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Vapor-Phase Chlorination of Chlorobenzene over Solid-Acid Catalysts

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Received February 7, 1995

Catalytic chlorination of chlorobenzene was studied in vapor phase using various solid-acid catalysts such as silica-alumina, alumina, zeolite and a modified clay prepared by impregnating bentonite with ferric chloride. The conversions of both chlorine gas and chlorobenzene showed high over silica-alumina, alumina and modified clay catalysts. However relatively large amounts of polychlorinated benzene derivatives were also observed. The active species of catalytic activity in chlorination of chlorobenzene in vapor phase were proved to be as Lewis acid sites by *in-situ* IR experiments. The strength of Lewis acid sites which were effective for the vapor-phase chlorination seemed to be having Hammett acidity $H_o > -3.0$. The selectivity to dichlorobenzenes was proved to be high over the zeolite catalyst due to their shape-selective properties. *p*-Dichlorobenzene or dichlorobenzene selectivities were improved more or less by changing the reaction conditions.

Introduction

Chlorination of aromatics has long been investigated using Lewis acid catalyst such as ferric chloride or antimony pentachloride.¹ Recently, solid-acid catalysts have been utilized in the catalytic chlorination of benzene and/or benzene derivatives.² The high *para*-selectivity of dichlorobenzene could be expected by using solid-acid catalysts comparing with Lewis acid catalysts such as $FeCl_3$, $AlCl_3$, $MnCl_2$ and $SbCl_5$,

etc.³ Many studies have been carried out for the effects of modification of zeolites by cation exchange or addition of various additives to improve the *para*-selectivity among dichlorobenzenes.⁴⁻⁷ Zeolite L, offretite and erionite were reported to exhibit the high *para*-dichlorobenzene selectivity by combination of additives such as aliphatic carboxylic acid, sulfur compound and ether.⁸ van Bekkum *et al.*⁴ reported that L type zeolite could produce *para*-dichlorobenzene with high selectivity due to its particular pore structure. In addition, Miyake *et al.*⁹ observed the salt bearing effect using inorganic salts on NaY zeolite which narrow the NaY pore

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preventing the consecutive reaction which could produce polychlorinated benzenes in liquid-phase chlorination of chlorobenzene. However, liquid-phase chlorination had some problems separating products from catalysts, which can be overcome by the vapor-phase reaction. Sekizawa *et al.*¹⁰ showed that cation exchanged offretite/erionite have high *para*-selectivity in vapor-phase chlorination. These enhancement in *p*-selectivity of the alkali metal cation exchanged offretite/erionite catalysts were attributed to the decrease of acid strength. The objective of this study was to investigate the catalytic activity and selectivity of chlorination of chlorobenzene in vapor-phase reaction using different types of solid-acid catalysts. The relationship between activity and acid types as well as acid strength of catalysts was investigated because chlorination activity had been considered to be under the influence of acidic properties. This work also included the study of reaction conditions to enhance the reaction process.

Experimental

Catalysts. The catalysts used for this study were four types of solid-acid groups as-received or modified catalysts. The zeolite Y catalysts were obtained from Union Carbide. The silica-alumina was prepared by the thermal decomposition of its corresponding hydroxide mixture. This hydroxide was prepared by coprecipitating the mixed aqueous solution of sodium silicate and aluminum nitrate with aqueous ammonia at 70–80 °C on water bath with stirring until the pH of mother liquid reached about 8. The coprecipitate of $\text{Si}(\text{OH})_4$ - $\text{Al}(\text{OH})_3$ formed was washed thoroughly with distilled water, nitrate ion was not detected. The precipitate of $\text{Si}(\text{OH})_4$ - $\text{Al}(\text{OH})_3$ was also washed with hot solutions of ammonium nitrate and subsequently with hot distilled water to remove the remaining sodium ion. The alumina catalyst was prepared by precipitation method similar to preparation of silica-alumina catalyst. Modified clay was prepared *via* impregnating bentonite obtained from Pure Chemical Co. with FeCl_3 . In the preparation of these catalysts, the slurry was filtered after stirring at room temperature for 6 hrs and dried in a vacuum dry oven at 80 °C overnight. The washed precipitates were dried at 110 °C in air, and used as catalysts after calcination at 400 °C for 1.5 hrs. The catalysts used for the vapor-phase chlorination were listed in Table 1, in which the catalysts having each component of silica-alumina, alumina and zeolite designated as SIAL, ALU and ZEO, respectively and the modified clay was designated as HLA.

