Research Article


Atheel Hassan Alwash, 1,2 Ahmad Zuhairi Abdullah, 1 and Norli Ismail 3

1 School of Chemical Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia
2 Department of Chemistry, College of Science, Al-Nahrain University, Al-Jadirya, Baghdad, Iraq
3 School of Industrial Technology, Universiti Sains Malaysia, 11800 Nibong Tebal, Penang, Malaysia

Correspondence should be addressed to Atheel Hassan Alwash; atheel_eng78@yahoo.com

Received 26 January 2013; Revised 2 June 2013; Accepted 10 June 2013

Academic Editor: Jose M. Guisan

Copyright © 2013 Atheel Hassan Alwash et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Lanthanide ions loaded TiO$_2$ encapsulated into Y zeolite catalysts were synthesized and used in sonocatalytic degradation of Amaranth dye in aqueous solution. The support zeolite Y was modified by different loading of Ti and La species using ion exchange method. The sonocatalytic reaction condition was carried out at 10 mg/L initial dye concentration, original pH, 1.5 g/L of catalyst loading with low ultrasonic frequency of 40 KHz. Different characterization techniques were used to reveal the physicochemical characteristics of the catalysts. Successful loading of TiO$_2$ and La/TiO$_2$ into zeolite Y was achieved. The framework of zeolite Y remained unchanged after the loading of TiO$_2$. Titanium species was bound to the framework of zeolite through Ti–O–Si bonds through isomorphous substitution of Si in the zeolite. The ultrasonic degradation of Amaranth dye was enhanced by the TiO$_2$ encapsulation with a maximum degradation efficiency of 50% after 120 min of reaction. However, the activity of the catalyst decreased after the loading of lanthanum. This decrease was attributed to the poor contact between the metal crystallites located on the external surface and the titanium encapsulated into cages of zeolite Y.

1. Introduction

Titanium dioxide is generally considered to be a very efficient photo- or sonocatalyst that is nontoxic, stable, and cheap [1]. It exhibits high durability, corrosion resistance, and high oxidation potential of the valence band that ensures its general applicability to a wide range of substrates [2]. On the other hand, fast charge carrier recombination, low interfacial charge-transfer rates, and recycling difficulties were the main drawbacks of using bare TiO$_2$ [3]. In order to overcome these problems, two methods have been suggested to increase its activity. The first one is through doping of the transition metal ions into titanium dioxide to suppress the recombination of electrons holes. Song et al. [4], Jamalluddin and Abdullah [5], Wang et al. [6], and many other researches have reported the differences in the catalytic activity of titanium oxide with different types of doping metals. Secondly, loading of titanium dioxide onto suitable supports could reduce the problem of catalyst separation after the reaction. Loading of TiO$_2$ nanoparticles on porous supports has been attempted using activated carbon [7, 8], fiber glass [9], clay [10], and zeolites [11] as the support materials.

Zeolites are good adsorbents and eco-friendly materials possessing high surface area and high thermal stability. Additionally, these materials possess amphoteric properties such as Lewis acidity (denotes electron-accepting ability) and Lewis basicity (describes their electron-donating property) [12, 13]. The nature of modification depends mainly on the specific zeolite structure, framework composition, nature of cation, and pore structure. The behavior of the catalyst and its practical applications will be influenced by the properties of the zeolites such as particle size, surface area, pore diameter, mechanical strength, microbial resistance, thermal stability, chemical durability, hydrophobic/hydrophilic character, ease of regeneration, loading capacity, and cost [14].
The possibility for titanium encapsulation into the pores of zeolite is interesting as far as catalysis is concerned due to the high internal surface area of zeolite. Titanium encapsulation into zeolite has been recently investigated for its use in photocatalytic reaction [15]. Chen et al. [16], Liu et al. [15], and Zhang et al. [17] have reported the characterization and the photocatalytic activity of titanium encapsulated into the pores of zeolite for the degradation of different organic compounds while a certain degree of success has been reported.

