Role of Platinum Deposited on TiO$_2$ in Photocatalytic Methanol Oxidation and Dehydrogenation Reactions

Luma M. Ahmed,¹ Irina Ivanova,² Falah H. Hussein,³ and Detlef W. Bahnemann²

¹ Chemistry Department, College of Science, Karbala University, 56001 Karbala, Iraq
² Institut für Technische Chemie, Leibniz Universität Hannover, Callin Strasse 3, 30167 Hannover, Germany
³ Chemistry Department, College of Science, University of Babylon, 51002 Hilla, Iraq

Correspondence should be addressed to Falah H. Hussein; abohasan_hilla@yahoo.com

Received 30 November 2013; Revised 4 January 2014; Accepted 5 January 2014; Published 20 February 2014

1. Introduction

Titanium dioxide is regarded to be one of the most common photocatalysts, having a wide range of properties, such as a strong resistance to chemical and photocorrosion, strong oxidation capability, low operational temperature, low-cost, being and nontoxic [1]. These properties make TiO$_2$ an attractive candidate for its utilization as a photocatalyst in the photocatalytic processes. TiO$_2$ has been extensively studied and demonstrated to be suitable for numerous applications such as, destruction of microorganisms [2–5], inactivation of cancer cells [6, 7], protection of the skin from the sun [8–11], photocatalytic water splitting to produce hydrogen gas [12–14], manufacture of some drug types [15–17], degradation of toxic organic pollutants in water [18–20], and self-cleaning of glass and ceramic surfaces [21]. Even though TiO$_2$ is the most used semiconductor material, it exhibits some disadvantages, such as low surface area and fast recombination rate between the photogenerated charge carriers and the maximum absorption in the ultraviolet light region.

Different attempts have been performed to improve the efficiency of TiO$_2$ depressing the recombination process of the photoelectron-hole pairs. Some of them include the modification of TiO$_2$ surface with other semiconductors to alter the charge-transfer properties between TiO$_2$ and the surrounding environment [22, 23], sensitizing TiO$_2$ with colored inorganic or organic compounds improving its optical absorption in the visible light region [24–28], bulk modification by cation and anion doping [29–38], and fabrication of TiO$_2$ surface from polyhedral to produce hallow TiO$_2$.
2 International Journal of Photoenergy

[39, 40]. TiO$_2$ nanoparticles are considered to be more active photocatalysts as compared with the bulk powder. The ratio of surface area to volume of nanoparticles has a significant effect on nanoparticles properties. This leads to a higher chemical activity and loss of magnetism and dispersibility [41].

This work was focused on the characterization of the prepared Pt-loaded TiO$_2$ (Hombikat UV 100) samples. Moreover, the photocatalytic oxidation and photocatalytic dehydrogenation of methanol have been studied employing both the bare and Pt-loaded TiO$_2$ in the O$_2$ and N$_2$ atmosphere. The methanal formation was determined using Nash method at a wavelength of 412 nm.

2. Materials and Methods

A known weight (2 g) of TiO$_2$ (Hombikat UV 100, Sachtleben, Germany) was suspended under continuous stirring at 250 rpm in a solution containing 40 cm$^3$ of 40% aqueous methanal (Chemanol), 10 cm$^3$ of methanol (Hayman), and the appropriate volume of hexachloroplatinic acid (Riedel-De-Haen AG) dissolved in HCl. The reaction mixture was maintained at 303 K, purged with nitrogen gas (20 cm$^3$/min) and irradiated by UV-A light employing Philips Hg lamp (90 W) with the light intensity of 3.49 mW/cm$^2$ (Eibe-Schon 6 lamps) for 4 h. This period of irradiation time was found to be the most sufficient time for the complete photodeposition process of metallic platinum. The concentration of platinum was monitoring by the atomic absorption spectroscopy (Shimadzu-AA-6300, Japan). The milky white suspension turns to the pale grey colour with the deposition of Pt. The suspension solution was filtered and washed by absolute methanol, throwing in a desecrater overnight. At the end the product was dried in an oven at 100°C for 2 h [31, 32]. Band gap energies of bare and Pt (0.5)-loaded on TiO$_2$ surface were determined, via the measurement of reflectance data $R$ by (Cary 100 Scan) UV-visible spectrophotometer system. It is equipped, with using a Labsphere integrating sphere diffuse reflectance accessory for diffuse reflectance spectra over a range of 300–500 nm by employing BaSO$_4$ as reference material.

