

METAL DOPED TITANIUM DIOXIDE FOR REMOVAL OF FORMALDEHYDE VAPOR

NGHIÊN CỨU TỔNG HỢP VẬT LIỆU TiO_2 TÂM KIM LOẠI ĐỂ XỬ LÝ HƠI FORMALDEHYDE

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Abstract: Formaldehyde (HCHO) is one of the most popular volatile organic compounds (VOCs), which is toxic to human health. HCHO in indoor air is often of anthropogenic sources such as construction materials, home appliances, new furniture, office equipment, detergents, and refrigerants. In addition, HCHO is a product of cooking and burning incense daily in household. This work studies on the photocatalytic removal of formaldehyde in air with catalysts such as pure and metal doped titanium dioxides. Experiments to remove HCHO were carried by photolysis, adsorption and photocatalysis. The results showed that efficiency of photocatalysis was 1.6 and 3.8 times higher than those of adsorption and photolysis, respectively. The experiments were then conducted using TiO_2 (P25) modified at different temperatures, metal oxides, and metal/titanium ratios. Under test condition, the results showed that zinc doped P25 with Zn/Ti ratio of 0.5% and annealed at 500°C had the high removal efficiency of 98%. These results imply that zinc doped TiO_2 is a promising photocatalytic material for control of HCHO in air.

Keywords: HCHO, VOCs, photocatalytic oxidation, TiO_2 , doping metal

Classification number: 2.3

Tóm tắt: Formaldehyde (HCHO) là một trong những chất hữu cơ dễ bay hơi (VOCs) phổ biến và độc hại cho sức khỏe con người. HCHO trong không khí tại nhà thường có nguồn gốc nhân tạo như từ các vật liệu xây dựng, đồ gia dụng, đồ nội thất mới, thiết bị văn phòng, các chất tẩy rửa và chất làm lạnh. Ngoài ra, HCHO còn là sản phẩm của quá trình đun nấu và đốt nhang hàng ngày trong các hộ gia đình. Nghiên cứu này nhằm mục tiêu ứng dụng phương pháp quang xúc tác để xử lý hơi HCHO trong không khí sử dụng xúc tác TiO_2 tinh khiết và tâm với kim loại. Thí nghiệm được tiến hành để xử lý hơi HCHO với các phương pháp quang hóa, hấp phụ và quang xúc tác. Kết quả cho thấy phương pháp quang xúc tác cho hiệu quả xử lý HCHO cao gấp 1,6 lần phương pháp hấp phụ và 3,75 lần phương pháp quang hóa. Thí nghiệm quang xúc tác xử lý hơi HCHO sau đó được tiến hành với xúc tác P25 nung ở các nhiệt độ khác nhau, tâm kim loại khác nhau và tâm kim loại ở các nồng độ khác nhau. Kết quả thí nghiệm cho thấy xúc tác P25 tâm kẽm với tỉ lệ Zn/Ti là 0,5% và nung ở 500°C cho hiệu quả xử lý HCHO cao nhất, lên tới 98%. Các kết quả này cho thấy tiềm năng của vật liệu xúc tác TiO_2 tâm kẽm trong việc kiểm soát HCHO trong không khí.

Từ khóa: HCHO, VOCs, quang xúc tác, TiO_2 , tâm ion kim loại.

Chỉ số phân loại: 2.3

1. Introduction

Volatile organic compounds (VOCs) are one of the most common contaminants in indoor air, negatively affecting human health. According to the U.S. Environmental Protection Agency (EPA), the majority of

VOCs in indoor air come from household paints and furniture. Concentration of indoor VOCs are occasionally five times higher than outdoor VOCs [1]. VOCs are capable of irritating the eyes, nose, and skin and causing problems related to the lungs and airways. In

addition, VOCs cause headaches, dizziness, and liver and kidney damage [2].