It is well known that the TiO$_2$ is irradiated by the absorption of the UV light generated from the ultrasonic process that is 375 nm leading to high oxidation potential and the generation of e$^-$.h$^+$ pair. This fact is similar to the photocatalytic process. However, the use of ultrasound as an irradiation source for the heterogeneous catalysts instead of photocatalytic process can be useful in many aspects such as the higher penetrating depths of ultrasonic up to 20–30 cm which is the superior characteristic of ultrasonication process compared to the low penetrability during the photocatalytic process in water medium (limited to several millimeters), improvement in the diffusion of reactant from the bulk solution to the surface of catalyst, continuous cleaning of the catalyst surface which is ascribed to the desorption of the generated product during oscillation. In addition, ultrasonic process prevents the aggregation of the catalyst particles due to the fragmentation of the particles into smaller sizes thus increasing the active surface area available for the reaction [18]. Therefore, it is of great interest to investigate the use of similar material in sonocatalytic reaction since this process does not have the problems of low light penetration, long reaction time, or the need for specific system design. In this study, La$^{3+}$ has been loaded onto the encapsulated TiO$_2$ on the hypothesis that the presence of dopant can retard the recombination between e$^-$.h$^+$ pair generated from the irradiated TiO$_2$ nanoparticles encapsulated into zeolite to consequently improve the catalytic activity [17]. The incorporation of both La and Ti into the framework of zeolite will give the chance to occupy most of the internal and external surface areas of zeolite with active metals thus enhancing the catalytic activity. As such, specific characteristics and sonocatalytic behaviors of encapsulated TiO$_2$ into zeolite Y with and without the presence of lanthanum dopant have been elucidated to investigate the ability of the catalyst to degrade Amaranth dye as a probe substance in this work. Amaranth is an anionic azo dye with three sulfonic groups in its structures usually; it is used for dying the fibers, wool, and textile printing silk as well as photography.

### 2. Experimental

#### 2.1. Materials

H–Y zeolite with Si/Al ratio of 15 was obtained from Zeolyst International. Amaranth dye, potassium titanooxalate dehydrate (99%), and sodium chloride bixtra (99.5%) were obtained from Sigma–Aldrich, while lanthanum nitrate III hexahydrate (99.999%) was obtained from Aldrich. The important properties of the dye molecules are given in Table 1. Distilled deionized water was obtained by purifying distilled water with an Elga-Pure Water Purification (UHQ W) system. It was used in the preparation of dye solutions used in the study.

#### 2.2. Catalyst Preparation Method

2.2.1. Preparation of Na–Y Zeolite. The dried H–Y zeolite was first converted to its sodium form by means of an ion exchange method [19]. The material was washed with 1 M NaCl at 80°C for 4 h in such a way that the ratio of zeolite Y to sodium chloride solution was 1: 80. The slurry was then filtered and washed with distilled dionized water to remove excess NaCl. In order to get a sufficient exchange of sodium with the zeolite, the previous procedure was repeated twice. The sample was then dried over night at a temperature of 80°C and then calcined in a muffle furnace at 550°C for 5 h.

2.2.2. Introduction of TiO$_2$ into Na–Y Zeolite. Several samples of Na–Y zeolite incorporated with TiO$_2$ were prepared using the procedure reported by Liu et al. [15]. Different concentrations of potassium titanooxalate (from 0.56–2.82 × 10$^{-2}$ mol/L) were dissolved in 100 mL of distilled deionized water. Then, 1.0 g of support (Na–Y zeolite) was added to each solution and they were kept under continuous stirring for 12 h to allow ion-exchange process. After the ion exchange step, the catalysts were filtered with a membrane filter (pore size 0.45 μm) and washed with excessive amount of water to avoid the physically adsorbed titanium species from aggregating on the external surface of the zeolite. Then, the catalysts were dried overnight in an oven at 100°C. The previous procedure was repeated to get higher loading of titanium and the catalysts were denoted as Ti$_1$-NaY, Ti$_2$-NaY, Ti$_3$-NaY, and Ti$_4$-NaY according to the increasing titanium content in catalyst. Next, the catalysts were calcined in a furnace at 550°C for 5 h with a ramping rate of 5°C/min. Prior their use in the reaction, the catalysts were ground into fine powder and kept in dry cabinet.

