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Synthesis and photo-catalytic property of a hollandite-type compound ($K_2Ga_2Sn_6O_{16}$)

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Abstract

Hollandites crystallize with one-dimensional tunnel-like framework structures. The tunnels in the hollandite are usually occupied by alkaline or alkaline earth elements and a case in point is $K_2Ga_2Sn_6O_{16}$ (KGSO). This compound has been shown to be catalytically active in the decomposition of endocrine-disrupting chemicals, pentachlorophenol (C_6Cl_5OH) and heptachloro-dioxin ($C_{12}Cl_7O_2H$), under weak ultraviolet illumination. It was observed that the morphology and size of the prepared materials was a significant factor in determining the extent of catalytic activity. Fine powders of KGSO were prepared using a sol–gel route. However, variations in the hydrolysis step allowed for control of the morphology of the produced, fine powders which in turn produced variations in the catalytic activity. The morphology of these powders was observed to be a key in maximizing the photocatalytic oxidative decomposition of both C_6Cl_5OH and $C_{12}Cl_7O_2H$ with particles which had a more rounded morphology having the greater activity. KGSO is a promising photocatalyst for decomposition of harmful aromatic compounds and with careful chemical control of its synthesis, the material can be optimized for chemical activity.

Keywords: Sol–gel processes; Surfaces; Functional applications

1. Introduction

There is an increasing concern for the effects of endocrine-disrupting chemicals such as pentachlorophenol (C_6Cl_5OH) and heptachloro-dioxin ($C_{12}Cl_7O_2H$) on the generative function of living creatures.[1] This comes on the back of an overall concern for a wide range of possible chemical toxins that are seen to adversely effect the reproductive systems[2–4] and a concern as to how successful strategies can be developed to remove these toxins from the ecosystem. Photocatalysis is proving to be an effective route for removing these pollutants and to date those catalysts are based mainly on titanium dioxide (TiO_2) utilized in various forms such as single crystals[5,6] thin films[7,8] fine particles loaded with Pt or Ag and a range of other configurations with TiO_2 as a substrate.[9–11] These photocatalysists have specific properties which rely on the strong oxidative power of TiO_2 activated under ultraviolet (UV) or visible light illumination. However, with the increasing range of chemical that need to be neutralized from the environment, a wider range of photocatalysts which can operate over a wide band of environmental conditions will be required to cope with the demand.

The authors have previously investigated the catalytic properties of thermally activated hollandite compounds.[12–14] In addition, the authors have also previously shown the potential of the photo-catalytic properties of hollandites by selectively decomposing nitric oxide in the gas phase and nitrate ions in water.[15–18] As a result of these preliminary observations it was thought that this family of hollandites may be a most promising photocatalysts for a wide range of decomposition reactions.

Hollandites have one dimensional tunnel-like framework structure which have a local stoichiometry of $M^{IV}O_2$ and are bounded by rutile-type MO_6 linked octahedron. The tunnels in the hollandite are usually occupied by alkaline or

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alkaline earth elements in conjunction with the charge compensating partial replacement of M^{IV} with di- or tri-valent cations. $K_2Ga_2Sn_6O_{16}$ (KGSO) is a typical hollandite-type compound with Sn providing the framework cation and the K occupying the tunnels. This study describes the controlled preparation through a sol–gel route of KGSO powders with differing powder morphology and an examination of their subsequent photocatalytic activity of oxidative decomposition of C_6Cl_5OH and $C_{12}Cl_7O_2H$ under weak UV illumination.

2. Experiment

2.1. Synthesis and characterization of nano-sized KGSO powders

The nanometer range KGSO powders were prepared by sol–gel method. The starting materials used were metal alkoxides such as 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 °C to produce the precipitation of the precursor that was used to produce the final form of KGSO. To investigate the hydrolysis behavior, a part of the mixture was separated into the sol and gel components using a centrifuge (30,000 rpm). After separation of the sol, it was filtered and the K, Ga and Sn content determined by inductively coupled plasma (ICP) technique. The hydrolysis rate was calculated using the following equation:

$$\text{hydrolysis rate}\,(\%) = \frac{[\text{K, Ga, or Sn}]_i - [\text{K, Ga, or Sn}]_t}{[\text{K, Ga, or Sn}]_i} \times 100 \qquad (1)$$

where $[\text{K, Ga, or Sn}]_i$ is the concentration of K, Ga or Sn selected as a starting materials and $[\text{K, Ga, or Sn}]_t$ is the concentration of aforementioned elements in the filtrate t min latter. The morphology of the prepared powders could be controlled markedly by using different hydrolysis routes. To prepare materials with round shape, distilled water was used in the hydrolysis stage and for more elongated particles; urea solution (1 mol/l) was used. The dried gel from each of these processes was calcined at 750 °C for 2 h in air after being ground. The crystal phases in all products were characterized by X-ray powder diffraction. The chemical composition of the calcined KGSO was analyzed by ICP as before. The specific surface area for all specimens was obtained by applying the Brunauer–Emmett–Teller (BET) method. The particle morphologies were characterized using scanning electron microscopy (SEM).

