[Regular Paper]

Low-temperature Hydrodechlorination of Chlorobenzenes on Palladium-supported Alumina Catalysts

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(Received June 30, 2004)

Hydrodechlorination of monochlorobenzene (MCB), 1,4-dichlorobenzene (DCB), and 1,3,5-trichlorobenzene (TCB) was carried out on palladium-supported γ -alumina and alumina Lewis superacid catalysts at 298 K and ambient pressure in a stream of hydrogen, using a fixed bed flow reactor for the gas-phase reaction and a fixed bed semi-batch reactor for the liquid-phase reaction. Both catalysts showed higher activity for hydrodechlorination in the gas-phase reactions than the platinum catalysts supported on the same carriers. The completely hydrodechlorinated products consisted only of benzene and cyclohexane. Hydrodechlorination of MCB and DCB at $3900 \text{ g} \cdot \text{h} \cdot \text{mol}^{-1}$ resulted in conversions and cyclohexane yields of 100%, and for TCB the cyclohexane yield was also over 95% with a conversion of 90%. Slight activity decrease of the Pd catalysts due to chlorine accumulation on the catalyst was observed, but the chlorine amount was about one-fourth at 353 K compared to 298 K in spite of the remarkable increase in the number of reacted (dechlorinated) molecules, so catalyst deactivation was effectively reduced at higher reaction temperatures. Furthermore, even in the liquid-phase reactions at ambient temperature, which was lower than the reaction temperatures previously used, the palladium-supported catalysts had moderate activity for hydrodechlorination and formed benzene and cyclohexane. The hydrodechlorination of chlorobenzenes probably proceeded through reactions between the hydrogen atoms spilling over from the Pd surface to the alumina carrier surface and the chlorobenzenes adsorbed and activated on the Lewis acid sites of the alumina surface.

Keywords

Hydrodechlorination, Palladium catalyst, Alumina catalyst, Chlorobenzene, Dichlorobenzene, Trichlorobenzene

1. Introduction

Chloroorganic compounds are widely used in the chemical industry, agricultural chemistry, and medical chemistry. These chemicals have provided important contributions to better human life, but some have also caused damage to the environment. The more severe recent environmental problems have increased interest in preserving the global environment.

Chloroorganic compounds, especially dioxins and polychloro-biphenyls, must be removed from the environment, because of their high mutagenicity and carcinogenicity. Establishing a method to eliminate or decontaminate such harmful compounds is very important for the future. Many investigations are continuing on this problem, for example, high-temperature incineration technology¹⁾, development of new incinerators²⁾, and many microbiological studies^{3)–6)}. Partially

chlorinated and highly dispersed manganese oxide on a monolayer titania-modified alumina has a high and stable activity for the total oxidation of chlorinated aromatics, in which no chlorinated organic byproducts were detected in the effluent⁷⁾. However, oxidative decomposition or high-temperature incineration of organic chlorides is a temporary solution and also makes little economic sense, because the destruction of aromatic rings seems to have no advantages in the chemical industry or synthetic organic chemistry, because synthesis of organic compounds with aromatic structures from alkanes and alkenes or to aromatize alicyclic alkanes and alkenes requires processes absorbing more energy and economic costs.

The optimum approach is to convert the halogenated aromatics to non-halogenated aromatic or alicyclic compounds without losing the fundamental aromatic structure by catalytic reactions. Catalytic hydrodechlorination of chlorine-substituted aromatics has been reported. Hydrodechlorination of mono-, di-, tri-, and tetra-chlorobenzenes was performed on palladium catalysts at 303 K⁸⁾. Bimetallic catalysts of platinum

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and vanadium, molybdenum, or tungsten showed good activity for the hydrodechlorination of chlorobenzene at temperatures higher than 413 K⁹). Liquid-phase hydrodechlorination of monochlorobenzene over palladium-supported zirconia, magnesia and silica-aluminum phosphate catalysts at 313 K in methanol showed some different deactivation phenomena depending on the surface characters of the metal oxide carriers, which were caused by the hydrogen chloride generated during the reaction¹⁰). Selectivity for benzene of over 98% was obtained in the liquid-phase hydrodechlorination of monochlorobenzene at 413–473 K on alumina-supported palladium catalyst and palladium-iron bimetallic catalysts, which were prepared by a microwave heating method¹¹). Recently, liquid-phase hydrodechlorination of substituted chlorobenzenes over palladium-supported on aluminum phosphate-silica was found to proceed through electrophilic attack¹²).

