Kinetic approach for the adsorption-photodecomposition properties of mesoporous silica-titania

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We have fabricated mesoporous silica-titania by a sol–gel method and evaluated the photocatalytic activity using acetaldehyde. The synthesized mesoporous silica-titania was effective for the removal of acetaldehyde from gas phase by adsorption and photodecomposition. In this study, the kinetic approach was carried out in order to clarify the adsorption-photodecomposition property of mesoporous silica-titania. The adsorption, direct photodecomposition and concerted adsorption-photodecomposition can be separately described in our simulation curves, which indicates that the adsorbability strongly affects the removal of acetaldehyde in the early stage and the photodecomposition after the strong adsorption of acetaldehyde on mesoporous silica-titania is important for the complete removal of acetaldehyde from gas phase.

Key-words : Mesoporous silica-titania, Adsorbent, Photocatalyst, Kinetic analysis

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1. Introduction

The removal of environmental pollutants such as volatile organic compounds is one of the important issues in the world, because most of air pollutants affect environment and human body even at the low concentration. One of the solution strategy is using photocatalyst with adsorbent such as activated carbon with TiO₂ photocatalyst,¹–⁶ TiO₂-modified zeolite,⁷–¹⁰ mesoporous silica-titania.¹¹–¹⁹ Among them, we focused on mesoporous silica materials because of its large surface area and easy control of its acidity by addition of other metal oxide. Mesoporous silica has regularly-oriented mesopores formed by a sol–gel process using the self-assembly of organic surfactant as template.²⁰ The adsorbability of mesoporous silica is remarkably enhanced by substitution of other metal, especially Ti, for Si in silica network which forms acidic sites.²¹–²³ The composite of mesoporous silica with photocatalytic particles is also received a lot of attention for the removal of pollutant. We have fabricated mesoporous silica-titania by control of sol–gel reaction,²⁴–²⁸ resulting in formation of homogeneous silica-titania structure,²⁶ TiO₂ nanoparticles dispersed in silica matrix²⁷ and spherical morphology.²⁸ Homogeneous mesoporous silica-titania has a high adsorbability for methylene-blue in water and acetaldehyde in gas phase, whereas TiO₂ nanoparticles involved in silica matrix indicates not only adsorbability but also a high photocatalytic activity under ultraviolet (UV) irradiation.

Generally, the photocatalytic activity is evaluated only in qualitatively using typical TiO₂ as reference. In order to understand and to discuss essentially the effect of adsorption on photocatalytic activity, quantitative analysis is needed. The kinetic analysis is one of the effective approaches for the quantitative analysis of photocatalytic activity. When the target gas is set at low concentration and immediately decomposed on the surface of catalyst, the pseudo-first order rate equation derived from Langmuir–Hinshelwood model can be applied on the quantitative analysis of photocatalytic reactions. Kinetic constants from pseudo-first order rate equation of adsorbent-photocatalyst complexes have been calculated, although most of them is not agreed with their raw data so much.²⁹–⁴⁰ This is due to the elimination of adsorption step. On the other hand, some researchers have proposed the kinetic equation with considering adsorption step.⁴¹,⁴² Their calculation and simulation indicate a good fitting with experimental data.

In this study, the adsorption-photodecomposition property of mesoporous silica-titania was evaluated in quantitatively using kinetic analysis. Three types of mesoporous
silica-titania were fabricated by a sol–gel method and the photocatalytic activity was investigated for acetaldehyde in gas phase.

2. Experimental procedure

2.1 Preparation

Mesoporous silica-titania was synthesized by a sol–gel method using Si(OC2H5)4 (TEOS; Wako Pure Chemical Industries, Ltd.) as silica source. Three kinds of titania source were used such as Ti(OC2H5)4 (TEOT; Merck KGaA, Co.), TiOCl2 prepared using diluted TiCl4 solution (Wako Pure Chemical Industries, Ltd.) and P25 (Japan Aerosil Co., Ltd.), specific surface area; 40 m2/g, anatase: rutile = 3:1 as typical TiO2 powder. In S-TEOT system, TEOT was mixed with acetylacetone (Wako Pure Chemical Industries, Ltd.) at room temperature in dry N2 at the ratio of TEOT to acetylacetone = 1:2 in mol in order to replace the part of etoxy groups with acetylacetones. After stirring for 30 min, TEOS, stearyltrimethylammonium chloride (C18TAC; Tokyo Chemical Industry Co., Ltd.) as template and diluted HCl water (pH = 2) were added to the capped-TEOT solution, and then heated at 50°C for 12–18 h until complete gelation. In the cases of using TiOCl2 (S-TiOCl2 system) and P25 (S-P25 system), TEOS, surfactant and diluted HCl water were mixed and heated for 30 min, and then titania sources were added. The composition was set at TEOS:C18TAC:H2O = 1:0.2:2.20 in mol. The Ti/Si molar ratio in the composite was changed from 0 to 0.5. The obtained gel was calcined to remove the organic residue and pulverized with an agate mortar. The calcination condition was set at the heating rate of 2°C/min and the holding temperature and time at 600°C for 4 h in air.

