

Short communication

# A method for decomposition of hexachlorobenzene by $\gamma$ -alumina

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## Abstract

A method of decomposing hexachlorobenzene (HCB) by  $\gamma$ -alumina was investigated at low temperature of 300 °C. It was found that HCB was rather quickly decomposed under such a condition. Decomposition efficiency (DE) increases with increasing the surface area of  $\gamma$ -alumina. Pretreated  $\gamma$ -alumina has a better performance for the decomposition reaction. A high decomposition efficiency within the short reactive time of 60 min was achieved to be 94.2%, which was obtained by preheating  $\gamma$ -alumina with the surface area of 220 m<sup>2</sup> g<sup>-1</sup> at 450 °C for 2 h. High surface area and appropriate pretreatment temperature probably provide more reactive sites such as the isolated OH groups and Al<sup>3+</sup> sites surrounded by O<sup>2-</sup> sites. These sites may induce the decomposition of HCB via a main ring-cracking process. The present study, hopefully, holds the promise for the eliminating of HCB contained hazardous materials in industrial application.

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**Keywords:**  $\gamma$ -alumina; Hexachlorobenzene; Decomposition efficiency; Reactive sites

## 1. Introduction

Hexachlorobenzene (HCB) is an environmentally persistent organic pollutant. It has an adverse health effects on animals and humans and is classified as a probable human carcinogen by the US Environmental Protection Agency [1]. Elimination of HCB from the environment is therefore of high importance. Methods for the dechlorination of chlorinated organic compounds have been reported such as hydrodechlorination on carbon supported Pd–Ni bimetallic catalysts [2], dechlorination with potassium–sodium alloy [3] and Fe (II) [4], microbial dechlorination [5], and photolysis [6]. These methods are unique and excellent, however, they are generally difficult to operate and require uses of specific expensive reagents and/or devices.

Metal oxides and supported noble metals are active for many deep oxidations [7–10]. Metal oxides are easier to obtain compared with alloys and supported catalysts. Recently, aluminum oxide has been widely used for eliminating many organic pollutants [8–10]. Decomposition of carbon tetrachloride by alumina was reported by Khaleel and Dellinger [8]. It has been found that the high surface area  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder holds the remark-

able reactive property. Kim [9,10] studied the adsorption of triethylenediamine (TEDA) on partially and highly dehydroxylated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surfaces where Al–OH group and surface Lewis acid Al<sup>3+</sup> serve as the important adsorption sites for the decomposition of TEDA, respectively. Mawhinney [11] investigated the reaction of 2-chloroethylethyl sulfide with a high surface area Al<sub>2</sub>O<sub>3</sub> which served as a decontamination medium, and pointed out that the dehydroxylation process played a critical role during this reaction. In this paper, a new method for decomposition of HCB at relatively low temperature and short reactive time on  $\gamma$ -alumina was reported. The achieved results, hopefully, provide applications for eliminating the persistent organic pollutant HCB contained solid wastes.

## 2. Experimental section

Hexachlorobenzene (purity 99.9%) was purchased from Beijing Chemical Plant of China and used without further purification.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was obtained from Alfa Aesar (A Johnson Matthey Company, USA). The surface areas were 45, 100, and 220 m<sup>2</sup> g<sup>-1</sup>, respectively. It was thermally pretreated at 450 °C or 550 °C for 2 h or not before exposure to HCB. Decomposition experiment was carried out in sealed glass ampules (volume, 2.0 mL). 2.0 mg HCB (7023 nmol) and 200 mg  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were mixed and sealed under air atmosphere. Then, the samples were

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heated to 300 °C for the various time ranges from 5 min to 90 min. A blank test was also carried out without  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 300 °C for 60 min. All the experiments were performed in triplicate to ensure the repeatability of the results.