Vapor-phase Chlorination. The reaction was conducted continuously in a fixed-bed reactor made of pyrex glass, to which Cl_2 gas and gaseous chlorobenzene were introduced concurrently after pretreatment of the catalyst at 400 °C for 2 hrs under N_2 atmosphere as shown in Figure 1. The reaction temperature was 200 °C and the amount of catalyst was 2.4 g. The feed ratio of chlorobenzene to Cl_2 was 2 : 1 and space velocity upon these catalysts 0.91 hr^{-1} . Chlorobenzene entered the system through the preheating zone of 140 °C quantitatively *via* digital syringe pump, and the flow rate of Cl_2 gas was regulated by Matheson's mass flow controller (Model 8270). Unreacted Cl_2 gas and HCl formed passed through the scrubber containing the NaOH aqueous solution.

Table 1. Catalysts Used for Vapor-Phase Chlorination

Catalyst	Types of solid-acid catalysts	Compositions/wt%
SIAL	Silica-Alumina	Si/Al = 87 : 13
ALU	Alumina	92% Al_2O_3
HLA		Bentonite/ FeCl_3 = 83 : 17
ZEO	NaY	Si/Al = 2.2

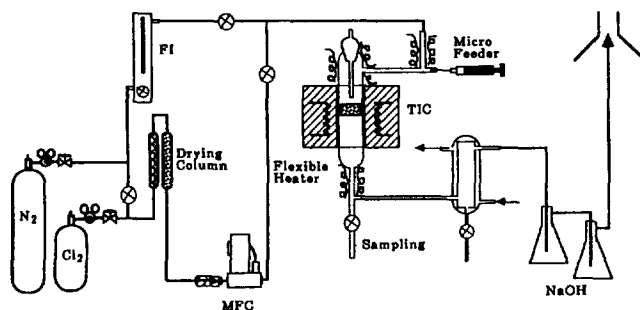


Figure 1. Experimental apparatus of vapor-phase chlorination.

The reaction products sampled periodically from the reactor were analyzed by Hewlett Packard 5890 gas chromatography equipped with a ultra-1 capillary column.

Acidity Measurements. Infrared spectra of pyridine adsorbed on the catalysts were obtained using BIO-RAD DIGILAB Division FTS 80 FT-IR spectrometer to investigate the type of acid sites on catalysts. The self supported disc in a in-situ IR cell was evacuated previously at 400 °C for 1.5 hrs and exposed to pyridine vapor for 30 minutes, followed by evacuation at 250 °C for 1 hr. The pyridine adsorbed IR spectra were also observed after treatment of the catalyst with the reactants at reaction temperature.

The acid strength of catalysts was measured under N_2 atmosphere after evacuation at 400 °C using a series of Hammett indicator.¹¹ The acid strength of each catalyst was identified *via* color change of indicators by spot test.

Results and Discussion

The vapor-phase chlorination using solid-acid catalysts has advantages in separation as well as regeneration and reutilization of the catalysts.¹² Our representative solid acid catalysts tested were listed in Table 1. The chlorination of aromatics could be possible in two ways. One is the electrophilic substitution, which is the major reaction over zeolite L and rare earth metal-exchanged Y-type zeolite (REY) and the other is the addition of Cl_2 to form mixed hexachlorocyclohexanes, which is the dominant pathway over ZSM-5 or mordenite.¹³ The compositions of chlorinated products over various catalysts including the conversion percentages of chlorobenzene and Cl_2 , selectivity of dichlorobenzene and *para* to *ortho* ratio of dichlorobenzene were shown in Table 2. Selectivity of dichlorobenzene was represented by the molar percentage of dichlorobenzene of all chlorinated products, and that of *p*-dichlorobenzene by the molar ratio of *para* to *ortho*-dichlorobenzene and denoted as *p/o*. Silica-alumina, alumina

Table 2. Catalytic Activities for Chlorination of Chlorobenzene over Solid-Acid Catalysts

Catalyst	Compositions in product mixtures, %							Conversion, %		Selectivity	
	CB	<i>p</i> -DCB ^a	O-DCB ^b	TCB ^c	TetCB ^d	PCB ^e	HCB ^f	Cl ₂	CB	<i>p/o</i>	DCB, %
SIAL	55.1	25.9	15.2	3.1	0.6	0.05		98.6	89.8	1.70	91.6
ALU	53.8	25.3	15.9	2.8	2.0	0.1		100	92.4	1.59	89.2
HLA	51.8	26.9	16.2	4.4	0.7			100	96.4	1.66	89.4
ZEO	72.3	18.4	7.8	0.7	0.5	0.2	0.1	60.8	55.4	2.36	94.6

Reaction conditions: weight of catalyst, 2.4 g; reaction temperature, 200 °C; feed ratio, CB/Cl₂=2 : 1; space velocity, 0.91 h⁻¹. ^a*para*-dichlorobenzene; ^b*ortho*-dichlorobenzene; ^ctrichlorobenzene; ^dtetrachlorobenzene; ^epentachlorobenzene; ^fhexachlorobenzene.