In order to investigate the effect of metal loading on the activity of the catalyst, different concentrations of lanthanum...
nitrate solution were dissolved in 100 mL of distilled deionized water and 1 g of Ti₄⁺-NaY was added to each solution, and they were kept under continuous stirring for 12 h at ambient temperature. Then, the catalysts were filtered with a membrane filter (pore size 0.45 μm) and washed. This procedure was repeated to get higher loading of La in the catalyst [20]. After drying overnight at 100°C and calcinations at 550°C for 5 h, the catalysts were ground and kept in a dry cabinet. The final catalysts are denoted as 0.32% La/Ti₄⁺-NaY, 0.64% La/Ti₄⁺-NaY, and 1.28% La/Ti₄⁺-NaY using the actual Wt% of La ions which was checked by the ICP technique.

2.3. Characterization Technique. Physicochemical characterizations of the catalysts with different analytical techniques were performed on the most potential catalysts. The loadings of titanium and lanthanum after the ion exchange process were checked by means of an inductively coupled plasma ICP-MS spectrometer. Meanwhile, X-ray diffraction patterns of the catalyst samples were determined using an XRD system (Philips Goniometer PW 1820). Surface analysis was also performed using nitrogen adsorption/desorption (Micromeritics ASAP 2020) based on N₂ adsorption process at 77 K. The energy dispersive X-ray analysis (EDAX) system from (Oxford INCA/ENERGY-350) was also used to analyse the type of metals at the catalyst surface. The reflectance of the solid samples was determined using UV-Vis spectrophotometer (Perkin Elmer) in a wavelength range between 190 and 1,100 nm. The FT-IR spectroscopic measurements were carried out using a Perkin-Elmer spectrometer in which the spectra were recorded in the range of 400–4,000 cm⁻¹ while transmission electron microscope (TEM) imaging was equipped with an image analyzer and operated at 120 kV. The roughness of the catalyst surface was checked using SPA 400 AFM technique.

2.4. Sonocatalytic Reaction. All experiments were carried out in a 250 mL cylindrical vessel and placed in an ultrasonic bath (Cole-Parmer) for up to 2 h. Before the ultrasonic reaction was initiated, the solution was stirred for 30 min at room temperature to maintain the good dispersion of catalyst with the dye solution. The experimental conditions were set at an initial Amaranth dye concentration of 10 mg/L, a catalyst amount of 1.5 g/L, and the solution pH was kept at its original level without any adjustment. The ultrasonic output power was fixed at 50 W with a frequency of 40 kHz. The catalytic activity was measured by calculating the degradation efficiency by means of a UV-Vis spectrophotometer. The performance of the catalysts was evaluated by adding 1.5 g/L of catalyst into the dye solution treated under ultrasonic irradiation. During the reaction, a sample solution was withdrawn at each time interval and centrifuged using a Kubota 5910 centrifuge to separate the supernatant. Then, concentration of the dye solution was determined at a maximum absorbance wavelength of 521 nm. The degradation efficiency of the catalyst was calculated based on the following equation:

\[
degradation\ efficiency\ (\%) = \left[1 - \left( \frac{C_t}{C_0} \right) \right] \times 100%, \quad (1)
\]

where \(C_0\) (mg/L) is the initial concentration of dye and \(C_t\) (mg/L) is the concentration of dye at certain reaction time, \(t\) (min).

3. Results and Discussions

3.1. Characterization of Catalyst

3.1.1. ICP Analysis. The results of ICP analysis for the actual amount of titanium and lanthanum in the zeolite catalysts prepared through ion-exchange method are shown in Table 2. The amount of titanium and lanthanum loaded into zeolite was found to increase with increasing concentration of Ti and La solutions used during the ion-exchange process. This was an expected result as higher concentration would shift the equilibrium in the ion-exchange process towards forward reaction. The highest loading of TiO₂ was achieved with Ti₄⁺-NaY with a loading of 0.30 wt.%. Meanwhile, the La content in the catalyst was varied between 0.32 and 1.28 wt%.