Sample analysis was described elsewhere [12]. After reaction, the ampule bottle was crushed and extracted by hexane (Fisher Scientific Inc.). The extracts were analyzed by an Agilent 6890 gas chromatograph equipped with a HP-5MS capillary column (30 m length, 0.25 mm i.d., 0.25  $\mu$ m film thickness) and interfaced to Agilent 5973N MSD. Quantitative analyzes of chlorobenzenes were performed in selected ion monitoring mode using two most abundant ions of the molecular ion clusters. The decomposition efficiency (DE) was calculated using following equation:

$$DE(\%) = \left( \frac{1 - R_{\text{HCB}}}{I_{\text{HCB}}} \right) \times 100 \quad (1)$$

where  $I_{\text{HCB}}$  is the molar number of HCB initially used.  $R_{\text{HCB}}$  is the residual molar number of HCB after the reaction.

### 3. Results and discussion

Table 1 lists the DE of HCB on the varied  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surfaces at 300 °C for the reactive time of 60 min. It could be observed that DE increased with increasing the surface area of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. When the surface area increased from 45 m<sup>2</sup> g<sup>-1</sup> to 220 m<sup>2</sup> g<sup>-1</sup> at the pretreatment temperature of 450 °C, DE increased from 42.5% to 94.2%. The trend was in agreement with the decomposition of carbon tetrachloride on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface [8]. It suggests that high surface area of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> favorably support the decomposition of HCB. On the other hand, it could be seen that the DE of HCB on the preheated alumina was higher than on the unpreheated one (room temperature). Obviously, the pretreated  $\gamma$ -alumina has a better performance for the decomposition reaction of HCB. For example, the DE was only 75.0% on the unpreheated alumina compared with 94.2% on the preheated one at 450 °C under the surface area of 220 m<sup>2</sup> g<sup>-1</sup>. However, when the preheated temperature of alumina increased from 450 °C to 550 °C, DE decreased from 94.2% to 85.0%. It is known that the alumina surface typically contains the defect sites which are terminated by hydroxyl groups or adsorbed water after exposure to the atmosphere [11]. Heating the powdered Al<sub>2</sub>O<sub>3</sub> produces some number of Lewis acid–base pair sites or Al<sup>3+</sup> sites surrounded by O<sup>2-</sup> except for the existence of the isolated hydroxyl groups [13]. According to the coordination

Table 1  
Decomposition efficiencies of HCB on varied  $\gamma$ -alumina surfaces at 300 °C for 60 min ( $n = 3$ , RSD < 10%)

Alumina	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Alumina preheated temperature (°C)	Decomposition efficiency (%)
Gamma_45	45	450	42.5
Gamma_100	100	450	66.7
Gamma_220	220	450	94.2
Gamma_220	220	–	75.0
Gamma_220	220	550	85.0

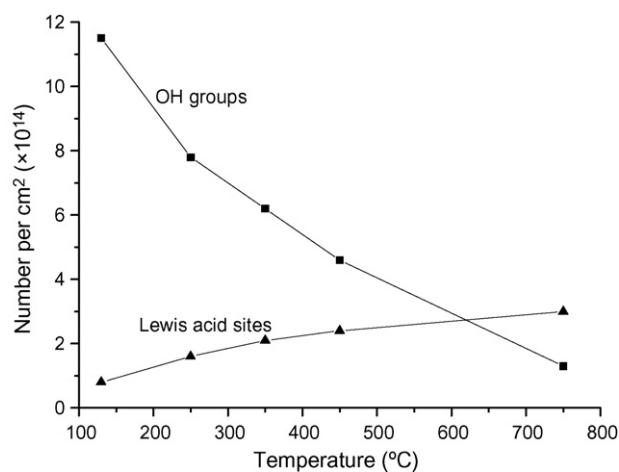


Fig. 1. Specific properties of  $\gamma$ -alumina at various pretreatment temperatures [15].