2.2. Examination of photocatalytic activity on KGSO

The photocatalytic decomposition reaction was performed in a quartz-glass cell. Approximately 7.5 mg (28.4 μmol) C_6Cl_5OH (molecular weight: 264) and 1 g (2.37 mmol) $C_{12}Cl_7O_2H$ (molecular weight: 422) were dispersed in acetone (3 ml) and toluene (3 ml), respectively. These organic chloride solutions were coated on KGSO powders and dried in air. A gas mixture consisting of oxygen (2 ml/min) and helium (8 ml/min) was introduced into the quartz glass cell, and the C_6Cl_5OH or $C_{12}Cl_7O_2H$ (dioxin) coated the KGSO powders were irradiated with a 1.3 mW/cm^2 black light. Carbon dioxide (CO_2) gas was analyzed with a photo-ionization detector on gas chromatography equipment incorporating a Porapak Q column. After photocatalytic reaction, the residual aromatic chlorides were extracted into hexane and quantitatively analyzed by GC/MS. To test the decomposition of dioxin, the yield of inorganic chlorine was estimated. The inorganic chlorines such as HCl and Cl_2 were extracted into sodium carbonate solution and quantitatively analyzed by absorptiometric method.

3. Results and discussion

Fig. 1 shows the relatiohnship between hydrolysis rate and hydrolysis time at 5 °C. The hydrolysis rate of K, Ga, and Sn tended to increase with an increase in hydrolysis time. The hydrolysis rate reached 100% within 20 min and since the hydrolysis behavior of each of the present cations was the same, it was expected that a homogeneous precipitation was prepared.

Fig. 2(a) and (b) present XRD patterns of calcination products. Both calcined products consited of a single phase of hollandite type structure with a tetragonal unit cell ($a = 1.0419$ nm and $c = 0.31328$ nm). No other phases were observed. A key to the successful preparation of on-composition materials was the control of the solubilty of potassium ions in water at room temperature. In order to min-

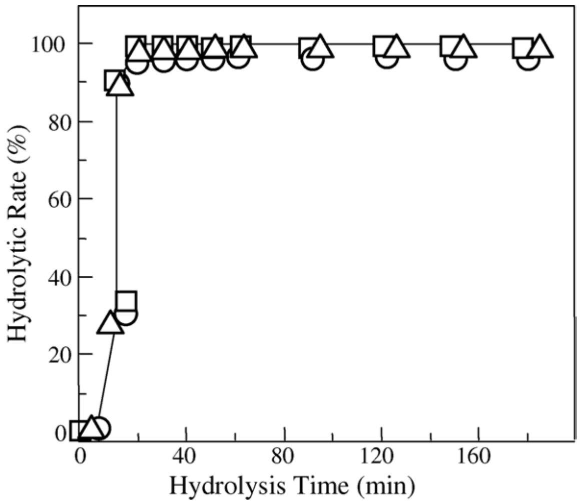

Fig. 1. The relationship between hydrolysis rate and hydrolysis time at 5 °C. Hydrolysis water dropping rate is 1.0 ml/min; (□) Sn, (△) Ga, (○) K.

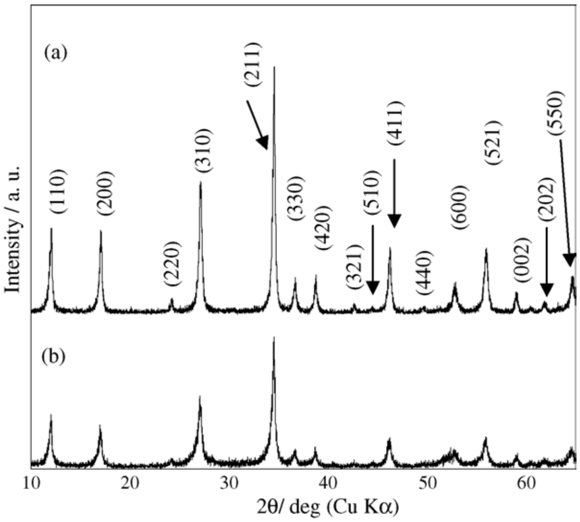

Fig. 2. XRD profiles of (a) nano size round shape particles and (b) nano size elongated particles, calcinations temperature: 750 °C, calcination time: 2 h.