HCHO is one of the most common and popular VOCs, widely used in industry and presented in many consumer products. HCHO is a colorless and smelly gas. It can be found in many construction materials such as plywood, glue, and paint. In medicine, HCHO is often used for preservation purposes. HCHO will decompose over time if it is in a single form and last longer if in the bonded forms. Since 2004, the World Health Organization (WHO) has included HCHO on the list of chemicals which are harmful to human health. It can harm the skin and respiratory system and cause leukemia and lung cancer [3]. HCHO is also included in group 1, a group of human carcinogens by the International Cancer Research Organization (IARC). HCHO can cause throat cancer, adenocarcinoma, and parts of the respiratory system [4].

There are many technologies for removal of VOCs in general and HCHO in particular such as absorption, adsorption, condensation, direct combustion, catalytic oxidation, and biological treatment. However HCHO in indoor air is often at low concentration which is not suitable for absorption, adsorption, condensation, or combustion methods. Biological measures are suitable for low concentration pollutants but it requires large area for equipment and can cause odor if improper operation. The catalytic oxidation method, especially photocatalyst, provides high removal efficiency for low concentration pollutants. Moreover, the photocatalytic device does not occupy much area to remove indoor air pollutants. Photocatalysis is the process of enhancing photochemical reaction by catalyst, which can be applied to remove pollutants in air and water environments. Catalysts commonly used in photochemical reactions are semiconductors (e.g., TiO_2 , ZnO , Fe_2O_3 , and CdS).

In recent years, the photocatalysis using titanium dioxide (TiO_2) has been considered as an effective and promising method to replace traditional methods for removing

organic substances in water or air environment [5-7]. TiO_2 is a material with strong oxidizing properties to decompose organic pollutants as well as hydrophobicity, chemical durability, long-term sustainability, non-toxicity, low cost, and transparent for various light [5, 8-11]. Because of the above advantages, TiO_2 has become more and more popular in scientific research as well as practical applications. Since pure TiO_2 usually has low activity, the doping and modification are usually conducted to improve its activity for water and air treatment [5-7, 12-14]. However, there is still little information on the using of metal doped TiO_2 for HCHO removal in air.

The photocatalyst initiated when photons, with higher energy than the bandgap (3.02 – 3.20 eV), are absorbed and promoted an electron to the conduction band (CB), leaving a hole in valence band (VB). These photo-excited electron (e^-_{CB}) and hole (h^+_{VB}) move to the surface to perform reduction and oxidation reactions directly or indirectly via mediated processes.

Both of e^-_{CB} and h^+_{VB} are capable to initiate oxidation – reduction while the semiconductor is not consumed [15-18]. In addition, e^-_{CB} and h^+_{VB} can also recombine to decrease a photonic efficiency and interfere the oxidation reactions. In most processes of photocatalytic decomposition, pure TiO_2 shows a photonic efficiency of less than 10% [19]. The metal is added to the catalyst to reduce the recombination e^-_{CB} and h^+_{VB} . Furthermore, doping of metal also showed many other effects on the properties of the photocatalysis, such as surface area [20, 21], magnetic susceptibility [20, 22], crystalline size [21, 22], reactivity of reduction and oxidation sites [23], and acidity.

In remove HCHO, the result of the research's Nakahira *et al.* [24] showed that the Pt nanocrystal-entrapped titanate nanotubes is capable of removing HCHO higher than the titanate nanotubes without Pt nanocrystals.

In this study, commercial TiO_2 was doping with many metals for improving the photocatalytic efficiency. The effects of

photolysis, adsorption, and photocatalysis were investigated. The experiments were also conducted in order to find the suitable metal, annealing temperature, and metal ratio for photocatalytic removal of HCHO.

2. Experimental

2.1. Experimental model

A continuous reactor was employed for HCHO removal tests under UV-A irradiation, with higher energy than the bandgap's TiO_2 (3.02 – 3.20 eV) (365 nm) using 3 UV light bulbs (8W) using 0.11 g of photocatalyst [25]. Concentration of HCHO was analyzed using a spectrometer analyzer (DR5000, Hach) at $\lambda = 580\text{nm}$. The mixed gas flow was controlled at a flow rate of lower 1 L/min, at room temperature and humidity, and HCHO concentration of 5.5 ppm.

