Photo Catalytic Activity of TiO$_2$ Immobilized on a 13X Zeolite Based in Removal of Ethyl Benzene Vapors under Visible Light Irradiation

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**Abstract**

Ethyl benzene is a volatile organic compound that is widely used in various industries. Ethyl benzene is a hazardous air pollutant not only for the environment but also for human health and hence there is a possibility of carcinogenesis in long-term exposure. Considering the fact that ethyl benzene is photo catalytic activity based in removal of VOCS vapors under visible light irradiation leading to serious health problems, the present study aimed to evaluate the gas-phase from airflow using photo catalytic property of titanium dioxide on 13X zeolite, in Ahvaz, Iran. In this experimental study, the characteristics of the catalysts were determined using BET method, X-ray diffraction (XRD), and scanning electron microscopy scanning (FESEM). Ethyl benzene vapors were produced using a dynamical condenser system and the efficiency of removal of ethyl benzene vapor depletion was investigated using 13X/UV and 13X/UV/TiO$_2$ (5 wt. %). The obtained results of the images and spectra from XRD, and FESEM showed good signs of immobilization. The findings revealed that the removal efficiency decreased by increasing the concentration from 25 ppm to 125 ppm and increasing the flow rate from 0.5 to 1.00. The removal efficiency at concentrations of 25, 75, and 125 was 57.8%, 37.2 %, and 24.64, respectively. The results showed that the use of substrates increased the efficiency of photo catalytic removal, by about 60%. It is therefore suggested that these adsorption and photo catalytic combination systems be used to remove other volatile organic compounds in the gas phase.
**Introduction**

A catalyst is a type of matter that reduces the activation energy of the reaction (the initial energy to perform the reaction) and thus increases the reaction rate. The metals that mediate the periodic table of elements are the most common catalysts. Catalysts are divided into two categories: Homogeneous and Heterogeneous. The catalyst is homogeneous, single atom, ion or molecule and is in phase with the reactants. In other words, homogeneous catalyst particles are easily dissolved in the reaction mixture. The homogeneous catalyst was consumed in the reaction and was produced (Recovery). Very high activity, selectivity and good efficiency are the advantages of this type of catalyst. Improvements in the performance of homogeneous catalysts can be achieved by attaching different organic and inorganic groups to the parent particle. The main problem with homogeneous catalyst technology is that after the reaction is complete, separating the dissolved catalyst from the final mixture is not an easy task. This problem is a major challenge, especially when the catalyst is consumed in small amounts.

