

COMBUSTION OF DIOXIN PRECURSERS ON A NEW ZEOLITE LIKE MATERIAL OCCLUDED RADICAL OXYGEN

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Introduction

Over the last several years, the release of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in combustion process has received much attention. Formation of PCDDs and PCDFs in combustion process of chlorine containing organic and inorganic materials have been frequently studied. A new material of mayenite, $[\text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{35}]$, with zeolite like structure is useful for controlling exhaust gases. $\text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{35}$ was able to capture HCl gas above 400°C with fixed bed reactor, and as a result, converted into chlorinate mayenite $[\text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{32}\text{Cl}_6]$ ^[1,2]. $\text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{35}$ occludes radical oxygen such as superoxide anion (O_2^-) and peroxide species (O_2^{2-}) in a cavity of the framework^[3]. The chloride ion in $\text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{32}\text{Cl}_6$ was fixed in the micro void ($\sim 4\text{\AA}$) of frameworks by substituting radical oxygen anion to chloride ion. The chloride ions in $\text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{32}\text{Cl}_6$ still remained after heating at high temperatures. Such high temperature the removal of chlorinated materials in exhaust can lead to the control of the downstream formation of hazardous byproducts such as PCDDs and PCDFs. The objective of the present study is to estimate the fixation of HCl gas using real gas phases for application in a combustion system. The experiments were performed in two type tests; the vertical reactor with flowing synthetic gases and the fluidized bed combustor. Furthermore, The combustion of chlorinated organic material such as chlorobenzene was performed with a conventional flow-type microreactor on $\text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{35}$.

Material and Methods

Material: $\text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{35}$ was formed by heating hydrogarnet $[\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{0.8}(\text{OH})_{8.8}]$ at 800°C $[5\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{0.8}(\text{OH})_{8.8} \rightarrow \text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{35} + 3\text{CaO} + 22\text{H}_2\text{O}]$. The hydrogarnet was hydrothermally synthesized from a stoichiometric mixture of alumina-sol, amorphous silica and calcium oxide. The water-to-solid weight ratio was 12:1. The autoclave included the mixture was placed in a temperature-controlled oven, the temperature was increased from room temperature to 200°C in 2 h. The mixture then was kept at 200°C for 15 h. The solid products were separated by filtration and dried at 110°C for 24 h.

Fixation of HCl by the vertical reactor with flowing synthetic gases: The experiment was started by heating the vertical tubular furnace at 700 or 800°C under flowing air of 45L/min (see **Figure 1**). The reaction gas, HCl of 1000ppmv diluted air, was introduced into the quartz glass reactor with $0.1\text{m}^{\phi} \times 4.5\text{m}^{\text{height}}$. **Table 1** shows gas composition used by this reactor $\text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{35}$ including CaO after calcining hydrogarnet was injected into the reactor at 0.4, 0.8, 1.2 and 1.6 g/min.

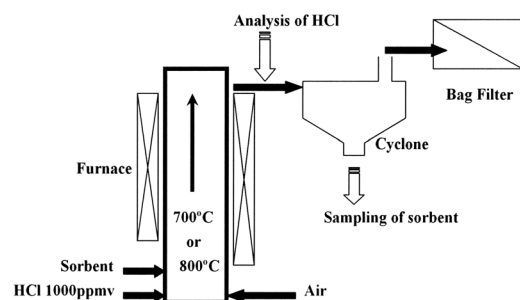


Figure 1: Schematic drawing of the vertical reactor

Table 1: Experimental condition in the vertical tube reactor

HCl	1000ppmv
O ₂	10%
CO ₂	10%
H ₂ O	10%
N ₂	balance
Gas flow rate (L/min)	45
Superficial velocity (m/s)	1.5
Residence time (s)	3
Reaction temperature (°C)	700, 800

Combustion of chlorobenzene with a conventional flow-type microreactor: The oxidation of chlorobenzene was performed using a conventional flow-type microreactor in the range from room temperature to 800°C. Synthetic air (80% N₂ and 20% O₂) was used. The concentration of mono-chlorobenzene was adjusted to 1000 ppmv by bubbling air through a temperature-controlled impinger. The total gas flow rate was 100 ml/min and the space velocity was 10000 h⁻¹. The catalyst (Ca₁₂Al₁₀Si₄O₃₅ including CaO) was sieved to a size of 300~500µm and placed in the reactor. The effluent gases were analyzed by an on-line gas chromatograph (SHIMADZU, Gas Chromatograph GC-8A).

