Performance of surface fluorinated P25-TiO$_2$ on the photocatalytic degradation of volatile organic compounds in indoor environment

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Abstract. Volatile organic compounds (VOCs) are considered as a major group of indoor air contaminants with several adverse health effects. Photocatalytic oxidation process (PCO) has been applied for the removal of indoor VOCs. In the PCO process, the adsorption extent of water molecules on the surface of photocatalysts is a decisive factor for PCO efficiency. Water molecules contribute in PCO process either as; a) the main hydroxyl radical’s source and enhance the removal efficiency, or b) compete with VOCs to adsorb on the super-hydrophilic surface of P25 and reduce the photodegradation efficiency. In this study, the effects of surface fluorination on the photocatalytic efficiency and surface hydrophilicity of commercial P25 were investigated. The fluorinated P25 (F-P25) nanoparticles were synthesized to remove methyl ethyl ketone (MEK) from the indoor environment. Surface fluorination formed the surface $≡Ti–F$ by an exchange reaction between the surface hydroxyl groups (OH) and fluoride ions (F$^-$) and decreased the water vapor adsorption on the photocatalyst’s surface. Herein, the photocatalytic efficiency of F-P25 was compared to P25 under a continuous-flow condition with a small residence time (0.026 sec) at four different relative humidity levels (0, 20, 40, and 60%). Furthermore, the performances of F-P25 and P25 on the generation of by-products, including formaldehyde and acetaldehyde were also evaluated. The results revealed that the F-P25 enhanced the photodegradation of MEK compared to bare-P25 in all tested relative humidity levels; however, the generation of the by-products increased as relative humidity increased.

1. Introduction
Indoor air pollution is considered as one of the top five environmental risks to public health, since people spend most of their time in indoor environments [1]. Volatile organic compounds (VOCs) are known as major indoor air pollutants, affecting human health, comfort, and productivity [2]. VOCs arise from many different household’s items and building material including, cleaning products, furniture, carpets, paint, etc. [3]. There is a need for efficient air purification systems that could be able to control the quality of the indoor air. Moreover, it is worth to investigate the performance of the air purification system under the conditions, which resemble real indoor applications. Heterogeneous photocatalytic oxidation (PCO) of VOCs, using the semiconductor photocatalysts, is a promising technology for air purification [4]. This process requires light illumination with sufficient energy to excite an electron from the valance band to the conduction band. The formation of the charge carriers (electron and hole) is a crucial step in the PCO process [5, 6]. Among a wide variety of semiconductor photocatalysts, TiO$_2$ has been widely used as an effective photocatalyst for VOC removal from the indoor environment, since it has great capability to decompose various VOCs [7-9]. Additionally, it has unique characteristic given TiO$_2$ low cost, chemical inertness, strong oxidizing power, and long-term stability against photo-corrosion [7, 10]. However, the high charge carrier’s recombination of TiO$_2$ limits its application. Moreover, its photocatalytic activity declines under high humid condition due to its super-hydrophilicity.

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Surface fluorination of TiO₂ is considered as a surface modification method, which can alter the surface characteristic such as surface area and surface charge. Fluorinated P25 can enhance the charge carrier separation and retard the recombination rate of electron and hole. This is because of the strong electronegativity of surface ≡Ti-F group and holding the photogenerated electron to reduce charge carrier recombination [11].

Weon et al. [3] reported that the surface fluorination enhanced the mobile OH radicals, facilitating the mineralization of VOCs by PCO process. They studied the toluene degradation in a closed-circulating reactor with a long residence time (30 min), which may not be feasible in real environments. Wu et al. [11] reported that the surface fluorinated TiO₂ reduced the charge carriers’ recombination rate and enhanced the photoactivity of the photocatalyst.

In the present work, the effect of surface fluorination on P25 photocatalyst is studied. By fluorinating P25, the surface hydrophilicity is reduced leading to decrease adsorption of water vapor on photocatalyst surface even at high relative humidity. As a result, there are higher chances for MEK to adsorb on photocatalyst’s surface in humid conditions. To investigate the performance of F-P25 photocatalyst, four different relative humidity levels (0, 20, 40, and 60%) were selected to study the MEK removal efficiency and by-product generation rates. To explore the effect of surface fluorination, the results were compared with those of untreated P25. The experiments are carried out at conditions close to the real applications such as humidity level (20-60%), low inlet contaminant concentration (1 ppm), and small residence time (0.026 sec).

2. Experiment

2.1. Experimental setup

The preparation of F-P25 photocatalyst is reported in our previous work [7]. Moreover, the results of different characterization tests including the N₂ adsorption-desorption, X-ray Photoelectron Spectroscopy (XPS), and Scanning Electron Microscopy (SEM) are provided in our previous work [7].

The schematic diagram of the experimental setup is provided in figure 1. As seen, a continuous type reactor with a dimension of 7 cm × 9 cm × 100 cm (height × width × length) is employed. The reactor is designed to be versatile in order to utilize a different number of lamps and photocatalyst layers. High-pressure mercury lamps are used to provide UV light irradiation.