The heterogeneous catalyst is not in the same phase with the reactants. The size and properties of the heterogeneous catalyst particles are such that they do not dissolve easily in the reaction medium, hence, its activity is limited (the total efficiency of the reaction decreases). Unlike homogeneous catalysts, heterogeneous catalysts are easily (with less cost, time, and materials) separated from the reaction mixture and do not cause impurities in the products. In order to compensate for the lack of active surface in such compounds, it is necessary to use a support in the role of catalyst support. The substrate is usually a porous structure with a high active surface. A suitable catalyst must have a large active surface and be separable. Nanotechnology can provide a very large active surface for the catalyst. Although the active level of nano catalysts is much higher than that of conventional catalysts, the active level of a nano catalyst is always lower than that of a homogeneous catalyst (the homogeneous catalyst is in complete contact with the reaction contents upon its dissolution). In contrast, catalytic nanoparticles are insoluble in the reaction solution and can easily be separated due to their larger dimensions than homogeneous catalyst particles. The high active surface, along with the ability to separate the catalyst at the end of the reaction, make the nano catalysts a bridge between homogeneous and heterogeneous catalysts. The complex process of producing some nano catalysts may be costly, but this can be overlooked because nanotechnology reduces the amount of catalyst, energy, and reaction time required. Volatile organic compounds (VOCs) are of low-risk concentrations. The most common pollutants are identified both in urban and industrial areas. They are costly, have short life spans, and lead to the production of secondary pollutants. They are emitted into the atmosphere from major industrial sources and especially petroleum derivatives that hydrocarbons hazardous for human health and the environment. In addition, VOCs emitted from indoor and outdoor air have hazardous air pollutants [1]. Ethyl benzene is one of the major VOCs that can cause many fatal or chronic health-related problems and irritation of nose and eyes. Also, it can bring about potentially various illnesses and toxic, mutagenic and carcinogenic effects [2]. According to the Environmental Protection Agency, acute exposure to ethyl benzene creates effects such as suppressing the central nervous system [3]. Ethyl benzene critically affects liver and kidneys and blood and convulsions, and respiratory paralysis. Thus far, zeolite-based catalysts have been studied extensively to remove ethyl benzene using effective technologies [4]. Therefore, catalyst development is needed to control the exposure to ethyl benzene. Today, photo catalytic removal methods have received a great deal of attention in comparison with other methods of removing pollutants. Therefore, target analyses of air quality monitoring are for abating the emissions VOCs and enforcing the development of effective technologies [5]. American Council of Governmental Industrial Hygienists recommends a threshold limit value (TLV) of 100 ppm and a short-term exposure limit of 125 ppm for ethyl benzene. The current Occupational Safety and Health Administration permissible exposure limit is equivalent to the TLV.
The photo catalytic process includes activation of semiconductors by UV visible light radiation [7]. The efficiency of photo catalysis depends on the process of separating electrons from the semiconductor photons, the electron-hole pair will produce the formation of hydroxyl radicals oxidizing and the process recombination of the pair hole-electron [8]. The properties of the nanoparticles are anatase with rutile from titanium dioxide (TiO$_2$) that have been the most widely studied material in the field of photo catalysis with UV light, the illumination of ultraviolet (UV) light [9]. For this purpose, Silica, alumina, zeolites, clay, bone char and Zeolites, proved already as an efficient absorbent and widely used material for the removal of all kinds of organic pollutants, were applied. Adsorbing efficiency is perfect support for this work due to the three-dimensional structure, high chemical resistance, and physical and crystalline also their uniform cavities unique structure [10-11]. Literature shows adsorbents such as zeolites are effective eliminating the pollutant and used as a photo catalyst on the adsorbent with high removal efficiency [12-13]. Therefore, the current study aimed to determine the efficiency of removal of ethyl benzene vapor from airflow using photo catalytic property of titanium Dioxide on 13X zeolite. The impregnation method is one of few environmentally safe processes for the preparation of photo catalysts based on 13X zeolite. Nanomaterials such as zeolite is an important field of study in toxic airborne contaminants degradation. This study considers pollution in air as representative of VOCs, and selected ethyl benzene. Zeolites such as 13X is widely used in the industry and possesses good light transmission. They have also been used to enhance the oxidation of the adsorbed VOCs [14-16]. Therefore, photo degradation rate using TiO$_2$/13X was investigated. Photo catalytic papers fabricated from 13X zeolite-based Nano titanium dioxide (TiO$_2$) for activation under visible light irradiation was considered [17]. The photo catalytic process includes activation of semiconductors by UV or appropriate visible light or photons, the electron-hole pair to produce hydroxyl radicals to eliminate various pollutants in a randomized process. The efficiency of photo catalysis depends on the process of separating electrons from the semiconductor and the process recombination of the electron-hole pair [18]. In photo catalysis, a known method for advanced oxidation processes is via the excitation of a semiconductor with UV light [19]. Titanium dioxide (TiO$_2$) has been the most widely studied material in the field of photo catalysis [20-22].

**Material and methods**

In this study, Zeolit 13X granolas with a diameter of 0.5-1 mm were used. Ethyl benzene (purity>99 %) and nanoparticles titanium dioxide (TiO$_2$) with a size of SSA of 35 m$^2$/g and diameter 40 nm (made in Sigma Aldrich-USA) were applied. Other required materials were purchased commercially from Merck Germany. In this experimental study, the characteristics of the catalysts were determined using Burner-Emmett-Teller, X-ray diffraction (XRD), and scanning electron microscopy scanning (FESEM). Ethyl benzene vapor was produced using a dynamical condenser system and the efficiency of ethyl benzene vapor depletion was investigated using UV/13X/TiO$_2$ similar to our previous study [26].

