Preparation and characterization of titanium dioxide nanotube array supported hydrated ruthenium oxide catalysts

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Abstract
This work aimed at preparing and characterizing TiO₂ nanotube supported hydrated ruthenium oxide catalysts. First of all, we succeeded in preparing TiO₂ nanotube arrays by electrochemical anodization of titanium metal at 20 V for 8 h in a 1M H₃PO₄ + 0.5 wt% HF solution as evidenced from scanning electron microscopy (SEM) and x-ray photoelectron spectroscopy (XPS) results. The hydrated ruthenium oxide was then deposited onto TiO₂ nanotubes by consecutive exchange of protons by Ru³⁺ ions, followed by formation of hydrated oxide during the alkali treatment. Further XPS measurements showed that the modified samples contain not only hydrated ruthenium oxide but also hydrated ruthenium species Ru(III)-OH.

Keywords: TiO₂ nanotube, anodization, hydrated ruthenium, catalytic oxidation.

Classification numbers: 2.03, 4.00, 5.06

1. Introduction
Incorporating metal-based species onto titanium dioxide surface is one of the well-known methods to improve catalytic activity of the resulting modified TiO₂ materials [1–6]. Among various metals such as copper, nickel, tin, gold, platinum, palladium ... the TiO₂ supported Ru catalysts have been proven to play an indispensable role with respect to wastewater treatment and energy storage applications [7–10]. During the past ten years, TiO₂ nanotubes have been widely investigated due to their practical applications in areas such as biomaterials, solar cell, rechargeable lithium batteries, gas sensor, and catalysts in particular [1, 10–14]. Indeed, the large cation exchange capacity of TiO₂ nanotubes allows a high loading of an active catalyst with even distribution and high dispersion. The open mesoporous morphology of the nanotubes, absence of micropores, and high specific surface area should facilitate transport of reagents during a catalytic reaction. The semiconducting properties of such new materials may result in strong electronic interaction between the support and a catalyst, which could improve catalytic performance in redox reactions [15]. As a result, studies on supporting ruthenium-based compounds on TiO₂ nanotubes are of potential interest [15–17]. In this sense, this work focuses on preparation of titanium dioxide nanotube array supported hydrated ruthenium oxide catalysts. As a cost-effective and high rate method, the use of electrochemistry to prepare TiO₂ nanotube arrays is described in the first section of the present paper. Part of the work is then devoted to the loading of hydrated ruthenium oxides onto the electrochemically anodized TiO₂ nanotubes.

It is remarkable to note that as a promising new catalyst for selective oxidation of many alcohols in aqueous media, hydrated ruthenium oxides have frequently been used in wastewater treatments [15]. However, the role of
ruthenium supported catalysts towards methanol oxidation in fuel applications is still an open topic for discussion [18, 19]. While some authors refer to the active ruthenium compound mainly as metallic Ru$^0$ in a bimetallic alloy, early research revealed that hydrated ruthenium oxide as a part of bimetallic Pt–Ru systems is the most active catalyst for methanol oxidation [18]. It is thus interesting to investigate the oxidation state of the Ru components deposited on our TiO$_2$ nanotube arrays. In this work, the formation of Ru-based species on the surface of TiO$_2$ nanotubes will finally be discussed as clearly as possible on the basis of x-ray photoelectron spectroscopy (XPS) results.

2. Experimental

2.1. Anodization of titanium metal

For the electrochemical anodization, a typical two-electrode configuration (figure 1) was employed with platinum foil as the counter electrode and titanium foil as the working electrode. Thickness of titanium foils (99.6% purity) was 0.5 mm. Effective area of the O-ring on the working electrode was 0.5 cm$^2$. Prior to any electrochemical treatment the foils were sonicated in acetone, isopropanol and methanol successively, followed by rinsing with deionized (DI) water and drying in a nitrogen stream. All anodization experiments were realized at room temperature in a 1 M H$_3$PO$_4$ (Merck) + 0.5 wt% HF (Sigma-Aldrich) solution. A potential of 20 V was applied through the system for 8 h. After each anodization, the obtained sample was rinsed by DI water and dried in a nitrogen stream. The as-anodized TiO$_2$ nanotubes were then recrystallized by heating at 400$^\circ$C for 10 h under nitrogen atmosphere. The obtained samples were characterized by means of scanning electron microscopy (SEM) and XPS techniques.

2.2. Deposition of hydrated ruthenium oxides onto TiO$_2$ nanotubes

The hydrated ruthenium oxide was deposited on TiO$_2$ nanotubes by consecutive exchange of protons by Ru$^{3+}$ ions, followed by formation of hydrated oxide during the alkali treatment. 200 mg of RuCl$_3$·3H$_2$O (Sigma Aldrich) was dissolved in 23 ml of water with addition of 2 ml of 0.5 M HCl. Then TiO$_2$ nanotube array samples were immersed in this solution for 60 min at 25$^\circ$C. After washing with a large amount of DI water, the samples were put in a beaker containing 1.0 M NaOH (Sigma Aldrich). After 1 h, the samples were taken out of the solution, rinsed by DI water, and then dried at 80$^\circ$C under vacuum condition for 2 h.

2.3. Microscopy study

The SEM images were recorded by a Hitachi S4800 equipped with a field emission gun (FEG-SEM).