![Figure 1. Schematic diagram of experimental setup.](image)

The light intensity of UV lamps was measured by a spectroradiometer (International Light Technologies). The light intensity at each side of the photocatalyst was 37 W/m². In this setup, all tubing
and fittings were made of PTFE and stainless steel. For supplying the carrier gas in this setup, two separate compressed air lines were used. To adjust the humidity of the carrier gas, one of the compressed air lines passed through a mass flow controller (MFC, OMEGA, model FMA5442ST), followed by a vessel of distilled water as the humidifier. The second compressed air line was used for adjusting the specific flow rate and humidity. A syringe pump (KD Scientific, Model KDS-210, USA) was employed to automatically inject the MEK contaminant into the setup with a certain injection rate. PID detector (ppb3000 RAE, USA) was used to continuously monitor the MEK concentrations at upstream and downstream to find out the saturation point of the photocatalysts.

2.2. Analytical instrument and method
A high-performance liquid chromatography (HPLC, PerkinElmer Flexar) was utilized to analyze the MEK concentration at inlet and outlet, as well as the generated by-products. For HPLC analysis, the target compounds and generated by-products were collected on the 2, 4-dinitrophenylhydrazine (2,4-DNPH) cartridges (Sigma Aldrich) by sampling pump at 1 L/min for 20 minutes. After sample collection, the adsorbed compounds on LpDNPH cartridge were eluted by acetonitrile and were analyzed by HPLC (column: SUPELCOSIL™ LC-18, 25 cm × 4.6 mm ID, 5 µm film thickness) with UV-vis detection. The samples were analyzed by EPA TO-11a method [12]. In this method, acetonitrile (72%) and deionized water (28%) were used as mobile phases with a flow rate of 1 mL/min. The injection volume was 20 µL.

2.3. Measurement of photocatalytic oxidation efficiency
The photocatalytic activity of F-P25 and P25 photocatalysts was evaluated at different relative humidity levels towards MEK degradation under UV light irradiation. Table 1 shows the operating parameters for MEK photocatalytic oxidation experiments. Once the experimental condition such as airflow rate, humidity, and temperature became stable, the injection of MEK contaminant with a specific injection rate was started. After 1h, when the adsorption of MEK on the surface of photocatalyst reached an equilibrium condition, the PCO reaction was initiated by turning on the UV lamps. After reaching a steady state, the sampling from the upstream and downstream ports were taken for HPLC analysis. The sampling was repeated three times, which showed stable repeatability with a standard deviation of less than 1%. The standard deviations are shown in figure 2 by vertical bars.

| Parameters                  | Value                      |
|-----------------------------|----------------------------|
| Temperature                 | 23 ± 1 ºC                  |
| Relative humidity           | 0, 20, 40, and 60 ± 1%     |
| Airflow rate                | 0.015 ± 0.001 m³/min       |
| Inlet concentration         | 2.95 mg/m³ ± 0.35 (1000 ppb)|
| Light intensity             | 37 W/m²                    |
| Volume of reactor           | 6.3×10⁻³ m³                |

3. Results and discussion
3.1. Effect of surface fluorination on PCO
Surface fluorination is an effective surface modification method to improve the photoactivity of semiconductor photocatalyst [13]. The surface fluorination could greatly alter the surface characteristics such as surface area, surface charge, polarity, and acidity. These factors influence the adsorption capacity and selectivity towards the challenge compounds. The strong electronegative fluoride ions on the surface (=Ti-F groups) lead to having more negatively charged surface on F-P25 photocatalysts. This modification process may cause higher adsorption of the positively charged compounds on the
surface [14]. In addition, it enhances the surface electron storage, inhibiting the charge carrier recombination [15]. The surface fluorination can be originated by a simple ligand exchange between surface hydroxyl groups (-OH) and fluoride anions (Equation 1) [13, 15]. According to Equations 2 and 3, it is expected that the surface fluorination of TiO₂ improves the interfacial charge transfer and surface-free hydroxyl radicals [3, 13].

\[
\equiv Ti - OH + F^- \leftrightarrow \equiv Ti - F + OH^-
\]  
\[
TiO_2 + h\theta \rightarrow e^-_{CB} + h^+_{VB}
\]  
\[
\equiv Ti - F + H_2O (or \ OH^-) + h^+_{VB} \rightarrow \equiv Ti - F + \bullet OH_{free} + H^+
\]

According to Equation 3, surface \equiv Ti-F groups facilitate the hole transfer in order to produce mobile OH radicals with higher oxidation potential compared to the surface bounded OH radicals, resulting in oxidizing the organic pollutants with higher efficiency [16].

3.2. Effect of relative humidity on photocatalytic activity

The single pass removal efficiency of both F-P25 and P25 photocatalysts for MEK degradation under UV irradiation is calculated by the following equation [17]:

\[
\eta (\%) = \frac{Q_{air}(C_{up}-C_{down})}{Q_{air}C_{up}} \times 100 = \frac{C_{up}-C_{down}}{C_{up}} \times 100
\]

where \( \eta \) (\%) is the single-pass removal efficiency of MEK contaminant, \( C_{up} \) and \( C_{down} \) are the upstream and downstream MEK concentration (mg/m\(^3\)), respectively, and \( Q_{air} \) is the airflow rate (m\(^3\)/min).