2.2 Characterization

The specific surface area of calcined products was determined from N2 adsorption isotherm by the BET method (BELSORP-mini II, BEL Japan, Inc.). The acidity was measured by an amine titration method in benzene using tetraamine as a titrant and p-dimethylaminoazobenzene as an indicator. The crystalline phases of calcined powder were identified by X-ray diffraction (XRD; SmartLab, Rigaku Co.) using CuKα radiation (40 kV, 30 mA). The particle morphology was observed by transmission electron microscopy (TEM; H-7500, Hitachi Co.).

2.3 Evaluation of photocatalytic activity

The photocatalytic activity was evaluated for decomposition of acetaldehyde in gas phase under UV irradiation. Black light (wavelength: 352 nm, FL6-BLB, Toshiba Lighting and Technology, Co.) was used as UV light source. The 0.025 g of powder sample was set on a glass plate in a glass chamber (ca. 1 L), and then the chamber was filled with N2 gas. After injection of acetaldehyde, the chamber was irradiated by black light, immediately. The concentrations of acetaldehyde and CO2 were analyzed by gas chromatography (GC-14B and GB-2014; Shimadzu Corporation).

3. Results and discussion

3.1 Structural analysis for three types of mesoporous silica-titania

Figure 1 shows the change in specific surface area and acidity with Ti/Si molar ratio. The specific surface area gradually decreased as rising Ti/Si ratio, but kept high value of about 1000 m2/g until 0.3 except S-TEOT system. In S-TiOCl2 system, as the amount of Ti content increased, the amount of acetylaceton also increased, which inhibits the formation of micelle template. This causes the decrease in specific surface area at high Ti/Si ratio. Acidity tended to be enhanced by small amount of Ti addition. This indicates the incorporation of Ti into silica network at low Ti/Si ratio.

Morphology of mesoporous silica-titania was observed by TEM (Fig. 2). In S-TEOT system, the monotone image was observed at 0.1, whereas some small deposits were observed and electron diffraction of anatase was detected at 0.3. These results suggest that titanium was incorporated into silica network until 0.1 and partially deposited as titania at 0.3.27) In S-TiOCl2 system, small nanoparticles were highly dispersed in mesoporous silica matrix. As Ti/Si ratio increased, the particle size also increased and agglomeration occurred. In S-P25 system, dispersed TiO2 particles were observed but particle size was larger than that of TiOCl2.

XRD patterns are shown in Fig. 3. Only halo pattern was detected on mesoporous silica because it has glass structure. In S-TEOT system, the peaks of anatase were detected at over 0.3. On the other hand, in S-TiOCl2 system, anatase peaks detected at 0.1 and partially deposited as titania at 0.3.27) In S-TiOCl2 system, small nanoparticles were highly dispersed into mesoporous silica. In S-P25 system, P25 particles were dispersed into mesoporous silica.
3.2 Adsorbability and photocatalytic activity of mesoporous silica-titania

The adsorbability and photocatalytic activity of synthesized mesoporous silica-titania were evaluated using acetaldehyde in gas phase. The starting concentration was set at 400 ppm. Under dark condition, the acetaldehyde concentration decreased at initial stage and then kept a constant value, indicating adsorption equilibrium state (not shown). The adsorbability of mesoporous silica-titania was enhanced compared to mesoporous silica, indicating some relationship with acidity but specific surface area.

Figure 4 shows the change in acetaldehyde and CO₂ concentrations with UV irradiation time. The result from P25 was also described as reference. In S-TEOT system, acetaldehyde concentration decreased at the early stage of reaction, but acetaldehyde remained in gas under UV irradiation for 3 h. In addition, CO₂ generation was hardly observed, indicating S-TEOT system has a low photocatalytic activity. On the other hand, in S-TiOCl₂ and S-P25 system, the decrease in acetaldehyde concentration and increase in CO₂ concentration were observed at the early stage of reaction. These results indicate that Ti in...
silica network cannot decompose acetaldehyde and the crystalline titania is needed for the photodecomposition of acetaldehyde. The amount of CO2 generation was largest in P25 among all samples, but the removal speed of acetaldehyde of some mesoporous silica-titania was higher than P25. These results suggest that the photocatalytic activity can be evaluated in qualitatively compared to P25, but it cannot be explained how adsorption affects on photodecomposition. Thus, we applied kinetic approach in order to evaluate the adsorption-photodecomposition activity in quantitatively as next section.