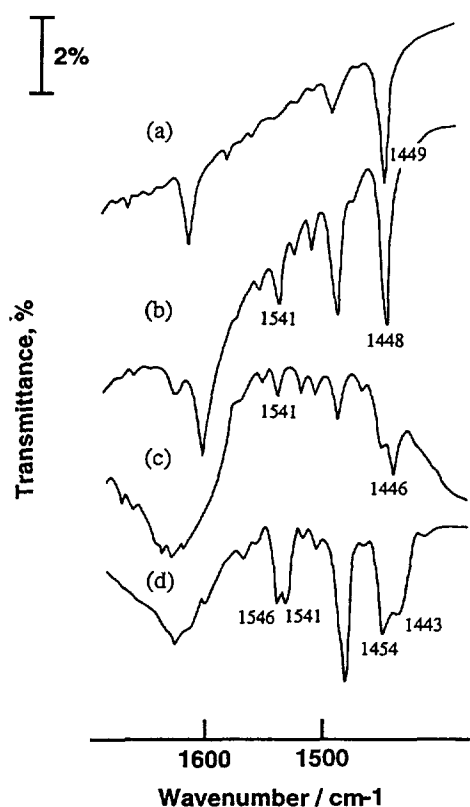


Figure 2. IR spectra of pyridine adsorbed on catalyst. (a) ALU, (b) HLA, (c) SIAL, and (d) ZEO.

and modified clay exhibited relatively higher catalytic activities than the zeolite, but the selectivity to dichlorobenzene was somewhat higher over the zeolite. The high dichlorobenzene selectivity and *p/o* ratio over the zeolite catalyst were due to its shape-selectivity. Comparing with zeolite catalyst, SIAL, ALU, and HLA had higher catalytic activities. The order of catalytic activity of four different catalysts observed was HLA>ALU>SIAL>ZEO. The conversions of Cl₂ reached 100% on the modified clay and alumina catalysts. Among the catalysts, HLA was the most active catalyst and had the highest formation of dichlorobenzene per unit time and unit amount of catalyst.

In the liquid-phase halogenation of aromatics, controlling factors for *p/o* ratio and activity has been reported as the acid sites with proper strength and the polarizing activity of halogen molecule.¹⁰ However, it has been rarely reported

Table 3. Acid Strength of Catalysts

Indicator	pKa	SIAL	ALU	HLA	ZEO
Methyl red	+4.8	+	+	+	+
Crystal violet	+0.8	+	+	+	+
Dicinnamal acetone	-3.0	-	+	+	+
Benzalacetphenone	-5.6	-	+	+	+
Anthraquinone	-8.2	-	+	+	+
<i>p</i> -Nitrotoluene	-11.35	-	+	+	+
<i>p</i> -Nitrochlorobenzene	-12.70	-	+	+	+
<i>m</i> -Nitrochlorobenzene	-13.16	-	+	+	+
2,4-Dinitrotoluene	-13.75	-	+	+	+
2,4-Dinitrofluorobenzene	-14.52	-	+	+	+

in the case of vapor-phase halogenation.¹⁴ To understand the effective active species or acid sites on the vapor-phase chlorination of chlorobenzene, Hammett indication method and *in-situ* IR experiment for pyridine adsorption were used. IR spectra of pyridine adsorbed catalysts used in this study were examined to probe the acidic properties affecting on the reaction activity. Figure 2 shows the IR spectra of pyridine adsorbed on ALU, HLA, SIAL and ZEO. The observed IR absorption band at 1449 cm⁻¹ and 1446 cm⁻¹ for ALU and SIAL were due to coordinatively bonded pyridine to Lewis acid sites. However, IR band due to pyridinium ion formed by Brønsted acid sites was hardly detected. HLA and ZEO catalysts showed not only the band characteristics of Lewis acid sites at 1454 cm⁻¹ and 1448 cm⁻¹ but also Brønsted acid sites at 1541 cm⁻¹ and 1546 cm⁻¹, respectively. ZEO catalyst had many Brønsted acid sites whereas SIAL catalyst had few Lewis acid sites. ALU had only Lewis acid sites. The order of Lewis site intensity found was HLA>ALU>ZEO>SIAL. Comparing the IR characteristics with their reaction activities, active species were established to be Lewis acid sites rather than Brønsted acid sites except for SIAL catalyst, and effective frequency region due to Lewis acid sites was around 1446-1454 cm⁻¹ vapor-phase chlorination. It seemed that IR band at 1443 cm⁻¹ of ZEO catalyst was assigned to C-C stretching one (ν CC(N)) of pyridine on hydrogen bonding of zeolite¹⁵ (Figure 2d). Parry¹⁶ suggested that more weakly surface bonded pyridine band was observed at the lower frequency. Thus, the high activity of SIAL catalyst in vapor-phase chlorination led us to investigate the relationship between activity and other acidic properties such as acid strength.