On bifunctional catalysts such as transition metal-supported metal oxides, hydrogen molecules adsorb dissociatively and the produced hydrogen spills over onto the support surfaces^{13)–15}). Especially over metal oxides with strong acidity and/or basicity, the dissociative hydrogen adsorption proceeds heterogeneously, followed by spillover of protons and hydride ions from the metal surface onto basic sites or surface hydroxyl groups and Lewis acid sites on the support, respectively^{16)–20}). Furthermore, since highly dehydrated aluminas have Lewis acid sites formed of aluminum atom vacancies^{21),22}) and the coordinative bond formation of Cl–Al between residual chloride ions and the Lewis acid sites enhances the Lewis acidities of the neighboring vacant aluminum atom sites^{23)–26}), the alumina surfaces modified by chloride ions accelerate the dissociative adsorption of hydrogen on platinum, followed by hydrogen spillover onto the alumina^{27),28}).

We have been studying the selective conversion of polychloro-substituted benzenes to pure benzene, cyclohexene, or cyclohexane without destroying the aromatic structure, using the active spillover of hydrogen. We previously reported that platinum-supported γ -alumina and alumina solid Lewis superacid (AmLSA) catalysts were active for the hydrodechlorination of monochlorobenzene (MCB), 1,4-dichlorobenzene (DCB) and 1,3,5-trichlorobenzene (TCB) to benzene and cyclohexane at room temperature and ambient hydrogen pressure²⁹). The reactions were promoted by the contribution of the active hydrogen spilling over from the platinum metal surface to the alumina surface. However, the catalysts were deactivated gradually by the irreversible adsorption of chlorine or chloride ions produced during the reaction onto the Lewis acid sites or the Pt surfaces.

In the present study, catalytic hydrodechlorination of chlorobenzenes was carried out on palladium-supported alumina catalysts at 298–353 K and ambient hydrogen

pressure, using a gas-phase and liquid-phase fixed bed reactor.

2. Experimental

2.1. Pd/Al₂O₃ Catalyst

Aluminas used were JRC-ALO-1 (160 m²·g⁻¹; 2.4 mm spherical particles) and JRC-ALO-6 (180 m²·g⁻¹; 1.6 mm spherical particles), which are Reference Catalysts of the Catalysis Society of Japan. Palladium was distributed on the alumina carriers by the impregnation of palladium(II) chloride. Details of the catalyst preparation were similar to those used for the platinum-supported alumina catalysts^{29),30}). The amounts of palladium were 0.25, 0.5, and 1.0 wt% of the carrier. Palladium-supported γ -alumina catalysts prepared from ALO-1 and ALO-6 were named Pd/ALO-1 and Pd/ALO-6, respectively. ALO-6 with small particle size and ALO-1 with large particle size were used in the gas-phase reaction and the liquid-phase reaction, respectively, by considering the characteristics of two types of reactor as described later. The catalytic activities and reaction selectivities of the two types of Pd-supported alumina catalysts were almost identical, as shown in Table 2.

2.2. Pd/AmLSA Catalyst

Pre-determined weights of alumina and amorphous palladium were separately put into quartz and Pyrex calcination tubes. The amorphous palladium was previously prepared on a cover glass using a high-frequency Ar⁺ sputtering device. The alumina was dehydrated at 1073 K, then exposed to dry chlorine, followed by outgassing at the same temperature. The chlorine-treated alumina contains strong Lewis acid sites, the so-called “alumina solid Lewis superacid (AmLSA)”^{26),31),32}). After chlorination of the alumina, palladium was deposited on the AmLSA as palladium chloride by the same CVD method as used in the Pt/AmLSA catalyst preparation^{28),29),33}), using chlorine and amorphous palladium. The palladium dichloride was finally reduced to metallic palladium by hydrogen at 673 K. The palladium-supported AmLSA catalyst prepared from ALO-6 was named Pd/AmLSA-6. The amount of Pd supported was 0.5 wt% of the carrier. The surface area of Pd/AmLSA-6 was 171 m²·g⁻¹, which was about 0.93 of the value of 183 m²·g⁻¹ for the Pd/ALO-6. Treatment of transient alumina in chlorine gas above 973 K gradually reduced the surface area with complicated phase-transformations³⁴). The AmLSA and the ALO-1 or ALO-6 chlorinated in the catalyst preparation were quite inactive for hydrodechlorination²⁹).