By-product generation rate during the PCO reaction of MEK is calculated by the following equation:

\[
\rho_{by-product} = \frac{Q_{air}(C_{down}-C_{up})}{m \times A_{BET}}
\]

where, \( \rho_{by-product} \) is the by-product generation rate (mg/m\(^2\). min), \( m \) is the photocatalyst mass (g), and \( A_{BET} \) is the BET surface area of photocatalyst (m\(^2\)/g).

Photocatalytic oxidation is hindered at high relative humidity due to the super-hydrophilic surface of TiO₂. Based on the reported literature, the presence of water molecules influence the MEK adsorption, photocatalytic degradation, and the generation of by-products in the PCO process [18, 19]. At high humidity level, water vapors adsorb on the surface of P25 and create a cluster, hindering the adsorption of MEK on the surface. In this study, the surface fluorination was employed as a surface modification technique to reduce the surface hydrophilicity of P25. Accordingly, to evaluate the performance of F-P25, four different relative humidity levels (0, 20, 40, and 60%) were selected. Figure 2 presents the results of MEK removal efficiency on P25 and F-P25 surface. As shown, F-P25 enhanced the removal efficiency in all humidity levels compared to P25. For both photocatalysts, by increasing the relative humidity from 0% to 20%, the MEK removal efficiency is enhanced. Further increases in the relative humidity from 20% to 60% decreased the MEK removal efficiency. This can be explained by the fact that the PCO process needs the hydroxyl radicals to oxidize the VOC pollutants and water vapor is the main source of hydroxyl radicals. The surface fluorination enhanced the surface area which further increases the PCO reaction on the surface. However, the excess amount of water vapor can occupy the active sites of the photocatalyst, since the surface of photocatalysts has a limited number of active sites. As a result, the MEK molecules could not be adsorbed on the surface of the photocatalyst to complete the degradation process. By surface fluorination, the hydrophilicity of surface is reduced and more number of MEK molecules could be adsorbed on the surface of F-P25 instead of water molecules, leading to a higher PCO efficiency of MEK. The improvement of the performance of F-P25 photocatalyst compared to P25 was more obvious at higher RH whereas there are more water molecules.
One of the main concerns of the PCO process is the generation of by-products during the process [20, 21]. Therefore, it needs further investigation to study the formation of the by-products under small residence time, diverse relative humidity levels, and low contaminant concentration conditions. In this research, besides the removal efficiency, the by-product generation rate is investigated and the results are tabulated in Table 2. Three by-products, including formaldehyde, acetaldehyde, and acetone, are detected by the applied HPLC method. As presented, for F-P25, increasing the relative humidity increased the acetaldehyde generation rate. While, acetone generation rates were quite stable in all humidity conditions for both photocatalysts. Formaldehyde generation rates for both photocatalysts were the lowest at 20% relative humidity, whereas the removal efficiency was also the highest. Further increasing in relative humidity from 20% to 60%, the formaldehyde generation rate was increased. This can be explained by the fact that the active sites of photocatalysts have limited adsorption capacity. Consequently, by increasing the relative humidity, the competition between water molecules with MEK and the generated by-products reduced complete mineralization of by-products.

Table 2. Effect of relative humidity on by-product generation rate of both P25 and F-P25 photocatalysts (mg/m².min × 10⁶).

| Photocatalyst | By-product | RH=0% | RH=20% | RH=40% | RH=60% |
|--------------|------------|-------|--------|--------|--------|
| P25          | Formaldehyde | 0.026 | 0.019  | 0.021  | 0.021  |
|              | Acetaldehyde | 0.060 | 0.057  | 0.077  | 0.094  |
|              | Acetone     | 0.002 | 0.004  | 0.004  | 0.004  |
| F-P25        | Formaldehyde | 0.031 | 0.020  | 0.032  | 0.036  |
|              | Acetaldehyde | 0.037 | 0.054  | 0.103  | 0.114  |
|              | Acetone     | 0.001 | 0.001  | 0.001  | 0.001  |
4. Conclusion
In the present work, the effect of surface fluorination of a commercial TiO₂-P25, was studied on the MEK removal efficiency and by-product generation. Surface fluorination considerably altered surface properties. This process increased the surface area and decreased surface hydrophilicity, which resulted in the improvement of the MEK removal efficiency at high humidity levels. To examine the photocatalytic activity of P25 and fluorinated-P25, four different relative humidity levels were selected. As results showed, the performance of F-P25 was improved compared to P25 in all tested conditions. This is due to the super-hydrophilic surface of P25, which adsorbs more water vapor instead of MEK molecules. In addition, the charge carrier’s recombination rate in F-P25 was lower than P25 because of storage of electron near the ≡Ti-F group on F-P25 surface.

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