Synthesis and adsorption-photodecomposition properties of mesoporous SiO$_2$–TiO$_2$/WO$_3$ composite

Shingo HIRATA$^1$, Aya INOUE$^1$, Miki INADA$^{2,3}$ and Junichi HOJO$^3$

$^1$Department of Molecular and Material Sciences, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6–1 Kasuga-Koen, Kasuga, Fukuoka 816–8580, Japan
$^2$Center of Advanced Instrumental Analysis, Kyushu University, 6–1 Kasuga-Koen, Kasuga, Fukuoka 816–8580, Japan
$^3$Education and Research Center of Manufacturing, Faculty of Engineering, Kyushu University, 6–1 Kasuga-Koen, Kasuga, Fukuoka 816–8580, Japan

Gaseous volatile organic pollutants may be removed from the environment through photocatalysts combined with adsorbents. Herein, a mesoporous SiO$_2$–TiO$_2$/WO$_3$ composite was fabricated by the sol–gel method in order to remove acetaldehyde in the gas phase. TiO$_2$ and WO$_3$ were well-dispersed in the SiO$_2$ matrix. The adsorption-photodecomposition properties of mesoporous SiO$_2$–TiO$_2$/WO$_3$ were evaluated through a three-step kinetic analysis, including direct-decomposition, adsorption, and adsorption-decomposition. The composition of WO$_3$ in the SiO$_2$–TiO$_2$ increased the acidity and improved the affinity between the photocatalyst and acetaldehyde. This effectively enhanced the initial removal rate of acetaldehyde. The atomization of WO$_3$ further improved the affinity between the photocatalyst and acetaldehyde and enhancing the photodecomposition rate constant.

©2021 The Ceramic Society of Japan. All rights reserved.

Key-words : Mesoporous SiO$_2$–TiO$_2$/WO$_3$, Adsorbent, Photocatalyst, Kinetic analysis

[Received February 10, 2021; Accepted May 10, 2021]

1. Introduction

Gaseous volatile organic compounds (VOCs) pollute the environment and are detrimental to human health, even at low concentrations. One of the techniques applied to remove VOCs pollutants involves combining photocatalysts with adsorbent, such as, activated carbon with TiO$_2$ photocatalyst,$^{1-5}$ TiO$_2$-modified zeolite,$^{6-10}$ and mesoporous SiO$_2$–TiO$_2$.$^{11-18}$ Belayachi et al. synthesized a TiO$_2$/activated-carbon composite using grape marc as the carbon source.$^{13}$ Kovalevskiy et al. synthesized a TiO$_2$/zeolite composite that adsorbed the initial pollutant by forming intermediates on the photocatalyst surface.$^6$ A total hazard index, accounting for the impact of all the reaction components in gas phase, was applied to investigate the photocatalytic activity. Liu et al. synthesized nanocomposites of mesoporous TiO$_2$ deposited onto SBA-15 forming a porous structure.$^{11}$ This mesoporous SiO$_2$–TiO$_2$ had a high specific surface area and exhibited high photocatalytic and adsorption capacities. Kim et al. reported that the photocatalytic activity of mesoporous SiO$_2$–TiO$_2$ prepared by the layer-by-layer technique is higher than that prepared by the sol–gel method.$^{12}$ Moreover, TiO$_2$ nanoparticles were formed on the surface of SBA-15 rather than in the pores. Activated carbon, zeolite, and mesoporous SiO$_2$ acted as a support for TiO$_2$, and substantially increased the adsorption capacity of the composite photocatalyst, so that it was more efficient than TiO$_2$ in removing organic compounds from the water and gas phases under ultraviolet (UV) irradiation. Additionally, the acidity of mesoporous SiO$_2$ can be regulated by adding other metal oxides.