2.4. XPS

XPS measurements were carried out with a Theta 300 (Thermo Scientific Instrument) equipped with a microfocusing monochromator x-ray source. The data were collected at room temperature, and the operating pressure in the analysis chamber was always below 10$^{-9}$ Torr. The core level spectra were referenced to the pollution C 1 s binding energy at 284.9 eV. Data treatment and peak-fitting procedures were performed using Avantage software.

3. Results and discussions

3.1. Electrochemical preparation of TiO$_2$ nanotube arrays

When a potential of 20 V is applied through the two-electrode configuration described in the experimental section, first of all, TiO$_2$ is electrochemically formed (Ti + H$_2$O $\rightarrow$ TiO$_2$ + 4e$^-$). Dissolution of titania then takes place thanks to the presence of fluoride ions in the solution and leads to the formation of soluble hexafluorotitanium complexes (TiO$_2$ + 6F$^-$ + 4H$^+$ $\rightarrow$ TiF$_6^{2-}$ + 2H$_2$O). With the help of electrical field, TiO$_2$ nanotubes finally formed as a function of the time [20, 21]. Figure 2 presents the SEM images of the resulting layers at different scales. The zoom-out SEM image (figure 2B) clearly shows the self-organized nanotubes as expected. It is also observed that the nanotube diameter is of approximately 100 nm (figure 2C). Such an obtained result is in a good agreement with the work of Bauer et al. [22], where the TiO$_2$ nanotube diameter was reported to be linearly dependent on the applied voltages and a diameter of about 100 nm was obtained with an applied potential of 20 V.

On the other hand, XPS measurements allow us to confirm that the self-organized nanotubes are titanium dioxide. As can be seen in figure 3 the survey spectrum of the sample is dominated by signals of titanium and oxygen as expected. Besides Ti and O peaks, we equally observe the presence of unavoidable contaminated carbon peak. This peak will be further discussed in the next section of this work. It is important to point out that the Ti 2p core level spectrum (figure 4(a)) shows the typical characteristics of titanium in TiO$_2$ with the 2p$_{3/2}$ and 2p$_{1/2}$ peaks centred at 458.8 and 464.3 eV, respectively [23].

XPS analysis also revealed that fluoride ions are strongly absorbed on TiO$_2$ surface, indicating the migration of F$^-$ ions is driven by the electrical field (figure 4(b)). In fact, under the influence of the electrical field, fluoride ions can even penetrate into the bottom of the nanotube as reported.
Figure 2. SEM images of TiO$_2$ nanotubes formed at 20 V for 8 h in 1M H$_3$PO$_4$ + 0.5 wt% HF at different scales.

Figure 3. XPS survey spectrum of anodized TiO$_2$ nanotube arrays.

Figure 4. Ti 2p and F 1s high-resolution spectra of TiO$_2$ nanotube arrays and C 1s + Ru 3d high-resolution spectra of the pristine and modified samples.

3.2. Titanium dioxide nanotube array supported hydrated ruthenium oxide catalysts

Figure 5 shows the XPS survey spectrum of TiO$_2$ nanotube arrays supported Ru. As is seen here, the XPS survey spectrum of TiO$_2$ nanotubes modified with Ru-based species looks very similar to that of pristine TiO$_2$ nanotubes. We do not observe clearly the presence of ruthenium on the spectrum. This however can be easily understood by noting the fact that the positions of Ru 3p are found to be very close to those of Ti 2p and also the Ru 3d$_{3/2}$ peak appears superposed to the C 1s line. In order to bring out the difference between the two samples, we wish next to concentrate on the C 1s elsewehere [24]. Furthermore, it should be kept in mind that fluoride anions are involved in the dissolution process of TiO$_2$ as mentioned above. Here, the most important point to be underlined is that simple anodization of titanium metal led to the formation of TiO$_2$ film which consists of individual tubes with a diameter of $\approx$100 nm as evidenced from the XPS and SEM results.

Before modification with ruthenium, the C 1s core level can be fitted by three components located at 284.9, 286.4 and 288.8 eV respectively (figure 6(a)). After modification, a typical behaviour of C 1s + Ru 3d mixed spectrum as already reported in many published works [9, 25–27] is
The obtained XPS data indicate that the resulting Ru/TiO$_2$ nanotube arrays contain both hydrated ruthenium oxide and hydrated ruthenium species Ru(III)-OH.

4. Conclusion

A one-step electrochemical method has been used to prepare TiO$_2$ layers that consist of arrays of individual tubes with a diameter of $\approx$100 nm. Thanks to the ion exchange reaction between the proton of the protonated

$$xMe^{n+} + H_2Ti_{3}O_7 \rightarrow Me_{x+}H_{2-x}Ti_{3}O_{7}^{(n-1)+} + xH^+.$$
form of a layered titanic acid and Ru$^{3+}$ cation in the bulk solution, hydrated ruthenium species Ru(III)-OH can be easily incorporated on TiO$_2$ nanotube surface. Part of such a ruthenium species was subsequently converted to hydrated ruthenium oxide by simple alkali and thermal treatments. Aside from Ru(III)-OH species, XPS allowed us to evidence the presence of hydrated ruthenium oxide on the surface of supported Ru/TiO$_2$ nanotube catalysts. As mentioned in the introduction, supported Ru/TiO$_2$ catalysts have been proven efficient in the selective oxidation of several organic alcohols. Testing the catalytic activity of the obtained Ru/TiO$_2$ nanotube catalysts is obviously the subject of our further works.

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