theory, Lewis acid–base pair sites on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surfaces are unsaturated. They are prone to bond with some functional groups that are adsorbed as ligands. Therefore,  $\gamma$ -alumina contains: (a) physisorption sites, that is, OH groups that adsorb organic molecules via hydrogen bonding and (b) adsorption locations that could give rise to Lewis acid sites adsorption [11]. However, the adsorption of too much water on the alumina surface lead to a high population of OH groups combined with Al<sup>3+</sup> resulting in hindering the reaction. On the other hand, the elevated temperature not only results in the increase of dehydroxylation but also increases sintering of alumina [14]. A measure of the OH groups per square centimeter compound to that of the Lewis acid sites was reported by Thomas [15]. As given in Fig. 1 (from reference [15]), when the preheated temperature was raised, OH groups decreased rapidly, whereas the Lewis acid sites increased slowly. Based on these reports and the present experimental results, it could be concluded that the more reactive sites on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for decomposing HCB should be from the cooperative contributions of both the isolated hydroxyl groups and Lewis acid–base pair sites. The overall observation from Table 1 shows that the

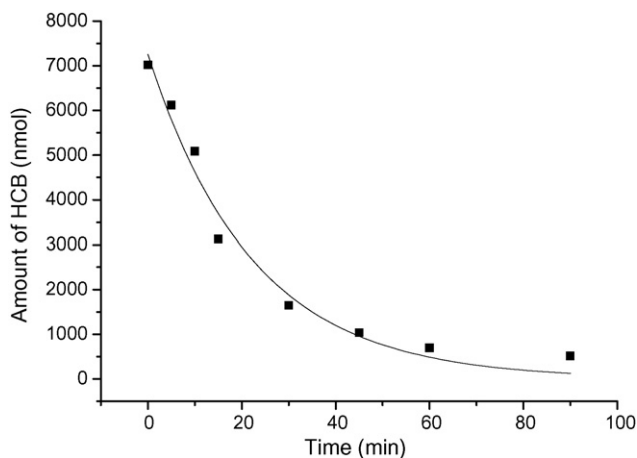


Fig. 2. Black spots (mean value of three replicates) show the changes of the residual HCB amount on  $\gamma$ -alumina dependent on the reactive time at 300 °C. The curve represents the corresponding fitted results.

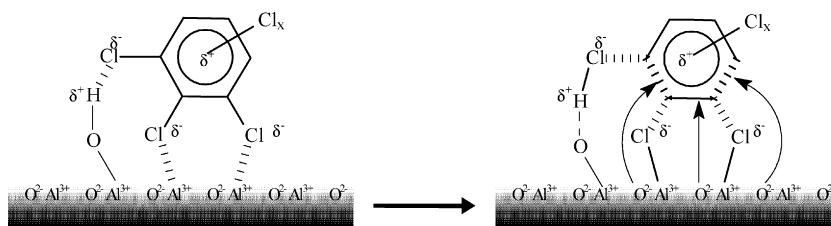


Fig. 3. Tentative schematic picture representation of HCB decomposition process on  $\gamma$ -alumina.

highest decomposition efficiency was achieved to be 94.2% at the pretreatment temperature of 450 °C. This signals that the high alumina reactive sites from the isolated hydroxyl groups and Lewis acid–base pair sites should be approached under such a condition. It is in agreement with the results reported by Mawhinney et al. [11] where a maximum  $\text{Al}_2\text{O}_3$  reactivity for decomposing 2-chloroethylethyl sulfide was achieved by pretreatment of  $\text{Al}_2\text{O}_3$  in the temperature range 400–500 °C and it was expected that both the isolated hydroxyl groups and Lewis acid–base pairs are involved in the reaction [11].