Figure 1 shows the structure of the experimental model used in this study to remove HCHO vapor. Air pump (1) pushes air flow through the device that is containing activated carbon (4) to adsorb unwanted components in the air flow before reaching the cross (5). Here, the air stream is divided into 3 flows. Flow 1 (HCHO) flows through the control valve (7) to adjust the desired flow rate before reaching impinger containing HCHO 37% (8). Flow 2 (dilute gas flow) flows through the control valve (6) before diluting with Flow 1 at the tee (11). Before entering the reactor, the synthetic flow is checked for flow rate through the flow meters (12, 14, 15). Flow 3 (washing gas flow) is used before conducting experiments with the new catalyst. The device will be cleaned with this washing gas stream to ensure that HCHO is no longer remained in the reactor. The reactor is arranged with 3 UV-A lamps (18) and equipped with catalyst covered on glass support materials. The gas samples of input and output were collected at gas sampling positions (17) and (22) and analyzed according to the 3500 method of the National Institute of Occupational Safety and Health (NIOSH).

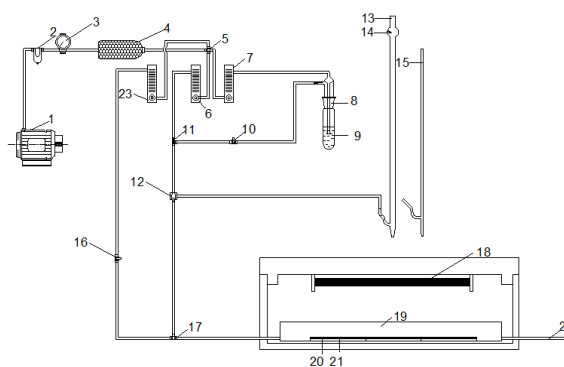


Figure 1. Experimental model to remove HCHO.

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|--|----------------------------|
| 1. Air pump | 12. Three-way valves |
| 2. Moisture absorption equipment | 13. Air flow test |
| 3. Pressure regulator valve | 14. Air bubbles |
| 4. Equipment containing activated carbon | 15. HCHO flow test |
| 5. Cross | 16. Air valve |
| 6. Clean air flow meter | 17. Sample input |
| 7. HCHO flow meter | 18. UV |
| 8. Impinger | 19. Reactor |
| 9. Solution HCHO 37 % | 20. Glass support material |
| 10. HCHO valve | 21. TiO_2 |
| 11. Tee | 22. Sample output |
| | 23. Air flow meter |

2.2. Research materials

P25 catalyst is a fine white powder of high purity (about 99%) with hydrophilic property due to the hydroxyl group on the surface. P25 mainly consists of synthesized particles with average diameter of about 21 nm. The structure of P25 includes two types of rutile and anatase, which belong to the quadratic structure (tetragonal). At 300 °C, anatase begins to transform slowly into a more stable rutile structure. P25 is considered to be suitable for many applications that require high photocatalytic activity.

Metal doped P25 catalyst materials used in this study were prepared according to the process illustrated in Figure 2. Metal salts used in this experiment include $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$.