We have fabricated mesoporous SiO$_2$–TiO$_2$ synthesized by sol–gel process and evaluated photocatalytic activity using acetaldehyde (CH$_3$CHO) gas.$^{19,20}$ Our mesoporous SiO$_2$–TiO$_2$ has a high adsorbability and photocatalytic activity for CH$_3$CHO gas under UV irradiation. Nowadays, we proposed a 3-step kinetic model as an alternative to the pseudo-first-order rate equation.$^{21,26}$ The effect of adsorption on the photocatalytic reaction is not observed as the target gas is assumed to decompose immediately (direct-decomposition). Our model considered the adsorption step. In addition, the change in the concentration of carbon dioxide, which is a decomposition product, was also included in calculation. As a result, it was found that the CH$_3$CHO gas was removed by adsorption and direct-decomposition in the early stage, then the adsorbed CH$_3$CHO was decomposed gradually. Thus, the photocatalytic activity of mesoporous SiO$_2$ composite should be enhanced without a decrease in adsorbability in order to accelerate the initial removal rate of CH$_3$CHO from gas phase.

Mesoporous SiO$_2$–TiO$_2$ is the base of the composite that maintains the adsorption capacity. The drawback of photocatalyst materials, such as TiO$_2$, is that the photogenerated
carriers are easily recombined.\textsuperscript{27) However, photocatalysts with narrow band gaps, such as WO\textsubscript{3} combined with TiO\textsubscript{2}, may overcome this limitation.\textsuperscript{27, 40) TiO\textsubscript{2}/WO\textsubscript{3} has heterojunction structures, and hole-electron pairs are separated efficiently. Thus, the prepared mesoporous SiO\textsubscript{2}–TiO\textsubscript{2}/WO\textsubscript{3} composite improves the specific surface area of TiO\textsubscript{2}/WO\textsubscript{3}.\textsuperscript{27, 41, 42) Chang et al. reported that SBA-15 complexed with W and Ti showed high visible-light photocatalytic performance for rhodamine B and 2,4-dichlorophenol in water.\textsuperscript{40} Cai et al. synthesized a WO\textsubscript{3}-deposited TiO\textsubscript{2}–SiO\textsubscript{2} nanocomposite and evaluated the contribution and mechanisms of the extended visible-light activity.\textsuperscript{42) However, the photocatalytic activity of mesoporous SiO\textsubscript{2}–TiO\textsubscript{2}/WO\textsubscript{3} for CH\textsubscript{3}CHO has not been reported yet, and the effects of organic compound adsorption on the photocatalytic activity have rarely been discussed.

Herein, we synthesized a mesoporous SiO\textsubscript{2}–TiO\textsubscript{2}/WO\textsubscript{3} composite using the sol–gel process, and evaluated its photocatalytic activity using CH\textsubscript{3}CHO. Our 3-step kinetic analysis was carried out to discuss the photocatalytic activity quantitatively.

2. Experimental procedure

2.1 Preparation of photocatalyst

Commercial TiO\textsubscript{2} (P25, Japan Aerosil Co., Ltd., specific surface area: 40 m\textsuperscript{2}/g, anatase:rutile = 3:1) and WO\textsubscript{3} (Nacalai Tesque, Inc.) were used as photocatalysts. WO\textsubscript{3} powder was prepared by wet milling using TiO\textsubscript{2}–SiO\textsubscript{2} nanocomposite and evaluated the contribution and mechanisms of the extended visible-light activity.\textsuperscript{42) However, the photocatalytic activity of mesoporous SiO\textsubscript{2}–TiO\textsubscript{2}/WO\textsubscript{3} for CH\textsubscript{3}CHO has not been reported yet, and the effects of organic compound adsorption on the photocatalytic activity have rarely been discussed.

2.2 Preparation of mesoporous SiO\textsubscript{2} materials

The mesoporous composite was synthesized by the sol–gel method. Si(OE\textsubscript{2})\textsubscript{4} (TEOS; FUJIFILM Wako Pure Chemical Corporation), stearytrimethylammonium chloride (C18TAC; Tokyo Chemical Industry Co., Ltd.) as template, and diluted HCl (pH = 2) were mixed with TEOS:C18TAC:H\textsubscript{2}O (1:0.2:20 in mol), and heated at 50 °C for 30 min with agitation. Then, the photocatalyst powder was added to the solution and kept at 50 °C overnight for complete gelation. The photocatalyst/Si molar ratio was 0.1. The obtained gel was calcined at 500 °C for 4 h to remove the organic residue. The calcined powder was then pulverized in an agate mortar and irradiated using UV light (wavelength: 352 nm, FL6-BLB, Toshiba Lighting and Technology, Co.) overnight.