3.3 Kinetic analysis based on Langmuir–Hinshelwood model

As first approach, Langmuir–Hinshelwood model was used. In this model, the target is low concentration and decomposed on the surface of catalyst immediately. The equation based on this model is pseudo-first order like Eq. (1).

$$\frac{dC}{dt} = kC$$

(1)

$C$ (mol/l): CH$_3$CHO gas concentration,  
$t$ (s): time, $k$ (s$^{-1}$): rate constant

The calculation results, as solid line, were filled in raw data as plots (Fig. 5). The results from P25 as reference indicated good fitting, whereas that of mesoporous silica-titania showed bad fitting. Table 1 shows the kinetic rate constant calculated by Eq. (1). There is a large difference in rate constant of between CH$_3$CHO decrease and CO$_2$ generation in mesoporous silica-titania system. In Langmuir–Hinshelwood model, the effect of adsorption did not take in consideration, which led to bad fitting between raw data and calculation curve.

3.4 Kinetic approach for adsorption-photodecomposition

We propose the 3-step model, based on modified Kusakabe’s model,

$$-\frac{dC}{dt} = N_{\text{sat}}[k_1C(1 - \theta) + k_{\text{ads}}C(1 - \theta) - k_{\text{des}}C]$$

(2)

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

(3)

$\theta$: CH$_3$CHO occupancy, $N_{\text{sat}}$ (mol/g): CH$_3$CHO saturated adsorption amount (calculated by Langmuir method), $C_0$ (mol/l): CH$_3$CHO initial concentration, $C_{\text{cat}}$ (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, $k_2$ (g/l s): adsorption-decomposition rate constant

The change in acetaldehyde concentration is described as direct decomposition and adsorption–desorption. The acet-aldehyde occupancy on surface of mesoporous silica-titania is explained as adsorption–desorption and adsorption-decomposition. $N_{\text{sat}}$ means the saturation amount of acetaldehyde estimated from Langmuir method. The direct decomposition and adsorption occur on the vacant surface site. Desorption and adsorption-decomposition relate with adsorption amount on the surface of mesoporous silica-titania.
titania. We obtained the change in acetaldehyde concentration from calculation of these equations. In addition, the change in CO2 concentration was also calculated from Eq. (4).

\[ C_{CO2} = 2(C_0 - C) \frac{C_{cat}N_{sat}}{C_0} \]

The calculation was carried out on S-P25 system at Ti/Si = 0.1 as simple model. Figure 7 illustrates raw data as plots and calculation curves as black solid line and broken line. The calculation curve indicates the good fitting with experimental data on both acetaldehyde and CO2 concentration. Usually, we can obtain only change in acetaldehyde and CO2 concentration by experimental from GC analysis. However, when this simulation is carried out, the change in adsorption amount of acetaldehyde on catalyst (gray line) and generated CO2 from direct-decomposition (red line) and adsorption-decomposition (blue line) are separately obtained. This simulation result indicates that acetaldehyde gas was removed by adsorption and direct-decomposition, then adsorbed acetaldehyde was decomposed gradually.

The effect of mesoporous silica-titania structure on photocatalytic activity was investigated at Ti/Si = 0.1.

**Table 1.** Kinetic rate constant calculated by Pseudo-first order Eq. (1) from Langmuir–Hinshelwood model

|               | S-TEOT, Ti/Si = 0.1 | S-TiOCl2, Ti/Si = 0.1 | S-P25, Ti/Si = 0.1 |
|---------------|---------------------|-----------------------|--------------------|
| CH3CHO (× 10⁻³/s) | 8.0 2.0 5.0         | 18 14 6.0             | 21 18 16           |
| CO2 (× 10⁻³/s)  | 2.4 0.03 0.16       | 1.3 1.8 0.9           | 0.8 1.4 2.4        |
In all systems, the simulation results indicate good fitting. The decrease in acetaldehyde concentration controlled by adsorption. In S-TEOT system, the decrease in acetaldehyde caused by adsorption only. In S-TiOCl₂ and S-P25 system, the amount of adsorbed acetaldehyde was almost same, but the phenomenon of CO₂ generation was quite different. These results strongly related to the difference in structure. Table 2 summarizes the kinetic constants obtained by simulation from Eqs. (2)-(4) at Ti/Si = 0.1.