<table>
<thead>
<tr>
<th>Catalyst sample</th>
<th>Composition (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti₄⁺-NaY</td>
<td>0.25</td>
</tr>
<tr>
<td>Ti₄⁺-NaY</td>
<td>0.30</td>
</tr>
<tr>
<td>0.32% La/Ti₄⁺-NaY</td>
<td>0.30</td>
</tr>
<tr>
<td>0.64% La/Ti₄⁺-NaY</td>
<td>0.30</td>
</tr>
<tr>
<td>1.28% La/Ti₄⁺-NaY</td>
<td>0.30</td>
</tr>
</tbody>
</table>

3.1.2. Surface Analysis. The BET surface area for zeolite (NaY), titanium encapsulated into zeolite (Ti₄⁺-NaY), and 0.64% La/Ti₄⁺-NaY were obtained by means of N₂ isotherm surface analyzer. It was observed that the surface area of zeolite was decreased after the encapsulation of TiO₂ into zeolite from 771 m²/g for NaY zeolite to 754 m²/g for Ti₄⁺-NaY with increasing loading of TiO₂. This slight reduction in surface area indicated the successful loading of titanium oxide during the repeated ion-exchange method. Severe drop in the surface area did not occur to indicate that porous exchange did not happen even at the highest TiO₂ loading. This could be due to the general characteristics of zeolite Y internal pores which are relatively large (7.4 Å) with a high void fraction of about 48% [21]. However, after the loading of 0.64 wt.% of La into Ti₄⁺-NaY, the surface area of the produced catalyst was decreased to 618 m²/g.

The pore volume of catalysts was also found to decrease from 0.249 nm for NaY zeolite to 0.242 nm for Ti₄⁺-NaY. This slight reduction was ascribed to the partial agglomeration of the TiO₂ cluster inside the pores of zeolite after the ion-exchange and calcination steps. Based on the special characteristics of this zeolite that has an external surface area of about 1% of the inner surface area (close to 6 m²/g), pore opening of 7.4 Å, and super cages diameter of 1.3 nm, titanium ions could be entrapped within the supercages of zeolite during the ion-exchange process depending on the size of TiO₂ cluster that formed [21]. It should be noted that potassium titanooxalate
formed a very clear solution due to its high solubility in water and it did not form any colloidal suspension. This high solubility allowed titanium ions to diffuse into the internal cavities of zeolite Y during the ion-exchange process. However, the maximum size of the TiO$_2$ cluster presented in the supercages might not be larger than 1.3 nm which is the diameter of the supercage.

For the case of 0.64% La/Ti$_4$-NaY the pore volume of the catalyst was reduced to 0.188 cm$^3$/g. The reduction in pore volume after the loading of La could be ascribed to the partial interaction of these ions with the framework of zeolite. However, it seems that there was an excess amount of La that could not any more enter the formwork of zeolite, and, instead, it was accumulated on the surface of it consequently causing this obvious reduction in surface area of the catalyst as it was mentioned earlier.

3.1.3. XRD Analysis. The crystalline structure of the catalyst particles was determined using X-ray powder diffraction method. The XRD patterns of selected catalysts with different TiO$_2$ loadings are shown in Figure 1. The high crystalline from of the parent zeolite (NaY) was very obvious from the diffraction patterns of XRD that exhibited reflections at 2θ values of 12, 15, 18, 20, 23, 31, and 34 which were typical to the structure of zeolite Y. These results were in agreement with those reported by Tayade et al. [19]. The structure of zeolite remained virtually unchanged after being loaded with titanium oxide (Ti$_4$-NaY and Ti$_2$-NaY) to indicate that the TiO$_2$ did not significantly affect the framework structure of the zeolite. However, no new peaks could be detected for anatase at 2θ 25.1° after TiO$_2$ loading into zeolite. This could be due to the low loading of TiO$_2$ as it was detected by the ICP technique or the TiO$_2$ clusters located within the zeolite pores that were very small leading to unclear diffraction patterns. Furthermore, the location of TiO$_2$ clusters within the internal pores could be difficult to be detected under XRD [17]. Chen et al. [16] reported that they did not observe any diffraction peak at low loading of titanium oxide incorporated into zeolite (below 83 mg/g of catalyst) since the amount of TiO$_2$ was not high enough to give clear diffraction peaks.

The XRD diffraction patterns for La/Ti$_4$-NaY at different loading of La are shown in Figure 1. It was clear that there was a reduction in the intensity of the peaks after the loading of small amount of lanthanum. All the peaks that are associated with the crystalline of zeolite were converted to wide and short peaks. Even though the loadings for both TiO$_2$ and lanthanum oxide were very small, but the difference in the intensities of the peaks after both loading was significant. The reduction in the intensity of the peaks for the case of La loading can give an indication that the lanthanum oxide mostly covered the surface of the support and, caused this reduction in peaks intensities. These results were in good agreement with the results of surface analysis.