**Immobilization of TiO$_2$ nanoparticles on surface 13X zeolite**

Adsorption sites of the 13X were improved through loading TiO$_2$ (five wt. %). So, double distilled water was prepared. Ethyl benzene vapor was measured using a Tiger PID Pho check device (a portable direct reading device for measuring the gaseous composition of VOCs using the ion detection method). All measurements were performed before and after air entering the pilot system. Finally, in the optimal photo catalytic process system, GC-MASS method was used to evaluate the output of by-products. Following the complete mixing, the solution was shaken for 30 min. Then, a specific amount of 13X zeolite was added to the suspension TiO$_2$ and exposed to ultrasonic waves for 30 min. In order to position the nanoparticles on the pores of 13X zeolite, the solution was fitted on a shaker for 2 h. Finally, for stabilization and calcination of TiO$_2$/13X, the mixture was kept at 300 °C for 2 h. TiO$_2$/13X catalysts were prepared following corresponding aqueous solution of metal nitrates.
and sieved to 20-40 mesh desired concentration. Common synthetic zeolites such as 13X are widely used to separate O\textsubscript{2} & N\textsubscript{2} from air by pressure-swing adsorption, and provide an immediate starting point for our work [23-25].

Setup of the photo catalytic system
Figure 1 shows a general experimental setup pumps (Model No. Hitachi Ltd. Tokyo Japan) 51 w with a pressure of 11.47 mmHg, pumping dry air through a reservoir of ethyl benzene liquid brought ethyl benzene gas. After that, the gas was mixed and diluted in air mixer to meter ethyl benzene into an air atomizing nozzle (Spraying Systems). To provide illumination, three six w UV-lamps outside of the reactor with three UV-A lamps 8 w (8 W) were located horizontally on top of the reactor. They emitted light at a primary wavelength of 365 nm. A fiberglass film horizontally situated 1 cm higher than the UV lamp supported the catalysts. The detection system involved the Pho Check Tiger (model 5000, UK) to analyze the ethyl benzene concentration. The ethyl benzene vapor with the humid and clean air was injected for full transfer of radiation of UV with a reactor (with a length, diameter, and thickness of 280, 20, and 2 mm, respectively). Adsorption of ethyl benzene on the surface of raw the13X zeolite in each cycle is listed at concentrations of 25, 75, and 125 ppm, different flow rate (i.e., 0.50, 0.75, and 1.00 L/min) with and without UV lamp. Pumping dry air through a reservoir of ethyl benzene vapor was carried out dynamically and in a gas phase intervals (5 min) on 13X/UV and 13X/UV/TiO\textsubscript{2} nanoparticles. Organic compounds on the deactivated supports or catalysts were extracted and analyzed by GC–MS [26].

![Figure 1. Photo catalytic reactor setup](image)

**Figure 1. Photo catalytic reactor setup**

Characteristics of photo catalysts
Morphology of the characteristics of photo catalysts as images produced by scanning electron microscopy and compared using a field emission sweep electron microscope (FESEM) indicated that pores on 13X and/13X TiO\textsubscript{2} were occupied providing coverage in a homogeneous manner. Measurement of S\textsubscript{BET} indicated that specific surface area of 13X zeolite was reduced after putting catalyst onto 13X where this reduction was due to penetration of catalyst 13X/TiO\textsubscript{2} into porosities of 13Xzeolite (Table1).

**Note:** Scanning electron microscopy (Philips-XL30 the Amsterdam, Netherlands), micrographs of raw ZSM-5 zeolite (a), 13X-TiO\textsubscript{2} (c), pure TiO\textsubscript{2} (b) photo catalysts calcined. Surface appearances of catalysts were performed on a Hitachi Philips-XL30 the Amsterdam, Netherlands model, and emission
scanning electron microscopy (FESEM) with the acceleration voltage was 150KV manufactured [27].

Figure 2. SEM images of: (a) raw 13X zeolite; (b) TiO2; and (c) 13X/TiO2 5 wt.