Subsequently, the behavior of the HCB decomposition as a function of the reaction times was investigated selectively on the  $\gamma$ - $\text{Al}_2\text{O}_3$  material with the surface area of  $220 \text{ m}^2 \text{ g}^{-1}$  at the pretreatment temperature of 450 °C. Black spots in Fig. 2 represent the changes of the residual HCB amount dependent on the heating time at 300 °C, exhibiting a decaying quasi-exponential relationship. HCB was rapidly decomposed from 7023 nmol to 694 nmol in 60 min and further decreased to 518 nmol in 90 min. It hints that  $\gamma$ - $\text{Al}_2\text{O}_3$  material is an effective way for eliminating the hazardous waste HCB. The result is roughly fitted as shown by the curve in Fig. 2 and quantitatively described by the below equation:

$$R_{\text{HCB}} = I_{\text{HCB}} \times \exp(-kt) \quad (k = 0.045) \quad (2)$$

$I_{\text{HCB}}$  is the molar number of HCB initially used.  $R_{\text{HCB}}$  is the residual molar number of HCB after the reaction. The value of  $k$  represents the HCB reaction rate constant for present study.  $t$  is the reaction time. From Eqs. (1) and (2), we can further deduce the followed equation:

$$\text{DE} (\%) = [1 - \exp(-0.045t)] \times 100 \quad (3)$$

It shows that DE has a quasi-exponential relationship with the reaction time  $t$  in present study.

In addition, the decomposition products were primarily analyzed after each reaction for exploring the decomposition mechanism of HCB on the  $\gamma$ -alumina material. During the overall reactions, less chlorinated benzenes were not detected except for the small amount of pentachlorophenol and pentachlorobenzene (<10 nmol), which suggested that the dechlorination could be neglected and the HCB decomposition may be a ring-cracking process. Further, based on the reported literatures [11–16], a possible mechanism for decomposing HCB by  $\gamma$ -alumina was described as follows (see Fig. 3). The HCB molecules adsorbed on the partially hydroxylated alumina via the hydrogen bonding and  $\text{Al}^{3+}$ – $\text{Cl}^-$  interaction. This step was followed by the nucleophilic attack on the carbon of the ring by the  $\text{O}^{2-}$  Lewis base. The reaction proceeded by the cleavage of

the carbon–chlorine bond to produce an  $\text{Al}^{3+}$ – $\text{Cl}^-$  bond and the formation of some ring-cracking species. Similar reactions occurred to 2-chloroethylethyl sulfide with  $\text{Al}_2\text{O}_3$  surfaces [11]. This process was essentially a reaction that requires the continuous renewing of the metal oxide surface by  $\text{O}^{2-}$ / $\text{Cl}^-$  exchange [11,14,15]. Thus, mobility of oxygen and chlorine atoms in the surface of the material became important. For the regeneration ability of aluminum oxide, it is predicted that the  $\text{AlCl}_3$  could be changed to  $\text{AlCl}_3 \cdot n\text{H}_2\text{O}$ , which will turn to  $\text{Al}_2\text{O}_3$  and  $\text{HCl}$  after calcination.

This is a very simple method using one metal oxide ( $\gamma$ - $\text{Al}_2\text{O}_3$ ) as a decomposition reagent, which is more easily to obtain than some composite oxides [12] or bimetallic catalysts [2,3]. The highest decomposition efficiency was achieved to be 94.2%, which is higher and effective than other decomposition methods [5]. A comprehensive study is in progress.

#### 4. Conclusion

Decomposition of HCB by  $\gamma$ -alumina was investigated at low temperature of 300 °C. The results show that  $\gamma$ -alumina is an effective way of eliminating hazardous waste HCB. DE increases with increasing the surface area of  $\gamma$ -alumina. Pretreated  $\gamma$ -alumina has a better performance due to the more active sites. A high DE within the short reactive time of 60 min was achieved to be 94.2%, which was obtained by preheating  $\gamma$ -alumina with the surface area of  $220 \text{ m}^2 \text{ g}^{-1}$  at 450 °C for 2 h. A quasi-exponential relationship between DE and the reactive time was revealed. In addition, the primary analysis of the decomposition products show that the decomposition of HCB on  $\gamma$ -alumina may be mainly induced by a ring-cracking process, which was carried out by the nucleophilic attack on the carbon of the ring by the  $\text{O}^{2-}$  Lewis base. The present results promisingly take an important role in the eliminating of persistent organic pollutants.