Fluidized bed combustor: RDF (Refuse Derived Fuel) composing the mixture of polyvinyl chloride (PVC), plastics waste and paper was burnt in a 1.2×1.2×9 m bubbling type fluidized bed combustor. The gas flow rate is 500Nm³/h and the temperature of combustion is 750±50°C (see Table 2). The concentration of exhaust gases (HCl, CO, SO₂, O₂ and NO₂) were continuously recorded under experiment. The gas sampling positions were equipped in outlet of combustor (sampling a in Figure 2) and outlet side of gas cooler (sampling b in Figure 2).

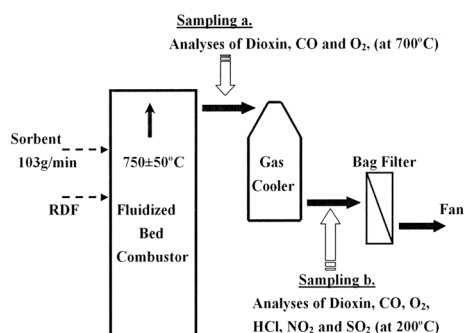


Figure 2: Schematic drawing of the fluidized bed combustor

Table 2: Experimental condition in the fluidized bed combustor

Gas flow rate (Nm ³ /h)	500
Superficial velocity (m/s)	1.0
Residence time (s)	6
Reaction temperature (°C)	750±50

The sorbent was injected into combustor at 103 g/min. The analyses of CO, O₂, SO_x and NO_x in the fluidized bed combustor were recorded by the multi-gas analyzer (Shimadzu Co., NSA-307). TEQ (Toxicity Equivalent Quantity) of dioxin (PCDDs, PCDFs and PCBs) was evaluated by Shimadzu Techno Research Co. which adopted selected ion monitoring method by using GC-MS (MICROMASS Co.).

Results and Discussions

In the vertical reactor with flowing synthetic gases, **Figure 3** shows concentration of HCl with introducing Ca₁₂Al₁₀Si₄O₃₅(+CaO) after heating hydrogarnet at 1.6 g/min.

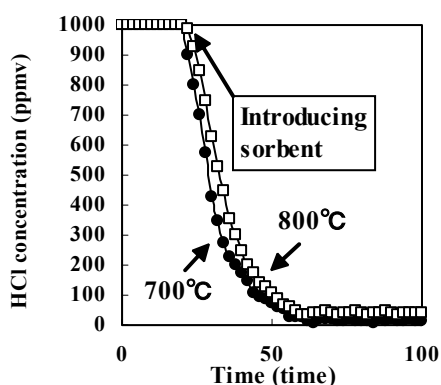


Figure 3: The concentration of HCl with introducing Ca₁₂Al₁₀Si₄O₃₅(+CaO) at 1.6 g/min.

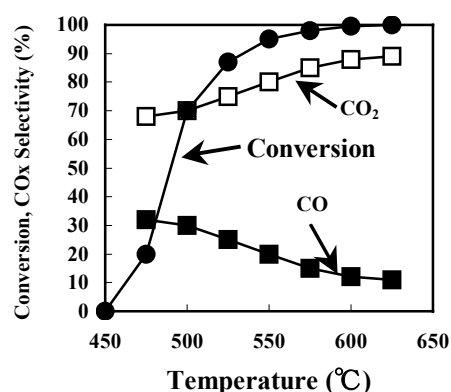
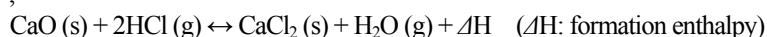


Figure 4: The conversion of chlorobenzene to CO₂ and CO.