2.3 Characterization

The crystalline phases of the products were identified by X-ray diffraction (XRD; SmartLab SE, Cu K\textalpha, 40 kV, 50 mA, Rigaku Corporation). The particle morphology was observed using transmission electron microscopy (TEM; H-7650, Hitachi High-Tech Corporation) and using scanning electron microscopy (SEM-EDS; JSM-6701F, JEOL Ltd.). The specific surface area of the products was determined from the N\textsubscript{2} adsorption isotherm using the Brunauer, Emmett and Teller (BET) method (BELSORP-mini II, MicrotracBEL Corp.). The de-gas condition was set at 300 °C for 5 h in vacuum. The acidity was measured using an amine-titration method in benzene, with tetraamine as a titrant and p-dimethylaminobenzene as an indicator.

2.4 Evaluation of photocatalytic activity

The photocatalytic activity was evaluated for the decomposition of CH\textsubscript{3}CHO in the gas phase under UV irradiation. Black light (wavelength: 352 nm, FL6-BLB, Toshiba Lighting and Technology, Co.) was used as the UV light source. Powder samples (0.025 g) were placed on a glass plate in a glass chamber (1 L), and then the chamber was filled with artificial air (N\textsubscript{2}:O\textsubscript{2} = 80:20). After the injection of CH\textsubscript{3}CHO, the chamber was immediately irradiated with black light. The concentrations of CH\textsubscript{3}CHO and CO\textsubscript{2} were analyzed using gas chromatography (GB-4014; Shimadzu Corporation).

3. Results and discussion

3.1 Structural analysis of mesoporous SiO\textsubscript{2}–TiO\textsubscript{2}/WO\textsubscript{3}

The crystalline phases of the products were identified using XRD (Fig. 1). The halo pattern was detected only on mesoporous SiO\textsubscript{2} (MS) because of its glass structure; anatase and rutile peaks were detected on the mesoporous SiO\textsubscript{2}–TiO\textsubscript{2} (MST) due to the P25 crystalline phase; and, anatase, rutile, and monoclinic WO\textsubscript{3} peaks were detected on both MSTW and MSTBW. The peak intensity of WO\textsubscript{3} on MSTW and MSTBW was almost same.

The dispersibility of the photocatalysts in the SiO\textsubscript{2} matrix was observed by TEM (Fig. 2). Nanoparticles, with a particle size of approximately 20 nm, were dispersed on the MST; nanoparticles and large particles with a particle size of approximately 300 nm were dispersed on the MSTW. These results indicated that P25 and WO\textsubscript{3} were well-dispersed in the SiO\textsubscript{2} matrix. Additionally, P25 was located around WO\textsubscript{3}. We tried to get mapping image of MSTW and MSTBW by SEM-EDS. However, the spectra of W and mapping image were hardly obtained due to low W amount in the samples. Unfortunately, there was no data that could be pointed out the difference in MSTW and MSTBW, although the particle size of WO\textsubscript{3} was different as shown in Table 1.

Table 2 summarizes the changes in the specific surface area and acidity of mesoporous materials. The specific
surface area was maintained at approximately 1000 m²/g. The incorporation of photocatalysts enhanced the acidity of the samples. The acid-base properties of oxide powders in water depend on the point of zero charge (PZC) for each powder, which is related to the reciprocal thickness of the electrical double-layer around the solid. At the interface of the mixture, the acidity increased because the thickness of the electric double-layer changed. The PZC of SiO₂, TiO₂, and WO₃ were 1.8, 6.7, and ~0.5, respectively, and its quantitative relationship with acidity is unknown. However, the TiO₂–WO₃ interaction may have increased the acidity, resulting in the increases in direct-decomposition and adsorption.

The structure of mesoporous materials can be summarized as follows: mesoporous structure was observed in all the samples. The photocatalysts were dispersed in the SiO₂ matrix. In MSTW, both P25 and WO₃ particles were dispersed in the SiO₂ matrix, with P25 either independent or located around WO₃. WO₃ particles may disperse more in MSTBW than MSTW.