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#### References

- [1] ATSDR, ATSDR Public Health Statement: Hexachlorobenzene, Agency for Toxic Substances and Disease Registry, Division Toxicology, Atlanta, GA, 1999.

- [2] V. Simagina, V. Likhobolov, G. Bergeret, M.T. Gimenez, A. Renouprez, Catalytic hydrodechlorination of hexachlorobenzene on carbon supported Pd–Ni bimetallic catalysts, *Appl. Catal. B: Environ.* 40 (2003) 293–304.
- [3] K. Miyoshi, T. Nishio, A. Yasuhara, M. Morita, T. Shibamoto, Detoxification of hexachlorobenzene by dechlorination with potassium–sodium alloy, *Chemosphere* 55 (2004) 1439–1446.
- [4] W.H. Kang, I. Hwang, J.Y. Park, Dechlorination of trichloroethylene by a steel converter slag amended with Fe (II), *Chemosphere* 62 (2006) 285–293.
- [5] F. Brahusi, U. Dorfler, R. Schroll, J.C. Munch, Stimulation of reductive dechlorination of hexachlorobenzene in soil by inducing the native microbial activity, *Chemosphere* 55 (2004) 1477–1484.
- [6] J.C. Yu, T.Y. Kwong, Q. Luo, Z. Cai, Photocatalytic oxidation of triclosan, *Chemosphere* 65 (2006) 390–399.
- [7] J.J. Spivey, Complete catalytic oxidation of volatile organics, *Ind. Eng. Chem. Res.* 26 (1987) 2165–2180.
- [8] A. Khaleel, B. Dellinger, FTIR investigation of adsorption and chemical decomposition of  $\text{CCl}_4$  by high surface-area aluminum oxide, *Environ. Sci. Technol.* 36 (2002) 1620–1624.
- [9] S. Kim, O. Byl, J.T. Yates Jr., The adsorption of triethylenediamine on  $\text{Al}_2\text{O}_3$ -II: hydrogen bonding to Al–OH groups, *J. Phys. Chem. B* 109 (2005) 3507–3511.
- [10] S. Kim, O. Byl, J.T. Yates Jr., Adsorption of triethylenediamine on  $\text{Al}_2\text{O}_3$ -III: bonding to Lewis acid  $\text{Al}^{3+}$  sites, *J. Phys. Chem. B* 109 (2005) 6331–6333.
- [11] D.B. Mawhinney, J.A. Rossin, K. Gerhart, J.T. Yates Jr., Adsorption and reaction of 2-chloroethylethyl sulfide with  $\text{Al}_2\text{O}_3$  surface, *Langmuir* 15 (1999) 4789–4795.
- [12] X. Ma, M. Zheng, W. Liu, Y. Qian, B. Zhang, W. Liu, Dechlorination of hexachlorobenzene using ultrafine Ca–Fe composite oxides, *J. Hazard. Mater. B* 127 (2005) 156–162.
- [13] T.H. Ballinger, J.T. Yates Jr., IR spectroscopic detection of Lewis acid sites on  $\text{Al}_2\text{O}_3$  using adsorbed CO. Correlation with Al–OH group removal, *Langmuir* 7 (1991) 3041–3045.
- [14] K.J. Klabunde, *Nanoscale Materials in Chemistry*, John Wiley and Sons, Inc., New York, 2001.
- [15] J.K. Thomas, Physical aspects of radiation-induced processes on  $\text{SiO}_2$ ,  $\gamma\text{-Al}_2\text{O}_3$ , zeolites, and clays, *Chem. Rev.* 105 (2005) 1683–1734.
- [16] B.M. Weckhuysen, G. Mestl, M.P. Rosynek, T.R. Krawietz, J.F. Haw, J.H. Lunsford, Destructive adsorption of carbon tetrachloride on alkaline earth metal oxides, *J. Phys. Chem. B* 102 (1998) 3773–3778.