The chemical states and the crystal structures of the support of the active component on the catalyst detected by XRD technique were indicated. In this study there was x-ray powder diffraction in Figure 3. (XRD) model (TEM, Philips-PW1800- 15000 kv, IR) with the wavelength of the device by 1.54A with the producer 40 Kv, 40 mA. Determination of the specific surface area and pore size was from the BET (Quanta chrome Cheam device). As shown in Figure 3, the pattern indicates the characteristic sharp peaks at 2θ of 5.09, 10.98, 11.84, 14.08, 20.7, 25.55, 35.91, 37.72 and 45.64 by their intensities (561, 836, 734, 629, 868, 994, 254, 365 and 302). XRD patterns of 13X-TiO2 bed are given in Figure 4 that confirm the presence of TiO2 on the bed. The XRD pattern showed in Figure 3 was similar to that reported in literature [29]. Findings obtained from SEM and BET indicated that specific surface area of 13X reduced after putting catalyst onto zeolite [26-30].

Figure 3. XRD patterns of the fresh, deactivated, and regenerated (a) 13X and (b) 13X/TiO2.

Result and discussions
In the partial samples recovered pore volume and BET (Bruner-Emmett-Teller) were used. Specific surface area (SSA), BET Quanta chrome Cheam were based on adsorption or repulsion of liquid nitrogen methods. Surface area (m²/g) of 13X and 13X TiO2 Sample S_BET in the same experimental settings of the photochemical removal efficiency of ethyl benzene was improved as the irradiated light intensified. Specific surface area of the produced TiO2/13X catalysts (349 m²/g) decreased compared with the raw 13X (368.9 m²/g). Table1 shows the main reason may be attributed to the blocking of some of the mesoporous and micropores of the raw 13X with coating TiO2 on the surface, which caused a reduction of the surface area and the average pore diameter of the zeolite [31-35].
Because of such interesting properties, zeolites are widely used as catalysts and adsorbents for organic synthesis and decomposition as well as in waste-gas since 13X-zeolite, ZSM-5 (Si/Al=2.75) has relatively large pores (entry aperture: 0.74 nm; diameter: 1.3 nm) than other zeolites, such as zeolite 13X. The Si/Al ratio determined by ICP analysis, increasing from 21.6 to 23 at 13X zeolite.

The results of this study on the gas-phase photo catalytic degradation of ethyl benzene and using 13X/UV/TiO₂ nanoparticles supported 13X zeolite in a photo catalytic. The mixed polluted air was pumped into the photo catalytic reactor until adsorption reached equivalence. Analyzing 13X/UV/TiO₂ concentrations was performed using the Pho Check Tiger apparatus with a photoionization detector (PID) [31-35].

Table 1: Results of the BET tests

<table>
<thead>
<tr>
<th>Element</th>
<th>Zeolite (13X)</th>
<th>TiO₂/(13X)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Special surface m²/g</td>
<td>368.9</td>
<td>349</td>
</tr>
<tr>
<td>The average diameter of the cavities</td>
<td>5.23</td>
<td>0.22</td>
</tr>
<tr>
<td>Total volume cm³/g</td>
<td>0.27</td>
<td>0.19</td>
</tr>
</tbody>
</table>

Table 2: Results compared to Zeolite (13X) & (ZSM-5)

<table>
<thead>
<tr>
<th>zeolite</th>
<th>Zeolite type</th>
<th>Company</th>
<th>SiO₂/Al₂O₃</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5</td>
<td>zeolite (ZSM-5)</td>
<td>21.6</td>
<td>356.4</td>
<td></td>
</tr>
<tr>
<td>13X</td>
<td>Zeolite (13X)</td>
<td>23</td>
<td>368.9</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4: the effects of different concentrations and gas flow rates at the adsorption efficiency of ethyl benzene (on the surface of raw 13-x zeolite)

The results on ethyl benzene at a variety of concentrations (25, 75, and 125 ppm) and flow rates (0.5, 0.7, and 1.0 L/min) from volatile organic compounds to determine of adsorption efficiency are shown in Figure 4. The input ethyl benzene concentrations and flow rates were studied as effective functional parameters on the adsorption process [31-32].

Figure 5. Effect of different concentration and gas flow rates at efficiency of degradation reaction of ethyl benzene on the 13X / TiO₂
The removal efficiency at concentrations of 25, 75 and 125 ppm was 57.8%, 37.2%, and 24.64%, in the flow rate 0.5 L/min, respectively. Also, increasing the flow rate from 0.5 to 0.1 L/min, removal efficiency of ethyl benzene at concentration of 25 decreased from 57.8% to 50.8% to 42.8%, respectively from volatile organic compounds to determine of degradation reaction as shown in Figure 5. These findings are consistent with the studies done earlier [32-34].