**Table 2.** Kinetic rate constants calculated by simulation from Eqs. (2)-(4) at Ti/Si = 0.1

|                | (I) S-TEOT | (II) S-TiOCl₂ | (III) S-P25 |
|----------------|------------|---------------|-------------|
| \( k'_{ads} = k_{ads} \times N_{sat} \times (10^{-4}/s) \) | 41         | 27            | 28          |
| \( k'_{des} = k_{des}/C_{cat} \times (10^{-4}/s) \) | 15         | 0.4           | 0.5         |
| \( k'_1 = k_1 \times N_{sat} \times (10^{-4}/s) \) | 0          | 3.6           | 5.0         |
| \( k'_2 = k_2/C_{cat} \times (10^{-4}/s) \) | 0          | 1.0           | 0.5         |

(Fig. 8). In all system, the simulation results indicate good fitting. The decrease in acetaldehyde concentration controlled by adsorption. In S-TEOT system, the decrease in acetaldehyde caused by adsorption only. In S-TiOCl₂ and S-P25 system, the amount of adsorbed acetaldehyde was almost same, but the phenomenon of CO₂ generation was quite different. These results strongly related to the difference in structure. Table 2 summarizes the kinetic constants obtained by simulation. S-TEOT system did not show the photodecomposition ability, resulting in \( k'_1 \) and \( k'_2 = 0 \). This is due to no TiO₂ particles in silica matrix [Fig. 2(I-a)]. The \( k'_1 \) of S-TiOCl₂ system was lower than that of S-P25 system, whereas \( k'_2 \) of S-TiOCl₂ system was higher than S-P25 system. This indicates that a large TiO₂ particle dispersed into silica matrix [S-P25 system; Fig. 2(III)] contributes direct-decomposition, and highly dispersed TiO₂ nanoparticle into silica matrix like S-TiOCl₂ system [Fig. 2(II)] promote the adsorption-decomposition.

The effect of Ti/Si ratio on photocatalytic activity was evaluated quantitatively with S-P25 system. The simulation results and kinetic rate constant are shown in Fig. 9 and Table 3, respectively. When Ti/Si ratio increased from 0.1 to 0.3, the changes in amount of adsorbed acetaldehyde and CO₂ generation by direct-decomposition were little, but the CO₂ generation by adsorption-decomposition increased. Over 0.3, the effect of direct-decomposition dramatically increased. From 0.1 to 0.3, the dispersed P25 TiO₂ particles into silica matrix increased, which caused the promotion of adsorption-decomposition. Over 0.3, P25 TiO₂ particles agglomerated, leading to enhancement direct-decomposition [Fig. 2(III)].

**Table 3.** Kinetic rate constants calculated by simulation from Eqs. (2)-(4) in S-P25 system

|                | Ti/Si = 0.1 | Ti/Si = 0.3 | Ti/Si = 0.5 |
|----------------|-------------|-------------|-------------|
| \( k'_{ads} = k_{ads} \times N_{sat} \times (10^{-4}/s) \) | 28         | 26          | 17          |
| \( k'_{des} = k_{des}/C_{cat} \times (10^{-4}/s) \) | 0.5        | 0.6         | 1.2         |
| \( k'_1 = k_1 \times N_{sat} \times (10^{-4}/s) \) | 5.0        | 4.9         | 6.3         |
| \( k'_2 = k_2/C_{cat} \times (10^{-4}/s) \) | 0.5        | 1.1         | 1.8         |

**4. Conclusions**

Three types of mesoporous silica-titania can be synthesized by a sol-gel process. Acidic point can be made by incorporation of Ti into SiO₂ network, which tends to...
enhance the adsorbability of CH$_3$CHO. Crystalline TiO$_2$ is needed for photodecomposition of CH$_3$CHO. Effect of adsorption on photodecomposition should be included in kinetic equation. Kinetic approach based on direct-decomposition, adsorption and adsorption-decomposition indicates good fitting result with experimental data. Direct-decomposition and adsorption affect on initial removal of CH$_3$CHO gas, whereas adsorption-decomposition relates to later period. Highly dispersive TiO$_2$ nanoparticles in mesoporous silica matrix is effective structure on both direct-decomposition and adsorption-decomposition.

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