2.3. Chemicals

Palladium (99+%) and palladium(II) chloride (99%) were supplied by Nilaco Ltd. and Kishida Chem. Co., Ltd., respectively. Chlorine (Nissan Syoji Co., Ltd.; 99.5%) was distilled three times in a vacuum system

Fig. 1 Fixed Bed Flow Reactor System for Gas-phase Reaction

Table 1 Gas-phase Hydrodechlorinations of DCB on 0.5 wt% Pd/AmLSA-6 and 0.5 wt% Pt/AmLSA-6 Catalysts

Catalyst	W/F [g·h·mol ⁻¹]	Reaction time [min]	Conversion [%]	Composition [%]			r_{elm}^0 [mol·h ⁻¹ ·g ⁻¹]
				C ₆ H ₅ Cl	C ₆ H ₆	C ₆ H ₁₂	
Pd/AmLSA-6	780	60	90.1	12.0	72.4	15.6	1.16×10^{-3}
		180	77.4	7.0	80.9	12.1	
	2340	60	100	0	61.0	39.0	
		180	100	0	57.3	42.7	
	3900	60	100	0	0	100	
		180	100	0	0	100	
Pt/AmLSA-6	3900	300	100	0	0	100	6.05×10^{-5}
		60	23.6	0	0	100	
		180	17.6	14.8	0	85.2	
		300	16.9	15.5	0	84.5	

AmLSA-6 was prepared from JRC-ALO-6. Hydrogen flow rate was 4 ml·min⁻¹ and reaction temperature 298 K.

and stored in a 3-liter glass flask. Hydrogen (Air Water Inc.; 99.9999%) was dehydrated by passing through molecular sieve 4A absorbent cooled with liquid nitrogen. Nitrogen (Air Water Inc.; 99.99%) was dehydrated by passing through a diphosphorus pentaoxide-packed column. Monochlorobenzene (Kanto Chem. Co., Inc.; 98%) was distilled three times in a vacuum system. 1,4-Dichlorobenzene (>99%) and 1,3,5-trichlorobenzene (99%) supplied by Tokyo Kasei Kogyo Co., Ltd. were used without further purification.

2. 4. Reaction Systems

A conventional fixed bed flow reactor consisting of 4 mm i.d. Pyrex glass tubing and a new design of semi-batch reactor with gas-liquid-solid phases and a fixed catalyst bed were employed for the gas-phase reaction and the liquid-phase reaction, respectively. The schematic drawing of the apparatus used is shown in Fig. 1. In the liquid-phase reaction, the fixed bed semi-batch reactor was replaced with the reactor port in

Fig. 1. The catalyst weight was 0.25 g. In the gas-phase reactor system, chlorobenzenes were introduced into a stream of nitrogen using saturators, which were subsequently mixed with a hydrogen stream. The flow rates of hydrogen and nitrogen were 4 and 20 ml·min⁻¹, respectively. The partial pressures of MCB, DCB, and TCB were 1317, 75, and 20 Pa, respectively. In the fixed bed semi-batch reactor, the hydrogen stream (4 ml·min⁻¹) was introduced below the catalyst bed and the reactants were automatically stirred by the rising hydrogen bubbles. Analysis of the reactants and reaction products was carried out using two gas chromatographs. Although monitoring of the hydrogen chloride produced with process time was required, quantitative analysis was not carried out because simultaneous and accurate analysis was very difficult. Therefore, the formation of hydrogen chloride in the hydrodechlorination was qualitatively tested and confirmed several times using a 1.5×10^{-2} mol·l⁻¹ silver

Table 2 Gas-phase Hydrodechlorinations of Chlorobenzenes on 0.5 wt% Pd/alumina Catalysts

Reactant	Alumina	W/F [g·h·mol ⁻¹]	Reaction time [min]	Conversion [%]	Composition [%]				r_{elm}^0 [mol·h ⁻¹ ·g ⁻¹]
					C ₆ H ₄ Cl ₂	C ₆ H ₅ Cl	C ₆ H ₆	C ₆ H ₁₂	
C ₆ H ₅ Cl	ALO-6	3900	60	100	—	0	0	100	
			180	100	—	0	0	100	
C ₆ H ₄ Cl ₂	ALO-6	390	60	33.8	—	35.7	61.9	2.4	8.67×10^{-4}
			180	27.5	—	42.6	55.3	2.3	
	ALO-6	780	60	78.7	—	4.5	63.3	32.2	1.01×10^{-3}
			180	77.4	—	4.1	73.7	22.2	
	ALO-1	780	60	80.0	—	4.0	57.9	38.1	1.03×10^{-3}
			180	78.1	—	5.6	69.9	24.5	
C ₆ H ₃ Cl ₃	ALO-6	3900	60	100	—	0	0	100	
			180	100	—	0	0	100	
			60	91.3	2.9	0.9	62.1	34.1	
			180	89.4	2.7	0.8	63.0	33.5	

Reaction temperature was 298 K and hydrogen flow rate 4 ml·min⁻¹.

nitrate solution trap, which was connected to the outlet of the fixed bed flow reactor.