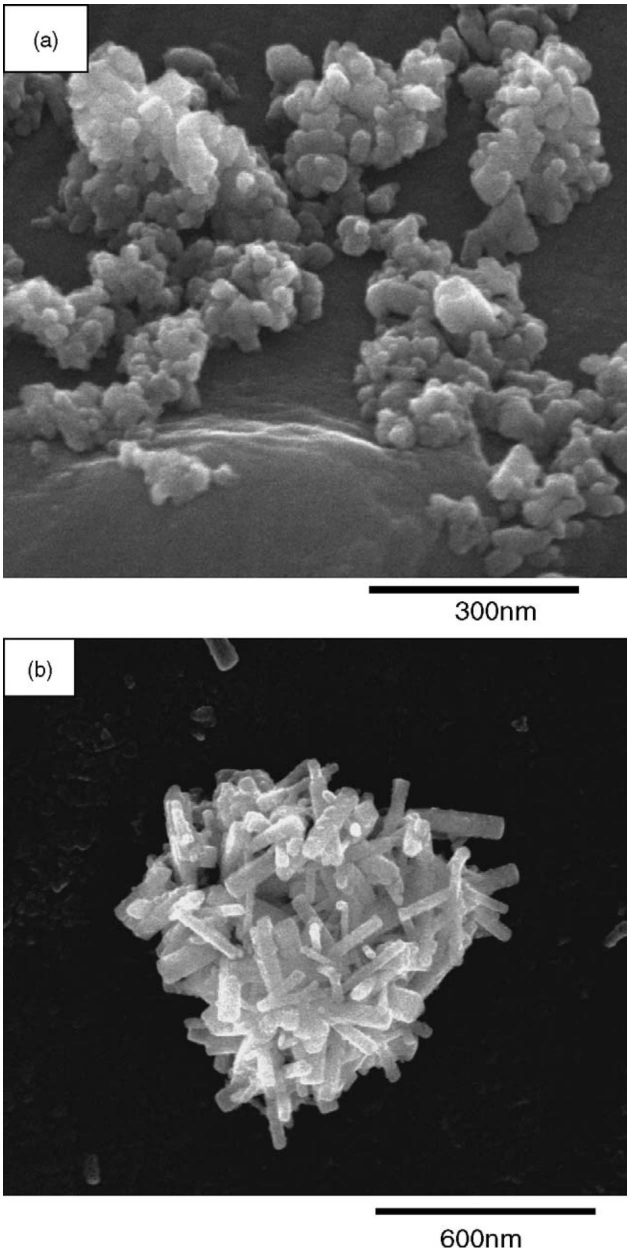

Fig. 3. SEM images of (a) round shape KGSO particles and (b) elongated KGSO particles, calcination conditions were equal to Fig. 2.

imize this, the hydrolysis temperature was lowered to around 5 °C. The resulting precipitration when calcined had a chemical compostion of $K_{1.85}Ga_{1.85}Sn_{6.15}O_{16}$, indicating that the composition of the KGSO could be controlled within a small deviation.

Fig. 3(a) and (b) show SEM images of each of the powder morphologies. Clearly they can be characterized roughly into round and elongated shape. The average particle size of the round shaped KGSO was 50 nm (Fig. 3 (a)). This powder has a specific surface area of 20.8 m^2/g. The round shape particles were well dispersed and did not appear to be agglomerated. On the other hand, the elongated particles were observed to form aggregates. The agglomeration was observed in the elongated particles (Fig. 3 (b)). The longer dimension of the elongated particles was approximately 300 nm with an overall aspect ratio of 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 have a porous structure. Since the morphology of KGSO was seen to be dependant on the chemical composition of the hydrating fluid, it is suggested that the 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. 4 shows the relationship between reaction time and photocataltyic activity of oxidative decompostion of C_6Cl_5OH on round shaped KGSO and elongated KGSO photo-catalysts, respectively. The decompostion product, CO_2 gas, was investigated as a function of UV irradiation. When 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 clearly indicates that photocatalysis is taking place. The activated surface of KGSO decomposed C_6Cl_5OH to CO_2 gas, even with a weak UV lamp. Under total UV irradiation time of 150 min, the conversions of C_6Cl_5OH on round shaped KGSO and elongated KGSO was 78.3 and 46.2%, respectively, indicating that the surface of the round shaped particles is substantially more active. We suggest that a rounded particle would have a greater percentage of terminating tunnels which we suggest, houses the active site for photocatalysis. The elongated particles grow with the tunnels along the growth axis and as a consequence the active exposed sites are at the termination of the particle. This is a difficult point to prove; however, a proposed study using transmission electron microscopy may provide some support of this idea. The difficulty is that these materials are