### 3.2 Photocatalytic activity of mesoporous SiO₂–TiO₂/WO₃

Figures 3 and 4 depict the concentration variations of CH₃CHO and CO₂ with UV irradiation time for the photocatalysts and mesoporous materials, respectively. In both P25 and TW, CH₃CHO concentrations decreased, and CO₂ concentrations increased. In contrast, the removal rate of CH₃CHO was faster and the amount of CO₂ generated at the early stage of the reaction (~1 h) was larger for mesoporous materials than that of each photocatalyst. However, after 3 h, the CO₂ generation of mesoporous materials was lower than that of the photocatalysts. These results suggest that CH₃CHO was adsorbed and retained on the catalyst surface. To quantitatively analyze the amount of adsorption and CO₂ generation, we applied kinetic analysis using the three-step model performed in the previous study.²⁰,²¹

### 3.3 Kinetic approach for adsorption-photodecomposition

We proposed a 3-step model for the adsorption-photodecomposition of CH₃CHO, which includes direct-decomposition, adsorption–desorption, and adsorption-decomposition (Fig. 5). The kinetic equations for this model were:

\[
\frac{dC}{dt} = N_{\text{sat}}[k_1 C(1 - \theta) + k_{\text{ads}} C(1 - \theta) - k_{\text{des}} \theta] \quad (1)
\]

\[
\frac{d\theta}{dt} = \frac{1}{C_{\text{cat}}}[k_{\text{ads}} C(1 - \theta) - k_{\text{des}} \theta - k_2 \theta] \quad (2)
\]

where \( C \) (mol/l): CH₃CHO in gas phase, \( \theta \): CH₃CHO occupancy, \( N_{\text{sat}} \) (mol/g): CH₃CHO saturated adsorption.

### Table 2. Specific surface area and surface acidity of mesoporous materials

|                | Specific surface area/m²/g | Surface acidity/µmol/m²-² |
|----------------|----------------------------|---------------------------|
| MS             | 1200                       | 2.52                      |
| MST            | 1050                       | 2.79                      |
| MSTW           | 1020                       | 3.41                      |
| MSTBW          | 1030                       | 3.37                      |

Fig. 1. XRD patterns of MST (a), MSTW (b), MSTBW (c) and MS (d).

Fig. 2. TEM images of MST (a) and MSTW (b).
amount (calculated by Langmuir method), $C_{\text{cat}}$ (g/l): catalyst amount, $k_{\text{ads}}$ (g/mol s): adsorption rate constant, $k_{\text{des}}$ (g/l s): desorption rate constant, $k_1$ (g/mol s): direct-decomposition rate constant, and $k_2$ (g/l s): adsorption-decomposition rate constant.

The CH$_3$CHO concentration variations were attributed to direct-decomposition and adsorption-desorption. The CH$_3$CHO occupy the sample surfaces through adsorption-desorption and adsorption-decomposition. $N_{\text{sat}}$ was estimated by the Langmuir method using the adsorption results under dark conditions. Thus, the CH$_3$CHO concentration variations were calculated using Eqs. (1) and (2). Moreover, the CO$_2$ concentration variation was also calculated as:

$$C_{\text{CO}_2} = 2\left(\frac{C_0 - C - C_{\text{cat}}N_{\text{sat}}}{C_0 C_{\text{cat}}}\right)^3$$

where $C_0$ (mol/l): CH$_3$CHO initial concentration.

Figure 6 depicts the plot and calculation data as solid (X) and dotted (Y) curves, respectively. The calculation curve indicates good fitting of the experimental data for both CH$_3$CHO and CO$_2$ concentrations. From these curves, the variation in amount of CH$_3$CHO adsorbed on the catalyst (gray), and CO$_2$ generated during direct-decomposition (red) and adsorption-decomposition (blue) were obtained.