3. Results and Discussion

3.1. Reaction on Pd/AmLSA

Gas-phase hydrodechlorination of DCB using the 0.5 wt% Pd/AmLSA-6 catalyst was first carried out at 298 K and $W/F = 3900 \text{ g} \cdot \text{h} \cdot \text{mol}^{-1}$ for 3 h. The catalyst indicated high activity for the hydrodechlorination and the only reaction product was cyclohexane, as shown in **Table 1**. Reduction of the contact time (W/F) resulted in gradual decrease in the conversion of DCB, but the product composition changed to include benzene and MCB as reaction intermediates (**Table 1**).

The reaction temperature was below the boiling points of the reactants and products, and carbon imbalance was observed between the inlet and outlet of the fixed bed flow reactor. The carbon imbalance resulted from the adsorption and adhesion of reactants and products on the catalyst surfaces and the inside wall of the reactor. However, the carbon-imbalance was almost eliminated by 45 min after starting the reaction.

Figure 2 shows the dependencies of the conversion and product composition on the W/F for the DCB hydrodechlorination on 0.5 wt% Pd/AmLSA catalyst. With increasing W/F , the conversion and the yield of cyclohexane in the product mixture increased, whereas those of benzene and MCB decreased. The change in the product composition with W/F clearly indicated that the hydrodechlorination proceeded in steps $\text{DCB} \rightarrow \text{MCB} \rightarrow \text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_{12}$. The DCB conversion decreased slightly with reaction time at $W/F > 780 \text{ g} \cdot \text{h} \cdot \text{mol}^{-1}$ (**Table 1**), but the apparent conversion remained at 100% even after 5 h beyond $1500 \text{ g} \cdot \text{h} \cdot \text{mol}^{-1}$. Since the mild decrease in catalytic activity observed in the short contact time was also observed on the Pd/ALO-6 catalysts, we will discuss the causes of the mild deactivation later.

The data were obtained at 5 h after starting the reaction.

Fig. 2 Dependencies of Conversion and Product Composition on Contact Time in the Gas-phase Hydrodechlorination of DCB on the 0.5 wt% Pd/AmLSA-6 Catalyst at 298 K

The results for the 0.5 wt% Pd/AmLSA-6 and the 0.5 wt% Pt/AmLSA catalysts, which were obtained at the same reaction conditions, are shown in **Table 1**. The catalytic activity of the Pd catalyst was at least 4 times that of the Pt catalyst. The activity decrease of the Pd catalyst with reaction time was significantly smaller than that of the Pt catalyst. The remarkable difference in catalytic activities seems to result from the chemical characteristics of the metals to hydrogen or DCB, since the carrier was identical.

3.2. Reaction on Pd/Al₂O₃

The toxicity of chlorine-substituted benzene derivatives increases with the number of chlorine atoms. Complete dechlorination of polychlorobenzene derivatives such as PCB and dioxins is one of the most important technologies in the environmental chemistry field. The present study investigated the hydrodechlorination of model molecules MCB and TCB compared with DCB, to assess the difficulty of dechlorination

The data were obtained at 5 h after starting the reaction.

Fig. 3 Dependencies of Conversion and Product Composition on Contact Time in the Gas-phase Hydrodechlorination of DCB on the 0.5 wt% Pd/ALO-6 Catalyst at 298 K

with number of chlorine atoms including in the molecule.

Table 2 shows the results of the gas-phase hydrodechlorination of MCB, DCB, and TCB on the 0.5 wt% Pd/ALO-6 catalyst. The catalyst showed good activity for all molecules and the main reaction products were benzene and cyclohexane. In the reaction of DCB, MCB was detected; in the reaction of TCB, the formation of DCB and MCB were observed as reaction intermediates. Since the amount of adsorbed hydrogen on the catalysts was unchanged as long as contact time and other reaction conditions were constant, the apparent hydrodechlorination rate or elimination rate (r_{elm}) was smaller in the order of MCB, DCB and TCB, because of the increase in the number of chlorine atoms in the reactant molecule. Consequently, the formation of DCB and MCB can be expected in the reaction of TCB.