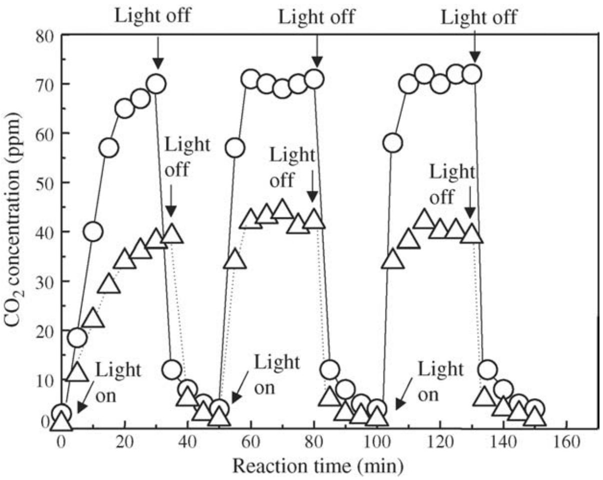

Fig. 4. CO_2 concentration vs. reaction time on round shape KGSO (○) and elongated KGSO (△) photocatalysts. Light source: black light (incident intensity: 1.3 mW/cm^2).

extremly beam sensitive and may not be amenable to high resolution examination.

Fig. 5 presents the relationship between reaction time and photocataltyic activity of oxidative decompostion of $C_{12}Cl_7O_2H$ on round shape KGSO photocatalyst. The conversion of dioxin on the round shaped KGSO reached 72% under total UV irradiation time of 16 h. The decompostion rate of dioxin on KGSO is sufficient for removal of dioxin ($C_{12}Cl_7O_2H$) under weak UV light if we consider that the concentration of dioxin (2.37 mmol) was much higher than that of C_6Cl_5OH (28.4 μmol) in the present test. In addition, the yield (72%) of inorganic chlorine ($HCl + Cl_2$) after UV irradiation of 16 h was exactly equal to the conversion of dioxin (72%). This indicates that round shape KGSO photo-catalyst has a unique selectivity for the decomposition reaction of $C_{12}Cl_7O_2H$ and produces no harmful organic chlorides as by-products. This high selectivity is an important factor in developing photocatalysts for the decomposition of endocrine-disrupting chemicals such as dioxin or its related compounds. Accordingly, it is expected that KGSO is one of the promising candidates for photocatalysts for the decomposition of harmful chemicals.

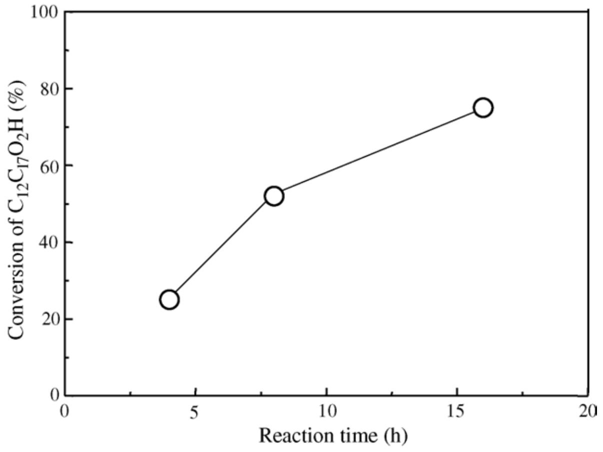

Fig. 5. The relationship between conversion fraction of $C_{12}Cl_7O_2H$ and reaction time on round shape KGSO photocatalyst. Light source: black light (incident intensity: 1.3 mW/cm^2).

4. Summary

The photocatalytic oxidation reactions on the hollandite type compound KGSO were examined for oxidative decomposition of endocrine-disrupting chemicals, C_6Cl_5OH and $C_{12}Cl_7O_2H$ under weak UV illumination. KGSO clearly showed the photo-oxidative decompositions of C_6Cl_5OH and $C_{12}Cl_7O_2H$ under weak UV illumination at room temperature. To examine the influence of particle morphology of KGSO on the photocatalytic activity against the decomposition of aforementioned harmful aromatic chlorides, powders with very different morphologies were prepared using a sol–gel method. The decomposition activity of C_6Cl_5OH on round shape KGSO was much efficient than that on specimens which showed an elongated shape. Also the round shape KGSO showed high selectivity in the decomposition reaction of $C_{12}Cl_7O_2H$. In addition, the control of hydrolysis temperature was important factors to prepare the fine KGSO powders. Accordingly, it is concluded that a control of morphology of KGSO is important for enhancement of catalytic activity and the design of a soft-chemical processing route is a key for development of KGSO photocatalyst.

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