**Figure 6.** TiO$_2$/13X photo catalytic degradation performance based on the concentration and flow rate

Analyzing the effect of primary input concentration from 25–125, ppm showed the rate of efficiency was reduced from 58% to 24.8% in the flow rate from 0.5 L/min and 50.8% to 19.6% in the flow rate 0.75 L/min and 42.8% to 16.8 % in the flow rate 1.01 L/min (Figure 6). Similarly, the rate of optimal radiation intensity of ray was acquired by 1.75 W/cm$^2$ in this study. The use of a hybrid photo catalytic system (TiO$_2$ Nano coupled oxide) and application of absorbent (13X) may be efficient and effective for refinement of ethyl benzene from airflow [36-38].

**Figure 7.** A comparison between adsorption efficiency of ethyl benzene on the surface of TiO$_2$/13X with/without UV lamp and with time at flow rate 0.5 L/min

A comparison was made between adsorption efficiency of ethyl benzene at 25-125 ppm concentration on the surface of raw 13X, 13X/TiO$_2$ with time at flow rate of 0.5-1 L/min. The finding showed on the surface of raw the13X zeolite was 98%, 41%, and 4% at the same time and flow rate was 0.50, L/min, respectively and on the surface of the13x zeolite with TiO$_2$ nanoparticles 98.64%, 56%, and 32% at flow rate was 0.50, L/min at the same time, respectively [36-39].

Unlike other studies conducted statically or in aqueous phase, this study was carried out dynamically in a gas phase. Our results showed that doping of TiO$_2$ nanoparticles could increase the energy of the bands of the semiconductor TiO$_2$ material. Moreover, this process promoted the photo catalytic activity of TiO$_2$. [40-42]. A synergistic effect was also observed when TiO$_2$ and 13X were simultaneously used for the photo catalytic degradation of Ethyl benzene. However, the saturation capacity of this system 13X TiO$_2$ Nano composite and hybrid photo catalytic system 13X TiO$_2$ could be assess in future research [42-46].
Conclusions
The efficiency results of TiO$_2$/13X/UV (5 wt. %) with use of a hybrid photo catalytic system efficiency of degradation of ethyl benzene under 25±1 °C, humidity: 35 ± 1 increased as it was added to radiation intensity under the same experimental conditions. These findings may be justified in the way that photo whole ray production has increased due to increase in intensity of radiation of this ray and finally this may increase efficiency of photo catalytic removal of ethyl benzene. The results indicated that 13X-TiO$_2$5% in the presence of UV irradiation more effectively removed Ethyl benzene because Ethyl benzene adsorbed by 13X-zeolite in the hybrids 13X-TiO$_2$ could then be continuously decomposed by UV in the presence of the TiO$_2$ photo catalyst on the hybrid. Using 13X-zeolite, the removal of Ethyl benzene from air occurs only by adsorption, as it does not have any photo activity. The maximum removal efficiency (58%) was found after action with photocatalyst13X TiO$_2$ nano coupled oxide for 11 hours on UV/13X-TiO$_2$ catalysts in both processes, adsorption of Ethyl benzene by the activated 13X-zeolite and its degradation by TiO$_2$photo catalysts, occurring at the same time. Since the adsorption process of the 13X-zeolite proceeds much faster than that by photo catalysis, the removal of Ethyl benzene occurs mainly by the former rather than the later. The removal of Ethyl benzene gradually increases, because of the combination of processes, adsorption and degradation. Therefore, in addition to the synergistic effect of TiO$_2$ loading, the findings of the present study suggest that the rate of stabilized TiO$_2$ nanoparticles on the 13X-zeolite is effective in the photo catalytic removal. Studies have suggested that the increase of the percentage of catalyst to a certain extent could be due to an increase in the contaminant removal. Use of a hybrid photo catalytic system (13X TiO$_2$ Nano coupled oxide) and application of absorbent (13X) may be efficient and effective for refinement of ethyl benzene from qualitative articles.

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Conflict of Interest
Conflict of Interests: The authors declare no conflicts of interest

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