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Oxidative Decomposition of Chlorobenzene over Calcium-Deficient Hydroxyapatite

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Gaseous chlorobenzene was decomposed into CO and CO_2 by the oxidative reaction at 400—450 °C over calcium-deficient hydroxyapatite (DAp) prepared by an aqueous precipitation procedure. Phenol and benzene were not detected after the reaction. Most of the Cl in chlorobenzene was captured as Cl^- in DAp by the reaction. On the other hand, the DAp prepared by the hydrolysis of α-tricalcium phosphate was inactive for the decomposition of chlorobenzene. The difference in the activity between the two DAp materials was attributed to the difference of their crystallinities.

Treatments of chlorinated organic compounds are important for controlling environmental pollution. Though incineration is a feasible treatment for these compounds, there is a possibility to form more toxic compounds such as polychlorinated dibenzo[*b*,*e*][1,4]-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) during the combustion. Safer treatment methods of various chlorinated organic compounds must be found quickly.

Recently, catalytic thermal combustion methods have been reported for the decomposition of chlorinated organic compounds.[1—3] Lee et al.[4] reported a decomposition procedure of chlorobenzene using a Pt catalyst, though the products in the reaction were not investigated. In some previous papers,[5—7] we reported on a oxidative vapor phase decomposition of trichloroethylene (TCE) and other chlorinated aliphatic compounds using a calcium-deficient hydroxyapatite (referred to as DAp), having this general formula:

$$Ca_{10-z}(HPO_4)_z(PO_4)_{6-z}(OH)_{2-z}\cdot nH_2O \quad (0 < z \leqq 1).$$

Catalytic reactions of some kinds of organic compounds, such as alcohol,[8,9] 1-butene,[10] and cyclohexanone oxime,[11] using DAp are well known. The vapor phase hydrolysis of chlorobenzene to phenol over DAp in water-saturated nitrogen is also a typical example.[12—14] However, a catalytic reaction of chlorobenzene over DAp in air has not been investigated. Chlorobenzene, an example of chlorinated aromatic compounds, was also known as one of the precursor compounds to PCDDs and PCDFs. In this paper, we describe the oxidative decomposition of chlorobenzene in the presence of two different types of DAp.

Experimental

The apparatus used for the chlorobenzene reaction over DAp was described in a previous paper.[5] CO_2 in the air used in this experiment was removed using Ascalite (sodium hydroxide on non-fibrous silicate carrier) tube.

Two kinds of DAp were used as catalysts. One (DAp-A) was prepared by an aqueous precipitation procedure (supplied from STK Ceramics Lab., Co.), and another (DAp-B) by the hydrolysis of α-tricalcium phosphate.[15] The DAp samples were sieved to 22—30 mesh for catalytic studies. Each DAp sample was heated to 450 °C in a stream of air prior to the reaction. The properties of the DAp are shown in Table 1.

Chlorobenzene vapor emitted from a diffusion tube was reacted with air at a space velocity of 12600 or 21000 h^{-1} through a 1 g bed of the DAp catalyst packed in a glass tube reactor with an inner diameter of 6 mm at 400—450 °C.

Chlorobenzene and produced organic products were analyzed by Hitachi 663-30 gas chromatograph with FID using a 3 m column of PEG-1000 on Chromosorb W. Inorganic products such as CO and CO_2 were also analyzed by an FID gas chromatograph equipped with a 3 m column of activated carbon after conversion to methane by a catalytic methanizer. Hydrogen chloride in flue gas produced in the reaction was analyzed by a Yokogawa Electric IC7000 ion chromatograph after absorption with distilled water. Chlorine in flue gas was analyzed spectrophotometrically using 352 nm after the absorption with a 0.1 M potassium iodide (1 M=1 mol dm^{-3}) solution. Cl^- amounts in DAp were determined spectrophotometrically using 460 nm after dissolution with 0.5 M HNO_3, dilution with distilled water, and then color development by mercury(II) thiocyanate.

X-Ray powder diffraction (XRD) patterns were recorded on a Philips PW1700 diffractometer. Fourier transform infrared (FTIR) spectra were measured with a JASCO 7300 equipped with a DR81 diffuse reflectance spectroscope (DRS).