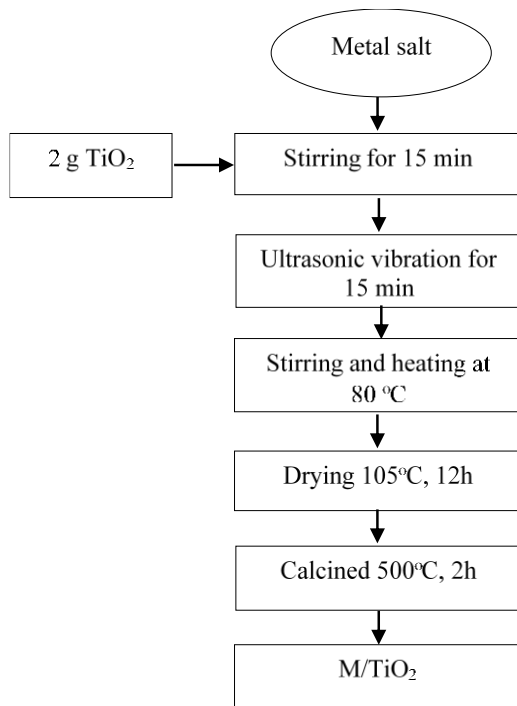


Figure 2. Procedure for metal doped P25 synthesis.

Supporting material consists of four glass panels with size of length \times width \times thickness = 100 mm \times 50 mm \times 2 mm. Before use, the glass is washed and dried at 105 °C for 20 min. P25 after doping with metal ion was coated on supporting material. The process of catalytic coating on glass is carried out as follows. 0.11 g of catalyst was put into 8 mL of distilled water. After shaking well, it was ultrasonic vibrations for about 1 h for suspension of the catalyst in the water. After that, 2 mL of the suspension solution was spread on the surface of each glass plate. These coated glassed was finally dried at 120 °C for 20 min.

3. Results and discussion

3.1. Effect of UV and catalyst

This experiment was conducted to compare the efficiency of photocatalytic (P25 and UV lamp) with photolytic (only UV lamp) and adsorption processes (only P25). As observed in Figure 3, the difference in removal efficiency is very clear in the three photocatalytic, photolytic and adsorption processes. During the photolysis, the removal efficiency was low (< 20%) under irradiation of UV lamp without catalytic material. This prove that the absence of catalytic material has

greatly affected the efficiency of HCHO degradation. During adsorption (only P25 catalyst material), removal efficiency reached about 38%. This is based on the pore structure and large specific surface area of the catalytic material. However the efficiency of adsorption process is still much lower than that of photocatalytic process (about 60%). This confirms the advantages of photocatalytic method as compared to adsorption and photolytic methods. From these results, it can be easily concluded that the removal efficiency of HCHO vapor of all three processes: photocatalysis > adsorption > photolysis. Particularly, the removal efficiency of the photocatalytic process was 1.6 and 3.75 times higher than those of adsorption and photolytic processes.

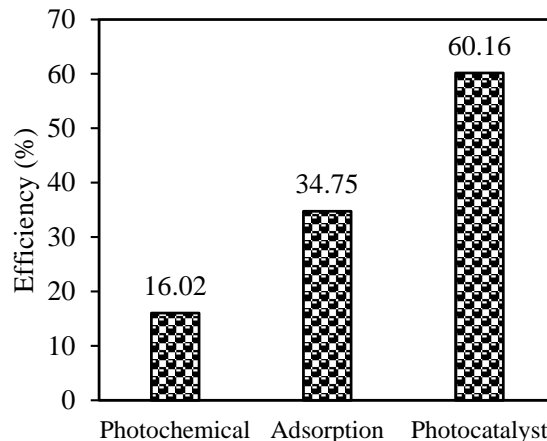


Figure 3. HCHO removal efficiency of photocatalytic, adsorption, and photolytic processes.

3.2. Effect of metal doping

P25 was doped with different metals (i.e. Cd, Sn, Cr, Ni, Sr, Mg, Co, Mn, Zn, Al, Fe, and Cu) with theoretical metal/Ti ratio of 1% and annealed at 500 °C. This experiment is conducted to find the metal that is doped with P25 for the highest HCHO removal efficiency. The experimental result after 90 min of irradiation is exhibited in Figure 4.