Table 4. Effect of Reaction Temperature on Cl₂ Conversion in the Vapor-Phase Chlorination of Chlorobenzene over Silica-Alumina Catalyst

Temperature (°C)	Conversion, % Cl ₂
150	79.3
180	91.5
200	100
250	100

Reaction conditions: Cl₂/CB=0.5, space velocity=0.91 hr⁻¹ (based on chlorobenzene)

Acid strength of catalysts was investigated by color change method using Hammett indicators to understand the relationship between the catalytic activity and acidity. The acid strength measured were listed in Table 3. The color of an indicator from a basic to an acidic state was indicated as + sign. HLA, ALU, and ZEO changed the color of 2,4-dinitrofluorobenzene to have Ho = -14.52. The acid strength of SIAL was Ho < +0.8, which indicates that the effective acid strength for chlorination was around Ho = +0.8, and chlorination activity seemed to be proportional to the acidity of this acid strength region. It should be noted that the catalytic activity depends on the acid type as well as on acid strength that seemed to be Ho > -3.0. Thus, the acid strength was an important factor for a catalyst to have a high chlorination activity, and it must be weak enough.

To investigate the effect of reaction conditions on catalytic activity and selectivity, various reaction conditions have been changed for the SIAL catalyst having high catalytic activity with weak Lewis acidity. Table 4 showed the catalytic activity of SIAL at various reaction temperatures. The conversion of Cl₂ was poor at 150 °C in vapor-phase chlorination. However, the conversion of Cl₂ was increased as the reaction temperature increased to 180 °C, and 100% conversion was obtained above 200 °C. Table 5 exhibited the conversion and selectivity over SIAL with changing the reactant feed ratio at 200 °C. The molar ratio of Cl₂ to chlorobenzene was varied from 0.25 to 1.0, and the conversion was actual value converted from reactant. Since chlorine was less than the stoichiometric amount, almost all of chlorine introduced to the reactor was consumed. The conversion of chlorobenzene increased and the selectivity to *p*-dichlorobenzene showed a parabolic type formation when the more chlorine was introduced. It has been known that substitution by more active electrophile depend less on the relative ability of *o*- and *p*-position in substituted benzene to supply an electron pair to bond with electrophile because most of collision in that case can lead to a reaction. Therefore, the feed ratio of Cl₂ to chlorobenzene must be high enough to increase the *p*-dichlorobenzene selectivity. Too much chlorine, however, caused a economical loss and environment pollution by unreacted Cl₂ gas. The effect of space velocity over SIAL catalyst was subsequently investigated. The feed ratio of Cl₂ to chlorobenzene was adjusted to 0.5 and reaction temperature was adjusted to 200 °C. The space velocity varied from 1.82 hr⁻¹ to 0.45 hr⁻¹. The contact time between the catalyst and reactants had an influence on the conversion of both reactants. The conversion of Cl₂ increased with decreasing the space velocity.

Table 5. Effect of Reactant Feed in the Vapor-Phase Chlorination of Chlorobenzene over Silica-Alumina Catalyst

Feed ratio Cl ₂ /CB	Conversion, % CB	<i>p/o</i> ratio
0.25	49.5	1.95
0.40	54.4	1.70
0.50	72.6	1.74
1.0	84.9	2.15

Reaction temperature = 200 °C

Table 6. Effect of Space Velocity on Cl₂ Conversion in the Vapor-Phase Chlorination of Chlorobenzene over Silica-Alumina Catalyst

Space velocity F/W (hr ⁻¹)	Conversion, % Cl ₂
0.45	95.2
0.90	90.2
1.35	73.4
1.82	61.6

Reaction temperature = 200 °C

city. However, dichlorobenzene selectivity increased with decreasing the space velocity. Thus, the space velocity must be regulated in considering the conversion of reactants in the catalytic chlorination of chlorobenzene. As shown from the above results, not only conversion but also *p*-dichlorobenzene or dichlorobenzene selectivities could be improved more or less by changing the reaction conditions.