Table 3 presents summarized information about the unit cell parameters and the unit cell volume of the NaY support before and after the loading of Ti and La metals. From the results of XRD diffraction, it was observed that the crystal structure was a polyhedral cubic form and it was able to keep its original structure even after the ion exchange with both Ti and La species. There was a significant reduction in the unit cell volume of zeolite from 14423.43 Å$^3$ to 14396.78 Å$^3$ after the loading of Ti species. This change was ascribed to the reduction in the unit cell parameter due to the replacement between the Ti and the framework of NaY. Similar result was reported by Zhao et al. [22] and Liu et al. [15]. After the loading of La ions onto Ti$_4$-NaY, an increase in the volume of the unit cell was observed with increasing loading of La. This increase in the unit cell volume could attribute to the deposition of lanthanum oxide on the surface of Ti$_4$-NaY to cause some deformation in the crystal lattice of the support.

3.1.4. FTIR Analysis. Infrared spectra of the NaY, Ti encapsulated zeolite with two different loadings of La, that is, 0.64% La/Ti$_4$-NaY and 1.28% La/Ti$_4$-NaY, are shown in Figures 2(a) and 2(b). A new absorption band at a wavelength of 950 cm$^{-1}$ appeared and it was attributed to Ti–O–Si bond. This result was in agreement with a reported work by Wang et al. [20]. The peak at 950 cm$^{-1}$ was detected for all zeolite catalysts loaded with TiO$_2$ and it was ascribed to the replacement of tetrahedral Si with Ti during the ion-exchange method [20]. The intensity was influenced by the amount of TiO$_2$ presented on the zeolite support [23].

For NaY, the peak at 950 cm$^{-1}$ is attributed to Si–OH bond [24], and from Figure 2(a), it is clear that there is no such peak. Thus, this peak was an indication of successful isomorphic substitution of Ti with Si to produce Si–O–Ti [25]. At 1,000 cm$^{-1}$, a slight shift towards higher frequency attributed

![Figure 1: X-ray diffraction patterns of various titanium-modified zeolite Y catalysts.](image)

**Table 3**: Unit cell parameters (Å) and (V) crystal volume (Å$^3$) of different catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>(V) Å$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaY</td>
<td>24.342</td>
<td>24.342</td>
<td>24.342</td>
<td>14423.43</td>
</tr>
<tr>
<td>Ti$_4$-NaY</td>
<td>24.322</td>
<td>24.322</td>
<td>24.322</td>
<td>14387.91</td>
</tr>
<tr>
<td>Ti$_2$-NaY</td>
<td>24.327</td>
<td>24.327</td>
<td>24.327</td>
<td>14396.78</td>
</tr>
<tr>
<td>0.64% La/Ti$_4$-NaY</td>
<td>24.342</td>
<td>24.342</td>
<td>24.342</td>
<td>14423.43</td>
</tr>
<tr>
<td>1.28% La/Ti$_4$-NaY</td>
<td>24.363</td>
<td>24.363</td>
<td>24.363</td>
<td>14460.79</td>
</tr>
</tbody>
</table>
to the T–O–T or O–T–O (T = Si or Al) stretching vibration of the framework was observed. This observation demonstrated the effect of the Ti species on zeolite framework [26]. Liu et al. [15] reported similar results in their attempt for Ti encapsulation into zeolite Y. The bands detected in the range from 500 to 700 cm\(^{-1}\) for all the samples were ascribed to pseudolattice vibrations while the bands below 400 cm\(^{-1}\) were ascribed to the lattice vibration [27]. However, a stretching vibration peak attributed to Ti–O bond was observed at 460 cm\(^{-1}\). Calcination of the catalyst samples at 550 °C caused some changes in the absorption bands in the low IR region. This result implied that partial aggregation of the Ti species in zeolite cavities might have occurred [24]. This was consistent with the partial drop in the pore volume as observed in the surface analysis.