In all photocatalytic experiments, 100 cm$^3$ of 40 mM aqueous methanol solution (HPLC grade, Sd fine-CHEM limited) was mixed with certain weight of bare TiO$_2$ or platinized TiO$_2$, and was suspended using a magnetic stirrer at 500 rpm. At different time of intervals 2.5 cm$^3$ of reaction mixture was collected in a plastic test tube and centrifuged (4000 rpm, 15 minutes) in an 800 B centrifuge. The supernatant solution was carefully removed by a syringe to a new plastic test tube and centrifuged again to remove the fine particles of bare TiO$_2$ or platinized TiO$_2$. The concentration of formed methanal was determined spectrophotometrically at 412 nm following Nash method [42, 43] using UV-visible spectrophotometer (T80+, PG Instruments Limited, England).

3. Results and Discussion

3.1. Characterisation of Bare and Platinized TiO$_2$

3.1.1. FTIR Analysis. The Fourier transform infrared spectra of bare and platinized TiO$_2$ are depicted in Figure 1. The illustrated peaks at 3350–3450 cm$^{-1}$ correspond to the stretching vibration mode of O–H bonds of free water molecules and at 1620–1630 cm$^{-1}$ correspond to the bending vibration mode of O–H bond of chemisorbed water molecules. The absorption intensity of surface O–H groups in TiO$_2$ is regularly increased with the increasing of the percentage of metals content. These findings are in a good agreement with the literature data [44–46]. The broad intense band below 1200 cm$^{-1}$ is due to Ti–O–Ti bridging stretching mode in the crystal. This peak appeared as unsymmetrical valley with the increasing of metal loading (or content) on TiO$_2$ exhibiting a maximum at 580 cm$^{-1}$. This change is related to the formation of Ti–O–M vibrations [47, 48]. The intense bands at 3621, 3645, and 3696 cm$^{-1}$ are found.

3.1.2. XRD Analysis. The XRD patterns of different TiO$_2$ samples (bare and platinum loaded) are shown in Figure 2. The mean crystallite size ($L$) of samples was calculated by Scherrer’s equation (3) and the crystallite size ($L$) of samples can be estimated from plotting the modified Scherrer’s
Increasing of the number of located of Pt\textsuperscript{4+} ions in TiO\textsubscript{2} lattice, which depresses the growth of TiO\textsubscript{2} Hombikate (UV 100) nanocrystals [54]. The results show that each particle consists of about 9 to 11 crystals, according to the results obtained from the calculation of Crystallinity Index values by employing the following equation [56]:

\[
\text{Crystallinity Index} = \frac{D_p}{L} \text{ or } \left(\frac{1}{\tilde{L}}\right),
\]

where \(D_p\) is the particle size which is measured by AFM analysis and \(L\) and \(\tilde{L}\) are the corresponding mean crystallite size and the crystallite size calculated by the Scherrer equation and the modified Scherrer equation employing XRD data, respectively.

The maximum value of average Crystallinity index for Pt (0.5)/TiO\textsubscript{2} is found to be 8.168. That referred to the suppression of the crystal defects number through decreasing the amorphous phase present in TiO\textsubscript{2} and overall enhancing the photocatalytic activity of TiO\textsubscript{2} [57].

