysis

A number of preparative scale experiments were carried out under galvanostatic scale experimental conditions to optimize the conditions for preparative electrolysis and to achieve high yield efficiency in the preparation of succinic acid from fumaric acid using both the electrodes. These results are summarized in Table. The current was varied from 1.0 - 4.0 A/dm^2 and varied temperature. It was found that the high yield of succinic acid was obtained by the electroreduction of fumaric acid using the electrode prepared by the thermal decomposition of $TiCl_3$ & HNO_3 at 600°C

Table 1 Comparative study of Ti/TiO_2 electrode by the thermal decomposition of $TiCl_3$ with HNO_3/H_2O_2

Method	Preparation conditions	XRD Structure	Yield of Succinic acid
Thermal decomposition of $TiCl_3$ & HNO_3	600°C, 0.15N of $TiCl_3$ with HNO_3	Anatase	93.00 (%)
Thermal decomposition of $TiCl_3$ & H_2O_2	600°C, 0.15N of $TiCl_3$ with H_2O_2	Rutile	47.00 (%)

Conclusion

This research work has optimized the parameters in the preparation procedure which can control the phase formation of TiO_2 on titanium substrate in its anatase phase. X-Ray diffraction studies, it was found that the phase formation of TiO_2 film on titanium substrate purely depend on the preparation variables, by which anatase phase formation is possible with high acidic pH and strong oxidizing agent like HNO_3. The findings were further confirmed by the high yield of succinic acid obtained by the electroreduction of fumaric acid using this electrode. Ti/TiO_2 electrode prepared by the above given methods can be used for reduction of various other organic carbonyl compounds and nitro compounds.

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