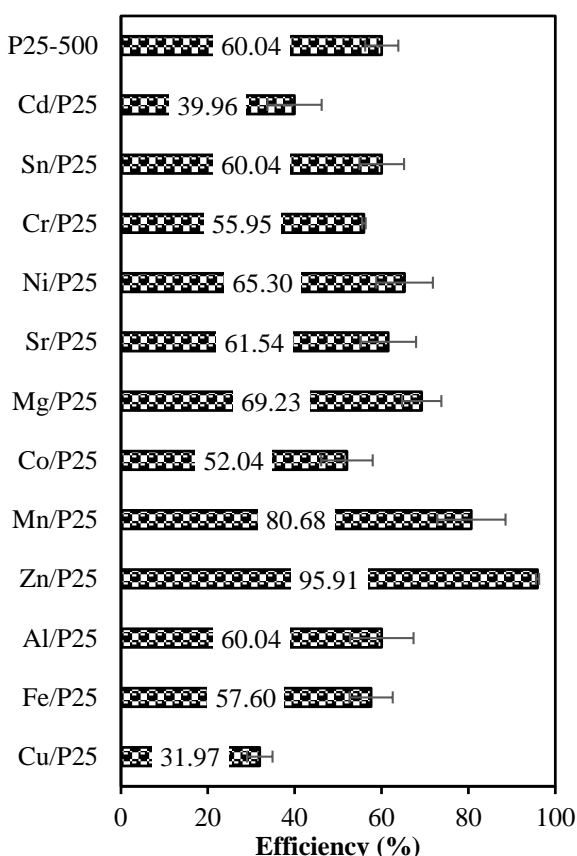


Figure 4. Removal efficiency of HCHO vapor using metal doped P25 ($M/Ti = 1\%$).

As seen in Figure 4, Zn/P25 catalyst had the highest removal efficiency of about 96% among the metal doped P25. This proves the high ability for removing HCHO molecules as well as the fast regeneration rate of the holes on Zn/P25 surface. The Mn/P25 catalyst had also high removal efficiency of about 81%. Generally, ZnO has smaller crystal size and larger surface area than MnOx. Therefore, the full and stable electron configuration in Zn ($[Ar]3d^{10}4s^2$) could create "charge traps" faster than that in Mn incomplete configuration of $[Ar]4s^23d^5$. Also, this increases the movement of electrons and holes to the catalytic surface, thus reduces the ability of electron-hole recombination [26]. Furthermore, the absorption spectrum of the Zn/P25 catalyst increases the photocatalytic activity of the catalyst under UV lamp irradiation.

3.3. Influence of annealing temperature

The annealing temperature can change the structure of TiO₂, so it is necessary to do

experiments using metal doped P25 material with different annealing temperatures. It is known that high temperature will increase the particle size and reduce the surface area of P25 TiO₂. The reduction of surface area is due to the aggregation of small TiO₂ particles to form larger ones. Moreover, when annealing temperature is too high, it will lead to the formation of fewer active rutile phase. This experiment is aimed to test the removal efficiency of HCHO using Zn/P25 annealed at temperatures of 300, 400, 500, and 600 °C. Figure 5 demonstrates the effect of annealing temperature on the removal efficiency of HCHO vapor.

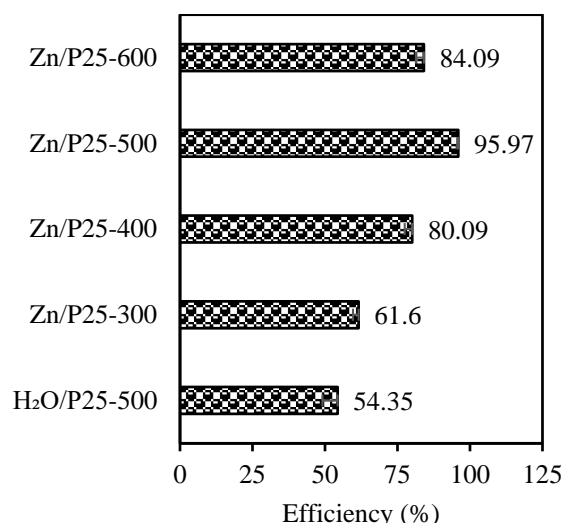


Figure 5. The removal efficiency of HCHO vapor of Zn/P25 at different annealing temperatures ($Zn/Ti = 1\%$).

