Improvement of oxidative decomposition activity on hollandite type photocatalyst against pentachlorophenol

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Abstract

Endocrine-disrupting chemicals such as pentachlorophenol (C6Cl5OH) are hazardous for the generative function of living creatures. Photocatalysts give us an effective route for removing these pollutants. Most of the reports are related to a photocatalyst of titanium dioxide (TiO2) fine particles loaded with metal particles such as Pt or Ag. However, a diversity of photocatalysts is required to deal with the increasing number of identified harmful chemicals which occur under a range of different conditions.

Hollandites have one-dimensional tunnel-like framework structure. K2Ga2Sn6O16 (KGSO) is one of hollandite type compounds. In this study, hollandite type KGSO fine powders were fabricated using sol–gel method. The hydrolysis route was carefully observed for preparation of KGSO fine powders with high photocatalytic activity. To prepare the fine powder, the influence of hydrolysis temperature on preparation of fine powder was examined. It was found that the control of aforementioned temperature was very important for preparation of nano-sized KGSO powders with high activity. In addition, the authors controlled particle morphology of KGSO using different preparation conditions. The oxidative decomposition activity against C6Cl5OH on round shape KGSO nano-particles (78%) was much higher than that on the elongated shape KGSO particles (46.2%). It is concluded that the control of morphology and size of KGSO particles maximized the photocatalytic activity on KGSO for oxidative decomposition of C6Cl5OH. In addition, KGSO did not produce organic chlorides as by-products in the photocatalysis. Accordingly, it is expected that KGSO will be one of promising photocatalysts for decomposition of harmful aromatic compound C6Cl5OH under weak UV illumination.

Keywords: Photocatalyst; Hollandite; One-dimensional tunnel structure; Pentachlorophenol; Sol–gel process; Weak UV irradiation; Oxidative decomposition; Selectivity; Endocrine disrupting chemicals; Hydrolysis rate

1. Introduction

Endocrine-disrupting chemicals such as pentachlorophenol (C6Cl5OH) are hazardous for the generative function of living creatures [1]. Social interest has been focused on the health risk assessment of a wide range of chemical toxicities, such as those that interfere with the reproductive systems [2–4] and the removal of these compounds from environment. Photocatalysis presents an effective route for removing pollutants especially at low concentrations [5,6] and it can be applied to the removal of harmful chemicals. Most of current studies on photocatalysis are related to titanium dioxide (TiO2) [5–12]. These photocatalysis were specified with the strong oxidative power of TiO2 activated under ultraviolet (UV) [8,9] or visible light illumination [10–12]. But a diversity of photocatalysts will be required in order to deal with a variety of harmful chemicals under different conditions. In a design of photocatalysis for decomposition of harmful aromatic chlorides, a development of the photocatalysts which produce no by-products in the photocatalysis is required.

The authors have investigated the catalytic properties of thermally activated hollandite compounds before [13–15]. Also, the authors examined the photocatalytic properties on the hollandites by selectively decomposing nitric oxide in
the gas phase and nitrate ions in water [16–19]. From these observations, it was expected that the hollandites can be one of promising photocatalysts for a wide range of decomposition catalysts.

Hollandites have one-dimensional tunnel-like framework structure with a stoichiometry of M IV O2 containing the rutile-type MO 6 octahedral linkage as shown in Fig. 1. The tunnels in the hollandite are usually occupied by alkaline or alkaline earth elements in conjunction with the partial replacement of M IV with di- or trivalent cations. K2Ga2Sn6O16 (KGSO) is one of hollandite type compounds.

In the present study, the route of sol–gel process was examined for a preparation of nano-size KGSO powder. Also the influence of particle morphology of KGSO nano-particles on photocatalysis for oxidative decomposition of C6Cl5OH was examined under weak UV illumination.