The FTIR spectra of 0.64 and 1.32 wt.% of La ions loaded on encapsulated titanium are shown in Figure 2(b). No new bands were detected after incorporating La ions into Ti\(_4\)-NaY. However, a small reduction in asymmetric stretching mode of external linkages bond was detected at 1050 cm\(^{-1}\) after the loading of La ions and this reduction was found to increase with increasing wt.% of La ions. A band at 450 cm\(^{-1}\) was observed and it was ascribed to T–O stretching vibration mode.

3.1.5. UV-Vis Spectrophotometer. The UV-Vis diffuse reflectance spectra for NaY, Ti\(_4\)-NaY, La/Ti\(_4\)-NaY are shown in Figure 3. Blue shifts towards shorter wave lengths about 376 nm were observed for Ti\(_4\)-NaY while the bare TiO\(_2\) (not shown for clearness) had a wave length of about 390 nm. This behavior was in agreement with Easwaramoorthi and Nataraajan [21]. The provenance of such blue shift towards shorter wave length was due to the quantum size effect for semiconductors as the particle size decreased after the modification of TiO\(_2\) into the pores of the zeolite.

The sudden fall in the reflectance at certain particular wave lengths indicated the presence of optical band gap after the ion-exchange of Ti species into zeolite [28]. However, doping of metals into semiconductors can generally reduce its energy gap to cause a shift in the reflection spectra towards higher wavelength. This red shift towards higher wave length will facilitate the excitation of electron from the valance band to the conduction band. Figure 3 showed that the doping of 0.64 wt.% of La into the Ti\(_4\)-NaY slightly enhances the shift towards higher wave length in comparative to that of Ti\(_4\)-NaY. However, increasing the concentration of La to 1.32 wt.% causes slight blue shift towards shorter wave length. This could be attributed to the difficulties of lanthanum ions to enter the lattice of Ti\(_4\)-NaY at higher concentration instead; it is merely dispersed at the external surface of zeolite and caused this slight enhancement in wavelength shift. Ökte and Yilmaz [3] also observed a decrease in wavelength shift with increasing the La concentration doped in TiO\(_2\)-ZSM-5.

The energy band gap for the samples was calculated from their reflection spectra. There were 3.55 and 3.70 eV for bare TiO\(_2\) and Ti\(_4\)-NaY, respectively. The change in the energy band gap indicated that titanium clusters could have been introduced into the internal pores of zeolite and the sizes of those titanium nanoparticles in the zeolites were smaller than those of bare TiO\(_2\) [17]. However, after the loading of La ions into Ti\(_4\)-NaY, a slight enhancement in the energy gap was observed about 3.60 eV for La/Ti\(_4\)-NaY samples in comparative to that of Ti\(_4\)-NaY.
3.1.6. EDAX Analysis. The energy dispersive X-ray (EDX) analysis is an effective technique to provide additional evidence on the success loading of the nanoscale metal on the surface of the support which was not detected in XRD analysis. In Figures 4(a) and 4(b), there were different elements detected on the surface of catalysts such as Si, Al and O which are considered as the main elements of zeolite framework. For instance, at various points in the same sample, different values were obtained at wider range due to the unequal distribution of these elements. Nevertheless, it was believed that the existence of signals attributed to the elements in these samples indicated the success of metals loading during the preparation method.

The EDAX analysis was carried out to verify the success in loading of metal on the surface of the support. Figure 4(a) shows that a small amount of lanthanum was detected on the surface of Ti$_2$NaY. On the other hand, Figure 4(b) did not show any signal for the Ti element on the surface of the catalyst. Thus, titanium oxide was successfully encapsulated inside the supercages of the zeolite. According to EDAX analysis, it was clear that titanium was encapsulated into the pores of zeolite and lanthanum nanoparticles agglomerated on the external surface. This conclusion was consistent with results of XRD and UV-Vis reflectance spectra.