3.1.4. UV-Visible Diffuse Reflectance Spectra. The UV-vis absorbance spectra of the bare TiO\textsubscript{2} and platinized TiO\textsubscript{2} (0.5\% Pt) powders were also measured to confirm the Pt-loading trend and to measure the effect of Pt loading. The results from UV-visible reflectance spectra as plotted in Figure 5 clearly show the shift of absorption edge towards longer wavelength for platinized TiO\textsubscript{2}. These results indicate that the excitation of metalized TiO\textsubscript{2} occurs with the narrowing and red shift of the band gap energy (\(E_g\)) peak [58]. These results were subsequently agreed with the increasing of the average Crystallinity Index [57].

3.2. Effect of the Metal Loading on Photocatalytic Activity of Methanol Solution. The photocatalytic activity of the platinized titanium dioxide was first increased with the increasing of the metal loading until a maximum was reached with the following decrease in the activity. Figures 6 and 7 show the results obtained with the samples containing different amount of platinum. The highest photocatalytic activity was observed with the Pt loading of 0.5\% wt. This loading percentage may give the most efficient separation of photogenerated electron-hole pairs [59]. The presence of Pt on the TiO\textsubscript{2} surface leads to an increase of the surface barrier and the space charge region becomes narrower. As a result of
Figure 3: Modified Scherrer equation plot of (a) bare TiO$_2$, (b) 0.25% Pt loaded on TiO$_2$, (c) 0.50% Pt loaded on TiO$_2$, (d) 0.75% Pt loaded on TiO$_2$, and (e) 1.00% Pt loaded on TiO$_2$.

Table 2: Particle size measured by AFM and Crystallinity values of bare TiO$_2$ and platinized TiO$_2$.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Particle size/nm</th>
<th>*Crystallinity Index</th>
<th>**Crystallinity Index</th>
<th>Average Crystallinity Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>80.940</td>
<td>7.046</td>
<td>7.988</td>
<td>7.517</td>
</tr>
<tr>
<td>Pt(0.25)/TiO$_2$</td>
<td>63.600</td>
<td>5.889</td>
<td>6.346</td>
<td>6.117</td>
</tr>
<tr>
<td>Pt(0.50)/TiO$_2$</td>
<td>77.020</td>
<td>8.233</td>
<td>8.104</td>
<td>8.168</td>
</tr>
<tr>
<td>Pt(0.75)/TiO$_2$</td>
<td>54.890</td>
<td>5.370</td>
<td>5.724</td>
<td>5.547</td>
</tr>
<tr>
<td>Pt(1.00)/TiO$_2$</td>
<td>73.130</td>
<td>6.981</td>
<td>8.851</td>
<td>7.916</td>
</tr>
</tbody>
</table>

*Crystallinity Index calculated by divided particle size on mean crystallite size and **Crystallinity Index calculated by divided particle size on crystallite size.
Figure 4: Three-dimensional AFM image of (a) bare TiO$_2$, (b) 0.25% Pt loaded on TiO$_2$, (c) 0.50% Pt loaded on TiO$_2$, (d) 0.75% Pt loaded on TiO$_2$, and (e) 1.00% Pt-loaded on TiO$_2$.

Platinum acts as electron scavenger hindering the recombination of the charge carriers and ultimately exhibiting the enhancement of the photoreactivity as shown in the following equation [31, 32, 63]:

$$\text{Pt/TiO}_2 + h\nu \rightarrow h^+_{\text{VB}} + e^-_{\text{CB}} \quad (6)$$

$$\text{Pt}_n + e^-_{\text{CB}} \rightarrow \text{Pt}^-_n \quad (7)$$

$$\text{O}_2 + \text{Pt}^-_n \rightarrow \text{O}_2^- + \text{Pt}_n \quad (8)$$

However, when the percentage of the metal reached maximum, the additional amount leads to making the space charge layer very narrow. As a result the penetration depth of light exceeds the space charge layer. The recombination of the electron-hole pairs will be favorable and the photocatalytic activity will be reduced [60]. Moreover, the presence of metal on the TiO$_2$ surface reduces the number of the surface hydroxyl groups leading to the reduction of the photoreactivity [64]. This means that the metal on the TiO$_2$ surface acts both as an efficient trap site and as a recombination center at the same time [65]. Hence the rate of the methanal (HCHO) formation will be slower while the conversion of methanal to formic acid (HCOOH) is a faster process. On the other hand, with the increasing of the metal amount, TiO$_2$ samples will become more grey in color. Thus, the changed optical properties of the samples could lead to the screening of the light towards the TiO$_2$ and suppression of the electrons excitation to the conduction band [31, 66].