Conclusion

Catalytic chlorination of chlorobenzene was conducted in vapor phase using four different catalysts. Lewis acid catalysts like ferric chloride can be used as heterogeneous catalysts *via* impregnating into bentonite, and this catalyst proved to be the most active catalyst. The characteristic IR bands showed that active species were Lewis acid sites rather than Brønsted acid sites. The acid strength was also an important factor for catalyst to have a high chlorination activity, and it seemed to be as Ho > -3.0. The catalytic activity and selectivity of chlorination reaction in vapor-phase could be improved by changing the reaction conditions such as reaction temperature, reactant feed ratio, and/or space velocity.

Acknowledgement. Authors are acknowledging Korean Ministry of Commerce and Industry, and Cossil Ltd. for the financial support.

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Electrochemistry and Direct Conductivity Determination of Thin Films of Prussian Blue

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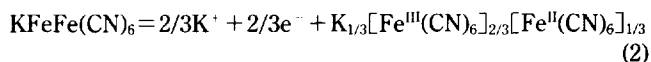
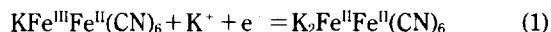
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Received February 13, 1995

Since much studies have been performed concerning the electrochemical behaviors and the practical applications of PB based devices, little has yet reported to investigate the best condition for the preparation for PB thin films. As considered some factors (peak shape, peak current, and peak separation) from the i-V curves, the optimal condition in the film growth were investigated under various immersion solutions. An electron-transfer processes of $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couples were considered by measuring the observed currents as a function of the rotation velocity. The standard heterogeneous electron-transfer rates for these films and bare Au disc electrode in 10^{-3} M $\text{Fe}^{2+}/\text{Fe}^{3+}$ solution, applied at +0.65 V vs. SCE, were 6.14×10^{-3} and 7.78×10^{-3} cm/s, respectively, obtained using a rotating disc electrode. In case of the addition of potassium ion, the rate constants for these $\text{Fe}^{2+}/\text{Fe}^{3+}$ system on thin films of PB and bare electrode were given a little high values. The electron transfer rates for 10^{-3} M $\text{Fe}(\text{CN})_6^{3-/4-}$ were 4.55×10^{-3} and 6.84×10^{-3} cm/s, respectively. The conductivity as directly determined during obtained the voltammogram, was 2.2×10^{-7} ($\Omega \cdot \text{cm}$)⁻¹. This value is similar magnitude to that calculated from bulk sample.

Introduction

Prussian Blue (PB) is presently well-known material among the polynuclear transition metal hexacyanides. Since the first study of thin films of PB on various metal and semiconductor substrates was performed,¹ a variety of researches in the electrochemistry of PB and related hexacyanometallates have been carried out.²⁻⁵ The thin films of PB can be reduced (-0.2 V vs. SCE) and oxidized (+0.9 V vs. SCE) in the solution containing potassium ion. Reduction of PB yields the colorless Everitt's salt (ES) and oxidation of PB to Berlin Green (BG) as shown in equation (1) and (2):



These reduced films can be electrochemically oxidized back to PB and cycled in electrolyte between the oxidized and reduced states with great stability. Several of PB analogues

are presumed to be the very similar structure because of their physical and chemical properties. These materials have the great potentiality of practical applications such as electrochromic devices,⁶⁻⁸ electro-optical devices,^{9,10} secondary solid cell,¹¹ highly reversible battery,¹²⁻¹⁴ potassium ion-selective electrodes,¹⁵⁻¹⁷ and electrocatalysts.¹⁸⁻²⁰ Further investigations are required to expand other technology areas and determine the best film growth of PB.

In this study the best condition for the preparation of PB thin films will be discussed. The rate constants of electron transfer for simple redox couples ($\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Fe}(\text{CN})_6^{3-/4-}$) on thin films of PB, electrochemically deposited under the optimal condition, will be described. The conductivity will be directly determined by measuring both the differential potentials and currents between the working electrode and the auxiliary electrode on simple redox couple ($\text{Fe}^{2+}/\text{Fe}^{3+}$).

Experimental

All experiments were carried out in a three electrode system consisting of working electrode, auxiliary electrode, and