As seen in Figure 5, the removal efficiency of HCHO using Zn/P25 catalyst increased strongly from 300 to 500°C (i.e. from 58% to 96%). The Zn/P25-500 catalyst achieves the highest removal efficiency of 96%. The efficiency was decreased slightly when the annealing temperature further increased to 600°C (about 84%). Annealing at high temperature is a method commonly used to increase the crystallization of nanomaterials, thus enhances the photocatalytic activity of the photocatalyst in this study.

3.4. Effect of metal content

The metal content of doped catalysts is also one of the factors that greatly affect the photocatalytic activity of P25. This experiment is conducted to investigate the removal efficiency of HCHO vapor using Zn/P25 annealed at 500 °C with different metal content to find out the suitable metal content. In this study, Zn/P25 catalysts were prepared with different Zn/Ti molar ratios of 0.1, 0.5, 1, 5 and 10% and the results are presented in Figure 6.

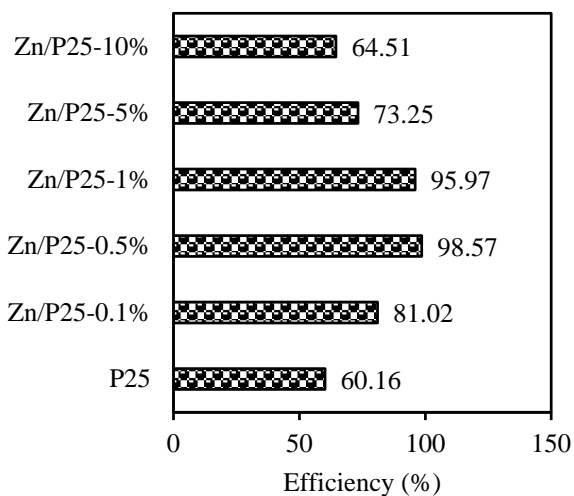


Figure 6. The removal efficiency of HCHO vapor of Zn/P25 at different metal contents.

It is clearly observed in Figure 6 that the removal efficiency of HCHO vapor of P25 increased significantly after doping with metal. At Zn/Ti ratio of 0.1%, the removal efficiency reached 78% after 90 min of irradiation. When Zn/Ti ratio increased to 0.5%, the removal efficiency increased significantly to 98.57%. However, the further increase of Zn/Ti ratio then caused a decrease in efficiency to 73.25% (Zn/Ti = 1%) and even 64.5% (Zn/Ti = 10%). These suggest that the 0.5% Zn content is the suitable doping ratio of Zn into P25 for HCHO removal. This can be explained as followings. When increasing the metal content of the catalyst (e.g., Zn/Ti ratio from 0.1% to 0.5%), the band gap energy of TiO₂ was reduced and energy required for the photocatalytic process was lower. Moreover, metal and metal oxide as electron traps increased the lifetime of electronic carriers and reduced the recombination ability of

photoexcited electrons and holes [6, 8, 10]. As results, metal doped TiO₂ had higher photocatalytic activity than pure TiO₂. However, when the metal content is too high, it will increase the recombination ability of electrons and holes, thereby reducing the catalytic activity. This result is consistent with the study of Liu et al. [27], where Zn/TiO₂ calcined at 500°C with Zn 0.5% content using solid phase reaction method had the highest efficiency for removal of Rhodamine B in water.

4. Conclusion

This study has successfully demonstrated that photocatalysis using P25 materials is more dominant than adsorption and photolytic methods in removing HCHO in air. Under the test condition, the study determined that Zn doped P25 at Zn/Ti ratio of 0.5% and annealed at 500°C had the high removal efficiency of 98%. Future works could focus on the effect of environmental factors such as irradiation intensity and time, catalyst amount, temperature, relative humidity, and exposed surface in order to obtain the suitable condition for photocatalytic removal of HCHO for future practical application □

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