Results and Discussion

Comparison of Activities of Two Types of DAp. The activities of the two types of DAp to vapor phase decomposition of chlorobenzene are shown in Table 2. DAp-A was catalytically active in the decomposition in air at both 400 and 450 °C. The decomposition did not occur without DAp-A at these temperatures, whereas DAp-B was inactive. It is not reasonable to think that the difference of the activities is

Table 1. DAp Samples and Their Characters

Sample	Starting meterial	Ca/P molar ratio	BET surface area/m^2 g^{-1}
DAp-A	CaO, H_3PO_4	1.58	68
DAp-B	α-TCP	1.53	15

Table 2. Activities of Two DAp Samples to Conversion of Chlorobenzene[a)]

		Chlorobenzene		Conversion/%	
Sample	Temp	Concn	Decomposition	to benzene	to phenol
	°C	ppm	%		
DAp-A	450	19.0	37	0	0
	400		28	0	0
DAp-B	450	22.2	0	0	0
	400		0	0	0

a) Reaction conditions: each DAp; 1 g, SV=21000 h^{-1}.

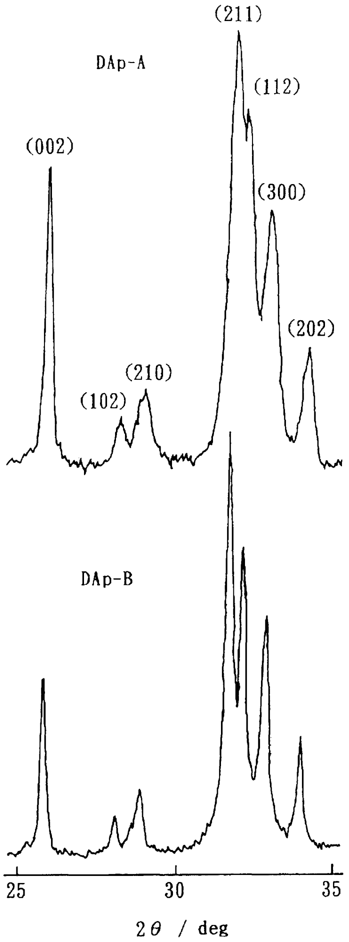

Fig. 1. X-Ray diffraction patterns of DAp samples.

Table 3. Effect of Contact Time to Chlorobenzene Conversion[a)]

Concn	SV	Conversion	Selectivity
ppm	h^{-1}	%	$(CO+CO_2)$%
40.1	12600	43	78
17.5	21000	35	75

a) Reaction conditions: DAp-A; 1 g, reaction temp; 450 °C, reaction time; 30 min.

due to the difference of surface area (Table 1), because DAp-B was completely inactive to the decomposition. Bett et al.[8)] concluded that the activity to the 2-butanol dehydration increased with increasing the calcium deficiency of DAp catalysts. The DAp catalysts with various Ca/P molar ratios less than 1.67 were prepared by an aqueous precipitation procedure using H_3PO_4 and $Ca(OH)_2$ in their experiment. The reasons why DAp-B with a calcium deficiency (Ca/P=1.53) more than that (Ca/P=1.58) of DAp-A was inactive in chlorobenzene decomposition must be considered later.

The XRD patterns of DAp samples are shown in Fig. 1. Generally, the broadening of XRD peaks reflects the lowering of crystallinity of the corresponding lattice directions. The crystallinity is influenced by crystal size and disorder. The XRD (300) peak of DAp-A broadened compared to that of DAp-B. On the other hand, the (002) peaks of the samples had similar sharpnesses. Therefore, the DAp-A crystals had a lower crystallinity than crystals of DAp-B toward the apatite *a*-axis, but a similar crystallinity toward the *c*-axis.

The FT-IR(DRS) spectra of the DAp samples are shown in Fig. 2. The split bands around 610 and 630 cm^{-1}, assigned to ν_4 of PO_4 and OH libration, respectively, were observed for DAp-B, though such a split is not clear for DAp-A. This fact supports the conclusion that DAp-A is more disordered than DAp-B. A similar result on catalytic activity was reported in oxidation of butane to maleic acid over $(VO)_2P_2O_7$ by Ozaki et al.[16)] They concluded that the difference of the oxidation activities seemed to be due to a different disorder of the catalysts. Consequently, the difference in the activity to chlorobenzene decomposition between the two DAp materials could also be due to a different disorder toward the *a*-axis of the DAp's.

Conversion of Chlorobenzene over DAp-A. The conversion of chlorobenzene to CO and CO_2 at 450 °C increased with decreasing SV, that is, increasing contact time of chlorobenzene to DAp-A, though little increase of selectivity was observed, as shown in Table 3. Phenol, which is known as a product in the chlorobenzene hydrolysis in water saturated nitrogen (Raschig method),[12)] and benzene were not produced in air condition, as shown in Table 2. The time courses of the conversion and selectivity are shown in Fig. 3. The conversion of chlorobenzene at the initial time (15—30 min) was 43%, then it decreased gradually to 20% after 6 h. However, the selectivity of CO and CO_2 was about 90% and remained almost constant after the first 1 h. The gradual decrease in the activity with the time on-stream was assumed to be due to the absorption of chlorine, as described below, and/or that of coke which was slightly observed on the DAp surface after the reaction.