3.1.7. Transmission Electron Microscopy (TEM). The TEM images were taken for the NaY, Ti$_2$NaY, and 0.64% La/Ti$_2$NaY catalysts in order to investigate the metal positions for both Ti and La with respect to zeolite structure. Figures 5(a) and 5(b) presents the hexagonal structure of zeolite at two different magnifications 8 k and 45 k, respectively. However, the structure of zeolite remained unchanged after the loading of Ti and La species after the ion-exchange method. In Figures 5(c) and 5(d) at 45 k magnification, there were dark and light spots distinguished at the outside and the inner side of the nanoporous structure. The light spots in Figure 5(c) existed between the lattice plan of zeolite ascribed to TiO$_2$ clusters, while the dark spots at the outer edge of the zeolite particle in Figure 5(d) were ascribed to La since the molecular weight of lanthanum is much higher than that of titanium. Thus, the TEM image of the former gave more dark spots than Ti. Due to the overlapping of the metals with the matrix of zeolite, it was rather difficult to measure the diameter of these metals nanoparticles.

3.1.8. AFM Technique. The three-dimensional images with a scan area of $10 \times 10 \mu m$ for the parent NaY, Ti$_2$NaY, and 0.64% La/Ti$_2$NaY were carried out using atomic force microscopy AFM technique to investigate the variation in the surface morphology for the prepared samples as presented in Figure 6. The results showed that both NaY and Ti$_2$NaY have similar surface characteristic and the roughness value for both catalysts was around 72–74 nm. This insignificant change in roughness value supports the previous characterization results and that the TiO$_2$ clusters were encapsulated into the cages of zeolite instead of its surface. However, for the case of 0.64% La/Ti$_2$NaY the roughness of the surface was decreased significantly to 44 nm due to the agglomeration of La oxide on the surface of zeolite. This result was in agreement with the XRD and TEM results.

3.2. Sonocatalytic Degradation Process

3.2.1. Control Experiment. Before starting the sonocatalytic reaction a preliminary study was carried out to investigate the color removal of Amaranth dye by the catalyst in the absence of ultrasonic irradiation. An aqueous solution of Amaranth with initial dye concentration of 10 mg/L was mixed separately with 1.5 g/L catalyst of Ti$_2$NaY and 0.64% La/Ti$_2$NaY at ambient temperature for 2 h in the absence of ultrasonic irradiation, and the pH of the dye around 5.6 was kept normal without any prior adjustment. No adsorption was indicated at the surface of the catalysts by using the magnetic stirrer for 2 h as it is shown in Figure 7. On the other hand, the degradation of the Amaranth by ultrasonic alone in the absence of catalyst was 12% only at the same reaction conditions of 10 mg/L of initial dye concentration, normal pH, and a catalyst loading of 1.5 g/L. This low activity of the ultrasonic was ascribed to the insufficient amount of $^\cdot$OH radicals generated by ultrasonic alone since radicals in this case were generated only through the dissociation of water molecules. As a result, the oxidation of the hydrophilic dye molecules could be only effective when these radicals were transferred from the interface of the caviation bubbles into the bulk solution [29]. However, encapsulation of titanium nanoparticles into the pores of zeolite gave significant enhancement in the sonocatalytic activity with maximum degradation efficiency of 50%. Increasing the sonocatalytic activity was completely ascribed to the synergistic between the encapsulated titanium and ultrasonic irradiation since no adsorption ability for the catalyst was detected. The effect of TiO$_2$ encapsulated into zeolite results will be discussed in details in the next section.

3.2.2. Effect of TiO$_2$ Amount Encapsulation into NaY. Sonocatalytic degradation of Amaranth dye with different amounts of titanium incorporated into the sodium zeolite was investigated and the results are as shown in Figure 8. The highest degradation value was 50% with Ti$_4$NaY which had the highest titanium loading among the materials tested. Increasing loading of titanium had minimal impact on the active catalytic surface due to the presence of Ti into the supercages in zeolite Y. As such, preference accumulation of titanium in these supercages would render the internal micropores of the zeolites to be virtually unaffected by the nanoparticles [20]. As such, minimal drops in the pore area and volume were demonstrated by the titanium-modified zeolite Y samples. The results also suggested that ultrasonic waves could reach the internal pores through the water medium. This was clearly the superior characteristic of ultrasonication process. Higher number of titanium sites enabled more generation of hydroxyl radicals upon ultrasonic irradiation to improve the degradation efficiency. The presence of the heterogeneous catalyst with the ultrasonic irradiation enhance, the activity of sonocatalytic process due to the effect of mechanical stirring produced by ultrasonic, the mass
transfer, and the activation of the catalyst surface leading to the generation of more reactive nucleation sites which were responsible for the production of more hot spots to enhance the production of free radicals [18].