The HCl gas was efficiently removed from the inlet gas and decreased (1000ppm→290, 160, 60 and 15ppm for 0.4, 0.8, 1.2 and 1.6 g/min, respectively at 700°C, 1000ppm→690, 380, 140 and 40ppm for 0.4, 0.8, 1.2 and 1.6 g/min, respectively at 800°C). These differences of residual HCl concentration in the reactor at 700 and 800°C are understood in terms of the idea that at 800°C, H₂O only suppresses CaCl₂ formation but not Ca₁₂Al₁₀Si₄O₃₂Cl₆ formation. The following reaction occurred in the sorption of HCl forms the solid product CaCl₂ [4],



The equilibrium is strongly shifted to the left above 767°C in the case of 10% H₂O presence [4]. The fixation of HCl under wet condition was demonstrated that Ca₁₂Al₁₀Si₄O₃₂Cl₆ and CaCl₂, and Ca₁₂Al₁₀Si₄O₃₂Cl₆ and CaO were formed below 700°C and above 800°C, respectively. This is in accordance to the above thermodynamics data. In combustion of chlorobenzene with a conventional flow-type microreactor, the conversion of chlorobenzene to CO₂ and CO is plotted in **Figure 4** as a function of the reaction temperature. With the catalyst, the oxidation begins at around 450°C and is completed at 625°C. The values of CO selectivity decrease with increasing temperature. **Figure 5** shows the relationship between conversion for chlorobenzene and chlorine contents of Ca₁₂Al₁₀Si₄O₃₂Cl₆ and CaCl₂ under 1% chlorobenzene, SV=10,00h⁻¹ and 600°C. The conversion dramatically decreases after the initial stable reaction period. In harmony with the decrease in the conversion of chlorobenzene, the cumulative amount of chlorine significantly increases

followed by a very mild increase to ca. 19wt% after the reaction for 360 min. The catalyst after the reaction of chlorobenzene was transformed into $\text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{32}\text{Cl}_6$ and CaCl_2 . The theoretical chlorine content for the mixture of $\text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{32}\text{Cl}_6$ and CaCl_2 was 22.1wt%. The formation of $\text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{32}\text{Cl}_6$ results from the exchange of oxygen species in the cavity of the $\text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{35}$ framework at $> 400^\circ\text{C}$ between O_2^- and Cl^- and between O_2^{2-} and 2Cl^- . Therefore, $\text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{35}$ has both the ability to oxidize chlorobenzene and to fix chloride ion in the cavity of the framework. In the fluidized bed, **Table 3** shows gas phase generated by RDF combustion. The initial content of HCl was 174ppm without catalyst, while concentration of HCl decreased to near 30ppm levels with sorbent. The initial dioxin concentration without sorbent (sampling a in Table 3) was lower than with sorbent because good combustion conditions indicated by the low CO concentration (687ppm) may possibly cause the reduction of dioxin formation (0.21ng-TEQ/m³N). It is noticed that the formation of dioxin at inlet side of gas cooler was depressed using $\text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{35}$ (+CaO) compared with blank test in spite of the different combustion conditions; the quantities of dioxins were 12 and 4.6ng-TEQ/m³N without and with sorbent. The cause of controlling dioxin is presumed as follow; $\text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{35}$ exhibited a high activity for the oxidation of chlorobenzene to carbon oxides due to the O_2^- and O_2^{2-} species present, and further, captured chloride generated from decomposition of chlorobenzene.

Table 3: The analysis results of exhaust gas in the fluidized bed combustor

Sampling a			Sampling b						
Dioxin (ng-TEQ/m ³ N)	O ₂ (%)	CO (ppm)	Dioxin (ng-TEQ/m ³ N)	HCl (ppm)	O ₂ (%)	CO (ppm)	SO ₂ (ppm)	NO ₂ (ppm)	
Blank	0.21	2.4	687	12	174	3.2	741	0	18
Sorbent	1.2	2.3	1010	4.6	35	2.3	>1100	0	21

References

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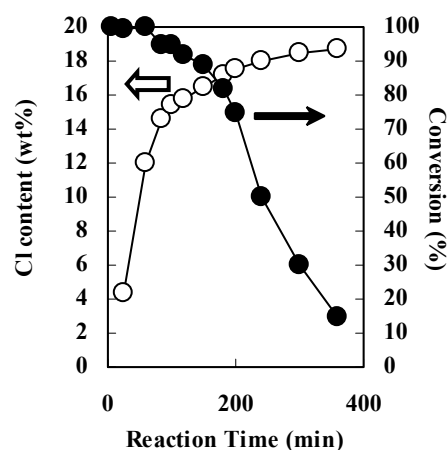


Figure 5: The relationship between conversion for chlorobenzene and chlorine contents of $\text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{32}\text{Cl}_6$ and CaCl_2 under 1% chlorobenzene, $\text{SV}=10,00\text{h}^{-1}$ and