Cl^- Amounts in DAp-A after Decomposition and Reaction Mechanism. The Cl^- amounts in fresh and reacted DAp-A are shown in Table 4. The Cl^- amount in DAp-A after the reaction was 86% of the total Cl amount in decomposed chlorobenzene. No Cl^- in DAp before the reaction was detected. HCl and Cl_2

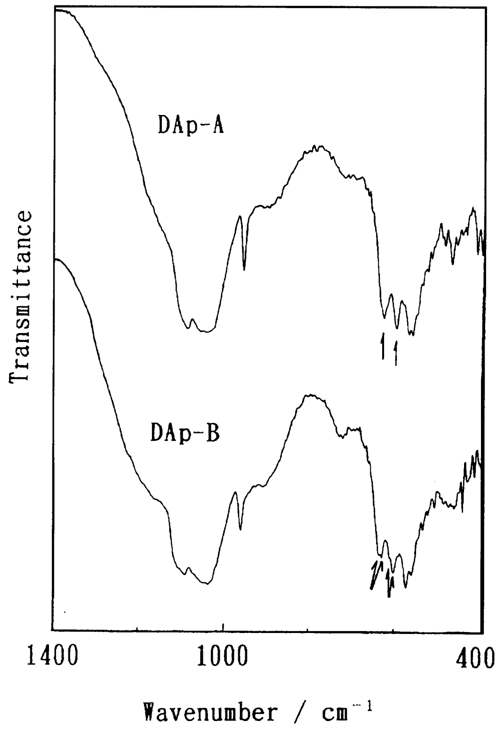

Fig. 2. FT-IR spectra of DAp samples.

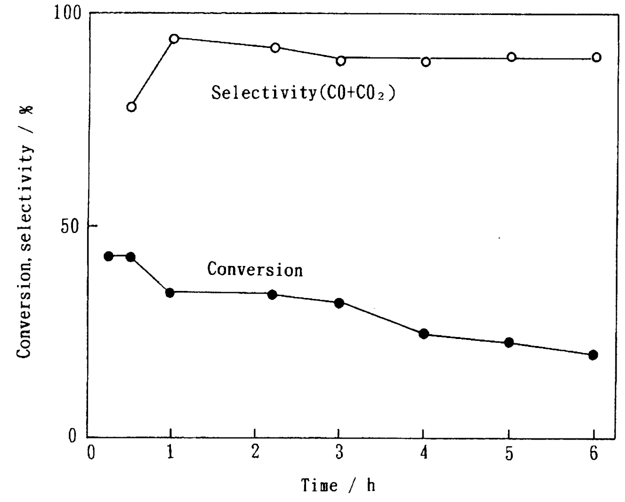

Fig. 3. Decomposition of chlorobenzene. Reaction conditions: DAp-A; 1 g, reaction temp; 450 °C, SV=12600 h^{-1}.

Table 4. Cl^- Amounts in Fresh and Reacted DAp-A[a)]

	Cl^-/DAp ($mg\,g^{-1}$)		A/B[c)]
	(A) Found	(B) Calcd[b)]	%
Fresh	None	—	—
Reacted	1.6	1.86	86

a) Reaction conditions: chlorobenzene; 40.1 ppm (v/v), DAp-A; 1 g, reaction temperature; 450 °C, b) Theoretical amount when the DAp-A was completely chlorinated with Chlorobenzene reacted. c) Cl^- amount in DAp-A to Cl amount in decomposed chlorobenzene.

were not detected in flue gas after the reaction. These results show that most of the Cl in decomposed chlorobenzene was fixed in DAp-A as Cl^- without volatilization as HCl or Cl_2. The fixed DAp was more inactive to the decomposition with dechlorination, as reported in the previous paper about the trichloroethyene/DAp reaction.[6)]

The main gaseous products in chlorobenzene decomposition over DAp-A were CO and CO_2. Phenol and benzene were not detected. And DAp-A after the reaction contained Cl^-. These facts supported the idea that the major part of Cl in decomposed chlorobenzene is captured by DAp as the Cl^- species in the chlorobenzene/DAp oxidative decomposition.

Consequently, the oxidative reaction must be given by

$$2C_6H_5Cl + \left(14 - \frac{x}{2}\right)O_2 \rightarrow xCO + (12 - x)CO_2 + 2HCl + 4H_2O \quad (0 < x \leqq 6)$$

The HCl formed would react immediately with DAp as follows:

$$HCl + DAp \rightarrow H_2O + Cl\text{-}DAp.$$

Therefore, we can explain why HCl is not detected in flue gas after the decomposition. A similar reaction was already clarified in the decomposition of trichloroethylene over DAp.[5,6)]

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