2. Experiment

2.1. Preparation of nano-size KGSO powder and its characterization

The nano-size KGSO powders were prepared using sol–gel method. The starting materials used were potassium n-propoxide, gallium n-propoxide and tin t-butoxide. These reagents were mixed at the molar ratio of KGSO in methoxyethanol, and the mixed solution was hydrolyzed at 5 or 20 °C to produce the precipitation of precursor of KGSO. To investigate hydrolysis behavior, a part of mixture was separated into a sol and a gel using a centrifuge (30,000 rpm). After separation of the sol, the sol was filtered. The K, Ga, and Sn content in the filter was determined by the inductively coupled plasma (ICP) technique, and the hydrolysis rate was calculated using the following equation:

\[
\text{Hydrolysis rate} = \frac{[K, Ga, or Sn]_i - [K, Ga, or Sn]_t}{[K, Ga, or Sn]_i} \times 100
\]

where [K, Ga, or Sn]i is the concentration of K, Ga, or Sn selected as starting materials and [K, Ga, or Sn]t is the concentration of aforementioned elements in the filtrate t minutes later. To prepare the round shape and elongated KGSO nano-size powders, distilled water and urea solution (1 mol/l) were used as hydrolysis water, respectively. The precipitation was dried in nitrogen gas flow for 3 days. The dried gel was calcined at 700 or 750 °C for 2 h in air after being ground. To remove the impurity on the surface of KGSO powder, the calcined powders were washed using distilled water three times. The crystal phases in all products were characterized by X-ray powder method. The specific surface area for all specimens was obtained by applying the Brunauer–Emmett–Teller (BET) method. The particle morphologies were characterized using field emission scanning electron microscopy (FE-SEM).

2.2. Examination of photocatalysis on KGSO

The oxidative decomposition reaction on KGSO photocatalyst was performed in a quartz-glass cell. About 7.5 mg (28.4 μmol) C6Cl5OH (molecular weight: 264) was dispersed in acetone (3 ml). The organic chloride solution was coated on KGSO powders and dried in air. O2 (2 ml/min) and He (8 ml/min) mixture gas was introduced into the quartz-glass cell, and the C6Cl5OH coated the KGSO powders was irradiated with a 1.3 mW/cm2 black light. CO2 gas was analyzed with a photoionization detector of gas chromatography system equipped with Porapak Q column. After photocatalytic reaction, the residual aforementioned aromatic chlorides were extracted into hexane and quantitatively analyzed by GC/MS. In the oxidative decomposition test of C6Cl5OH, the yield of inorganic chlorine and chloride (HCl + Cl2) were estimated. HCl and Cl2 were extracted into sodium carbonate solution and quantitatively analyzed by absorptiometric method. The conversion of C6Cl5OH and the yield of (HCl + Cl2) were calculated using Eqs. (2) and (3):

\[
\text{Conversion of C}_6\text{Cl}_5\text{OH} = \frac{[\text{C}_6\text{Cl}_5\text{OH}]_{150\text{ min}}}{[\text{C}_6\text{Cl}_5\text{OH}]_i} \times 100
\]

\[
\text{Yield of (HCl + Cl}_2) = \frac{[\text{Total (HCl + Cl}_2)]_{150\text{ min}}}{[\text{Total (HCl + Cl}_2)]_i} \times 100
\]

where [C6Cl5OH]i is the concentration of C6Cl5OH selected as a starting material, [total (HCl + Cl2)]i is the calculated...
content from the initial concentration of C$_6$Cl$_5$OH. [C$_6$Cl$_5$OH]$_{150\text{ min}}$ and [total (HCl + Cl$_2$)]$_{150\text{ min}}$ are the concentration of aforementioned C$_6$Cl$_5$OH, HCl, and Cl$_2$ in the filtrate 150 min latter.

3. Results and discussion

Fig. 2 shows the relationship between hydrolysis rate and hydrolysis time at 20°C in hydrolysis reaction temperature. The hydrolysis rate of K, Ga, and Sn tended to increase with increasing hydrolysis time in the remaining samples. The hydrolysis rate of Ga and Sn reached 100% within 20 min. But the hydrolysis rate of K did not reach 100%. The aforementioned rate reached the maximum at 88%. The difference of hydrolysis behavior among K, Ga, and Sn would be attributable to the solubility of precipitation against water. KOH has high solubility against hydrolysis water. K element did not completely precipitate into the solvent. To increase hydrolysis rate of K and to get a homogeneous precipitation, the hydrolysis reaction was performed at 5°C.