Two mechanisms for the photocatalytic oxidation (in the presence of O$_2$) and photocatalytic dehydrogenation (in the presence of N$_2$) of methanol with Pt (0.5)/TiO$_2$ are suggested as shown in Scheme 1. The scheme shows the differences...
between the mechanism of photooxidation and photodehydrogenation of methanol on platinized titanium dioxide. The formation of CaCO₃ in photooxidation process was indicated by passing the outlet gas in Ca(OH)₂ solution. However, no CO₂ formation was indicated in photodehydrogenation of methanol.

Differences in experimental conditions, such as, experimental equipment, type of photocatalyst, position of band edges of semiconductor compared to redox potential of O₂/O₂⁻ and −OH/−OH, and type and concentration of organic pollutant, cause difficulties in the comparison of photocatalytic activity of different materials. Xiang et al. [67] measured the formation rates of hydroxyl free radical for various semiconductor photocatalysts at the same experimental conditions. They discussed the difference of rates formation of hydroxyl free radical on various semiconductors. In another study Xiang et al. [68] showed that hydroxyl radicals are one of active species and indeed participate in photocatalytic reactions. They also found that the photocatalytic activity of Ag-TiO₂ exceeds that of P25 by a factor of more than 2. Our results are in good agreement with these findings.

The different yields that are suggested in the two mechanisms are HCOH and H₂O in the absence of oxygen (photocatalytic dehydrogenation of methanol) and HCOOH in the presence of oxygen (photocatalytic oxidation of methanol). The pH of the reaction suspension after one hour of irradiation was found 6.93 in dehydrogenation process while it was 4.82 in photooxidation process. This indicates the further oxidation of the formed formaldehyde to formic acid.

4. Conclusions

This study is focused on the elucidation of the mechanism of the methanol formation by the photocatalytic oxidation and/or photocatalytic dehydrogenation of aqueous methanol solution with bare and platinized TiO₂. The main conclusions can be summarized as follows.

1. The FT-IR spectra show that the peaks at 3450 cm⁻¹ and 1630 cm⁻¹ related to the surface O–H groups of TiO₂ are increased with the increasing of the platinum amount loaded on TiO₂ surface. The intense bands at 3621, 3645, and 3696 cm⁻¹ have been observed in all spectra which are characteristics for the tetrahedral coordinated vacancies designated as 4Ti⁴⁺–OH. Additionally, a disappearance of two bands at 3765 and 3840 cm⁻¹ attributed to 6Ti³⁺–OH has been observed as well.

2. The XRD data have been used to calculate the crystallite size of the bare and Pt-loaded TiO₂. The values obtained for the crystallite size of the bare TiO₂ showed a decrease with the increasing of platinum amount on TiO₂.

3. AFM images indicate that the shapes of both bare and platinized TiO₂ are spherical.

4. One particle consists of about 9 to 11 crystals.

5. In photoreaction, no reaction occurred with using bare TiO₂ under inert gas (N₂); however, in the presence of metal, the photoreaction occurred; that is, the existence of the metal substituted the needed
for the O\textsubscript{2}. In the existence of O\textsubscript{2} the reaction was carried on to form formic acid as a result of further oxidation of methanol while, in the absence of the O\textsubscript{2}, dehydrogenation of methanol occurred, and no further photooxidation occurred.

**Conflict of Interests**

The authors declare that there is no conflict of interests regarding the publication of this paper.

**References**