3.2.3. Effect of La Loading on Titanium Oxide Encapsulated into NaY. The catalyst with the highest titanium content that is, Ti4NaY, was chosen to load the lanthanum nitrate with different loadings, that is, 0.32, 0.64, and 1.28 wt.%, of La in order to investigate the effect of this metal on the sono-catalytic process. Figure 9 shows the degradation of Amaranth during the ultrasonic-assisted reaction at 10 mg/L initial dye concentration, original pH with a catalyst loading of 1.5 g/L for 2 h. No significant enhancement in decolorization efficiency was noticed after the loading of La onto
The catalytic activity with different wt.% La loading was reduced from 50% for Ti\textsubscript{4}-NaY to 33% for 1.28% La/Ti\textsubscript{4}-NaY. This reduction in catalytic activity was associated with the agglomeration of the lanthanum oxide, that is, La\textsubscript{2}O\textsubscript{3} nanoparticles which might be formed after the calcination step mainly on the external surface of the zeolite. Thus the nanoparticles, of La oxide could block the production of TiO\textsubscript{2} clusters and shield the irradiation source from reaching the titanium clusters encapsulated into zeolite. This result was in agreement with the XRD and the AFM results as most of La oxides formed were located at the surface of the Ti\textsubscript{4}-NaY catalyst. Furthermore, with increasing the La loading, the ability of these ions to separate electron-hole pairs will be reduced. These results can be supported by the results obtained from Uv-Vis analysis since slight enhancement in energy gap was only occurred and further increase in wt.% of La caused a blue shift to lower wave length thus causing more reduction in catalytic activity up to 33%.

Ökte and Yılmaz [3] reported that the loading of La into TiO\textsubscript{2}-ZSM-5 catalyst enhanced the catalytic activity for the degradation of methyl orange dye. However, the locations of the La and TiO\textsubscript{2} were both at the surface of ZSM-5. Inversely, the present work is dealing with the effect of La loading with titanium encapsulated into zeolite. The differences in the characteristics of the catalysts produced in this work...
were ascribed to the metal incorporation procedures and its location with respect to zeolite structure. Our earlier work [30] successfully synthesized the Fe loaded on TiO$_2$ encapsulated into zeolite and it was confirmed to be a promising catalyst due to its high decolorization efficiency. The Fe ions were able to enter the lattice of Ti$_4$-NaY due to the smaller size of Fe$^{3+}$ in comparison to that of La$^{3+}$ and cause a significant reduction in the energy gap of the produced catalyst up to 2.8 eV at loading of 0.8 wt.% of Fe ion. As such, important factors should be considered to get best catalytic activity, that is, selection of the suitable preparation method selection of the suitable dopant metal bearing in mind the ionic radius of the metal and the pore size of the support.

4. Conclusions

Different amounts of titanium were successfully encapsulated inside the cages of Y zeolite using ion-exchange method. Characterization results suggested that the structure of zeolite remained virtually unchanged after the encapsulation. There was no titanium atom observed on the surface of the zeolite catalyst according to the EDAX and AFM analyses to suggest the successful incorporation within the internal pores. The UV-Vis spectrum for Ti$_4$-NaY demonstrated blue shifts towards short wave lengths while a slight red shift was detected after the loading of 0.64% La into Ti$_4$-NaY. The maximum degradation efficiency of Amaranth in 2 h was 50% and it was observed with the highest titanium amount loading in Ti$_4$-NaY. The encapsulated titanium into zeolite improved the activity of the zeolite catalyst in the sonocatalytic process owing to the ability of the ultrasound to penetrate into the micro- or mesoporous supports that improved the generation of the radicals by the TiO$_2$ located within the zeolite host. On the other hand, the activity of the catalyst decreased after the doping with lanthanum. This reduction in catalytic activity was ascribed to the poor contact between the metal that was mostly existed at the external surface of the catalyst and the titanium nanoparticles that were encapsulated into the supercages of zeolite.

Acknowledgment

The Research University grant from Universiti Sains Malaysia to support this work is gratefully acknowledged.

References


Submit your manuscripts at
http://www.hindawi.com