Fig. 3 presents the relationship between hydrolysis rate and hydrolysis time at 5°C in hydrolysis reaction temperature. The hydrolysis rate of aforementioned three elements tended to increase with an increase in hydrolysis time. The hydrolysis behavior of all elements was almost same. This indicates that homogeneous precipitation is obtained in the present hydrolysis process.

Figs. 4(a) and (b) display XRD patterns of KGSO particles which were calcined at 700 and 750°C, respectively. The products which were hydrolyzed at 5°C consisted of a single phase of hollandite structure with a tetragonal unit cell (a = 1.0419 nm and c = 0.31328 nm) at calcination temperature 700°C. No other phases were observed using X-ray diffraction analysis. In contrast, the products hydrolyzed at 20°C had poor crystallinity at the aforementioned calcination temperature. The crystallization temperature of KGSO particles which were hydrolyzed at 5°C was lower than that of KGSO particles hydrolyzed at 20°C. This suggests that the homogeneous precipitation hydrolyzed at 5°C lowers the crystallization temperature of KGSO.

Fig. 5(a) presents SEM photograph of KGSO particles which were hydrolyzed at 5°C and calcined at 750°C. This figure indicates that particles interconnect with each other to make networks. The secondary particles were the cluster of round shape particles. The calcined powders were observed to be composed of uniformly sized, round shaped, and discrete particles. The average particle size of powders was approximately 50 nm. This powder had a specific surface area of 21 m$^2$/g. This indicates that the agglomeration in these particles is small. On the other hand, the KGSO particles which were hydrolyzed at 20°C and calcined at 750°C consisted of a mixture of round shape particles and elongated particles as shown in Fig. 5(b). The small agglomeration was observed in the mixture of round shape and elongated particles. The particle size in long length of elongated particles was 100–300 nm, although the particle size of round shape particles was almost as same as that of particles shown in Fig. 5(a). The aspect ratio of the elongated one was 5–10. This suggests that the different behavior among K, Ga, and Sn in hydrolysis process influences the heterogeneity of particle morphology in calcined particles. It is a key point that the hydrolysis temperature is controlled around 5°C to decrease the solubility of KOH. Accordingly, it is concluded that the control of hydrolysis behavior in sol–gel process is important to prepare round shape KGSO particles in nano-scale.

Fig. 6 demonstrates the relationship between reaction time and photocatalytic activity of oxidative decomposition of C$_6$Cl$_5$OH on the round shape KGSO and the mixture of round shape KGSO and elongated KGSO photocatalysts.
The decomposition product, CO$_2$ gas, was investigated as a function of UV illumination. When the sample was exposed to UV light, CO$_2$ gas concentration increased with increasing reaction time. When the UV light is turned off, CO$_2$ gas concentration gradually decreased. CO$_2$ gas concentration rapidly increased, however, when the sample was re-exposed to UV light. This tendency is a typical phenomena of photocatalysis. The activated surface of KGSO consequently decomposed C$_6$Cl$_5$OH to CO$_2$ gas even with a weak UV lamp. Under total UV irradiation time of 150 min, the conversions of C$_6$Cl$_5$OH on round shape KGSO and elongated KGSO were 78.3 and 60.2%, respectively. This indicates that a control of particle morphology in nano-scale is important for a development of photocatalyst with high activity.

To conclude the influence of particle morphology on photocatalytic activity, the elongated KGSO particles were synthesized using urea solution (1 mol/l) instead of hydrolysis water in sol–gel process. Fig. 7 shows XRD profiles of calcined KGSO powders which were synthesized using different hydrolysis solution. Both calcined products consisted of a single phase of hollandite type structure. No other phases were observed using X-ray diffraction analysis. Since the hydrolysis temperature was controlled at 5°C for preparation of both powders, aforementioned two powders consisted of single phase of hollandite structure. But the crystallinity of KGSO powders, which were hydrolyzed using urea solution, was poor as compared with KGSO powders hydrolyzed by distilled water. This indicates that the surface area of KGSO powders hydrolyzed by urea solution is much higher than that of KGSO hydrolyzed by distilled water.