Table 3 summarizes the kinetic constants obtained by simulation. The kinetic constants were normalized using $N_{\text{sat}}$ and $C_{\text{cat}}$. In MST, the simulation results indicated that CH$_3$CHO was removed by adsorption and direct-decomposition, and almost no adsorption-decomposition occurred. The CH$_3$CHO completely decomposed in 2 h in the previous study, but it was not decomposed even after 3 h here. The intensities of the UV irradiation in this study (0.43 mW cm$^{-2}$) is lower than that in previous study (0.86 mW cm$^{-2}$). Therefore, it is considered that this difference appeared. The $k_{\text{des}}$ values were also high. In contrast, $k_{\text{ads}}$ did not vary, and $k_{\text{des}}$ was smaller in MSTW compared to that in MST. These results indicated a relative increase in adsorption capacity, consistent with the increase in acidity. This implied that the SiO$_2$–TiO$_2$/WO$_3$ surface had a higher affinity for CH$_3$CHO than the SiO$_2$–TiO$_2$ surface. Therefore, the decrease of CH$_3$CHO concentration of MSTW was larger than that of MST. However, the values of $k_1$ decreased, and $k_2$ increased. The difference between MST and MSTW was that charge separation occurred between TiO$_2$ and WO$_3$. The charge separation may be the rate-determining step, and therefore, $k_2$ increased. The
simulation results indicates that CO₂ generation on MSTW is more slowly than that of MST. It is probable that CH₃CHO strongly adsorbs on MSTW. In addition, the amount of CO₂ generation at the early stage depends on direct-decomposition. The CO₂ generation increases rapidly in MST which \( k_1 \) is higher than MSTW.

Previous studies have shown that a large photocatalyst particle dispersed into the SiO₂ matrix contributes to direct-decomposition, and the well-dispersed photocatalyst nanoparticles promote adsorption-decomposition. Therefore, the effect of WO₃ atomization was investigated using MSTW to improve adsorption-decomposition. In MSTBW, CO₂ generation by both direct-decomposition and adsorption-decomposition increased. These results indicated that the dispersed photocatalyst particles in the SiO₂ network increased, causing the promotion of adsorption-decomposition. Additionally, an increase in the contact area between WO₃ and TiO₂ caused a relative decrease in the contact area between TiO₂ and another TiO₂. Thus, direct-decomposition improved with an increase in the exposed TiO₂ surface.

4. Conclusions

Incorporation of WO₃ into the SiO₂ matrix increased the acidity, which enhanced the adsorption of CH₃CHO. The photocatalytic activity showed that the photocatalysts incorporated into MS removed CH₃CHO effectively. Kinetic analysis indicated that incorporating TiO₂ into the SiO₂ matrix increased the direct-decomposition rate and incorporating WO₃ increased the adsorption and adsorption-decomposition rates. Hence, incorporating both TiO₂ and WO₃ into the SiO₂ matrix increased both direct-decomposition and adsorption-decomposition rates, and rapidly removed CH₃CHO from the gas phase. The photocatalyst can be dispersed by atomizing WO₃, which enhanced the adsorption-decomposition rate. Furthermore, an increase in the contact area between TiO₂ and WO₃ caused an increase in the direct-decomposition rate. The addition of WO₃ in MST mainly improved photocatalytic activity. In order to develop a material that rapidly removes CH₃CHO from the gas phase, it will be necessary to investigate the the factors related to the rate constant by detailed structural analysis of the material.

468

Table 3. Kinetic rate constants calculated through simulation in mesoporous materials

| Material | \( k'_{ads} = k_{ads} \times N_{sat} \) \((\times 10^{-4}/\text{s})\) | \( k'_{dec} = k_{dec}/C_{cat} \) \((\times 10^{-4}/\text{s})\) | \( k'_1 = k_1 \times N_{sat} \) \((\times 10^{-4}/\text{s})\) | \( k'_2 = k_2/C_{cat} \) \((\times 10^{-4}/\text{s})\) |
|----------|---------------------|---------------------|---------------------|---------------------|
| MST      | 11                   | 2.8                 | 5.1                 | 0.0                 |
| MSTW     | 11                   | 0.0                 | 3.4                 | 0.4                 |
| MSTBW    | 22                   | 0.0                 | 8.3                 | 1.0                 |

Fig. 6. Effect of addition of WO₃ on photocatalytic activity. The samples are MST (a), MSTW (b) and MSTBW (c). Simulation result from 3-step model on sample. Raw data as plots and the fitting curves of CH₃CHO gas (X) and CO₂ gas (Y) concentrations are described. The amount of CO₂ generated from direct-decomposition (A) and adsorption-decomposition (C), and adsorbed amount of CH₃CHO (B) were obtained from simulation.

References

1) H. Belayachi, B. Bestani, N. Benderdouche and M. Bellakem, Arab. J. Chem., 12, 2018–3027 (2019).
2) N. Wang, X. Li, Y. Yang, Z. Zhou, Y. Shang, Z. Zhuang and T. Zhang, J. Water Process Eng., 35, 101220