Fig. 8 displays SEM image of particle morphologies recorded from KGSO powder synthesized by urea solution. The elongated particles were prepared when the urea solution (1 mol/l) was used instead of distilled water.

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**Fig. 4.** XRD profiles of KGSO particles which were hydrolyzed at 5 and 20°C. Calcination temperature: (a) 700°C, and (b) 750°C.

**Fig. 5.** SEM photographs of KGSO particles which were hydrolyzed at (a) 5°C and (b) 20°C. Calcination temperature: 750°C.

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![Fig. 4. XRD profiles](image1)

![Fig. 5. SEM photographs](image2)
The elongated particles consisted of aggregates. The agglomeration was observed in the elongated particles, but the primary particles inside tend to separate from each other. The particle size in long length of elongated particles was approximately 300 nm. The aspect ratio of the elongated one was 10. These elongated particles have a specific surface area of 36.2 m$^2$/g. The SEM observation and the BET analysis indicate that elongated KGSO has porous structure and a large amount of N$_2$ gas penetrable to inside of the aggregates during BET analysis. Since morphology of KGSO was changed by distilled water or urea solution in the hydrolysis process, NH$_4^+$, OH$^-$ and CO$_3^{2-}$ content of the precipitate in the present process would determine the morphology of nano-size KGSO particles.

Fig. 9 shows the relationship between reaction time and photocatalytic activity of oxidative decomposition of C$_6$Cl$_5$OH on round shape KGSO and elongated KGSO photocatalysts. The tendency of photocatalysis profile of elongated KGSO was as same as that of round shape KGSO. But the activity on elongated KGSO was much lower than that on round shape KGSO. Under total UV irradiation time of 150 min, the conversions of C$_6$Cl$_5$OH on round shape KGSO and elongated KGSO were 78.3 and 46.2%, respectively. This suggests that the surface of round shape KGSO has many active sites as compared with the elongated one. Since round shape KGSO has many tunnel end plane on the surface, we concluded that tunnel end plane of KGSO is active site. As mentioned above, it is found that a control of morphology of KGSO particles in nano-scale is a key for development of KGSO photocatalyst. In addition, the yield (round shape KGSO: 78.1%, elongated KGSO: 44.5%) of (HCl+Cl$_2$) after UV irradiation of 150 min was...
equal to the conversion of C₆Cl₅OH (round shape KGSO: 78.3%, elongated KGSO: 46.2%). The relationship between conversion of C₆Cl₅OH and yield of (HCl + Cl₂) was summarized in Table 1. This indicates that KGSO photocatalyst has high selectivity for the decomposition of C₆Cl₅OH to (HCl + Cl₂) and no harmful organic chlorides as by-products are created in this photocatalytic decomposition reaction on KGSO. This high selectivity would be very important for a development of photocatalysts for the decomposition of endocrine-disrupting chemicals such as C₆Cl₅OH. Accordingly, it is expected that KGSO will be one of promising photocatalysts for decomposition of harmful chemicals such as aromatic chlorides.

4. Summary

The photocatalytic oxidation reaction on the hollandite type compound KGSO was examined for oxidative decomposition of C₆Cl₅OH under weak UV illumination. For a design of photocatalyst with high activity and its photocatalysis, the influence of processing route on morphology of KGSO powders was examined. Round shape nano-size KGSO powders were synthesized when the hydrolysis temperature was controlled at 5 °C. This temperature control was a key for preparation of nano-sized round shape KGSO powders. The elongated nano-size KGSO powders were synthesized when the precursor solution was hydrolyzed using urea solution instead of distilled water. KGSO clearly showed the photooxidoative decomposition of C₆Cl₅OH under weak UV illumination at room temperature. The decomposition activity of C₆Cl₅OH on round shape KGSO was much higher than that on the elongated shape one. Also KGSO showed a high selectivity for preparation of CO₂ and (HCl + Cl₂) in the decomposition reaction of C₆Cl₅OH. This means that no harmful organic chlorides as by-products are created in the present photocatalysis on KGSO. Accordingly, it is concluded that a control of morphology of KGSO in nano-scale is important for a design of catalytic activity and a development of KGSO photocatalyst.

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