Using the reaction of DCB, the changes in conversion and product composition with contact time were examined by changing the catalyst weight (W) from 0.027 g to 0.5 g. The results obtained at 5 h after starting the reaction are shown in **Fig. 3**. The conversion increased rapidly with W/F and reached 100% over $2340 \text{ g} \cdot \text{h} \cdot \text{mol}^{-1}$. In the range of 0 to $780 \text{ g} \cdot \text{h} \cdot \text{mol}^{-1}$, the conversion was almost proportional to the W/F . Also, the conversion *versus* W/F curve almost coincided with that for Pd/AmLSA-6. Therefore, the average initial reaction (elimination) rate, r_{elm}^0 , was given by $\Delta x / \Delta(W/F)$, as shown in **Tables 1** and **2**. The change in product composition with increasing W/F showed that the amount of MCB decreased rapidly and that of benzene decreased through a maximum at $W/F = 780 \text{ g} \cdot \text{h} \cdot \text{mol}^{-1}$. Just after the benzene content began to decrease, cyclohexane formation rapidly increased with W/F and reached 100% at $3900 \text{ g} \cdot \text{h} \cdot \text{mol}^{-1}$.

The data were obtained at 5 h after starting the reaction.

Fig. 4 Variations of Conversion and Product Composition with Amount of Pd in the Gas-phase Hydrodechlorination of DCB on the Pd/ALO-6 Catalyst at 298 K and $W/F = 390 \text{ g} \cdot \text{h} \cdot \text{mol}^{-1}$

mol^{-1} . The dependence of product composition on W/F was fundamentally similar to that for Pd/AmLSA-6 catalyst (**Fig. 2**), but more rapid reduction in the benzene content was observed with W/F than the Pd/AmLSA-6. Probably a benzene- π -complex forms between the benzene planar molecule and the strong Lewis acid site of the AmLSA, and the coordinated π bond is too strong to allow exchange with other basic organic molecules^{26,31,32}. Consequently, the hydrogen spillover rate from the Pd to the AmLSA surface or the cyclohexane formation would be reduced by the formation of the π -complex.

Figure 4 shows the change in the conversion and product composition at 5 h with the amount of Pd supported on ALO-6. Increased Pd promoted DCB hydrodechlorination and the product composition gradually shifted to the highly hydrogenated product. These results are due to the increase in the number of hydrogen atoms activated on the Pd surface, because the weight of the ALO-6 carrier used was almost unchanged, *i.e.*, the number of DCB molecules activated on the ALO-6 surface is considered to be almost constant.

Table 3 also shows that the catalytic activity for DCB hydrodechlorination at 298 K decreased gradually with reaction time. The deactivation was observed even if the amount of Pd was increased to 1.0 wt%. However, when the reaction temperature was raised to 353 K, the deactivation of the Pd catalyst was remarkably reduced. This effect seems to be due to the increases in the migration rate of spillover hydrogen and in the desorption of adsorbed chlorine with higher reaction temperature. Also, the effective reduction in residence times of the reactant and product molecules adsorbed on the alumina surface might be involved.

The amounts of chlorine remaining on the Pd/ALO-6

Table 3 Conversions and Product Compositions Obtained from DCB Hydrodechlorination on Pd/ALO-6 Catalysts with Different Amounts of Pd at $W/F = 390 \text{ g} \cdot \text{h} \cdot \text{mol}^{-1}$ and at 298 and 353 K

Supported Pd [wt%]	Reaction temp. [K]	Reaction time [min]	Conversion [%]	Composition [%]		
				C ₆ H ₅ Cl	C ₆ H ₆	C ₆ H ₁₂
0.25	298	60	13.4	70.7	29.1	0.2
		180	9.5	74.7	24.9	0.4
	353	60	74.7	4.8	49.2	46.0
		180	72.3	7.7	44.6	47.7
0.5	298	60	33.8	35.7	61.9	2.4
		180	27.5	42.6	55.3	2.3
	353	60	75.3	4.8	44.7	50.3
		180	78.6	7.3	44.4	48.3
1.0	298	60	52.0	20.5	72.9	6.6
		180	43.5	26.1	68.6	5.3
	353	60	93.0	0.7	8.1	91.2
		180	92.3	1.0	11.7	87.3

catalyst before and after the DCB hydrodechlorination were measured using the Volhard method³⁵⁾. The chlorine content of the fresh catalyst, $6.24 \times 10^{-4} \text{ mol} \cdot \text{g-cat}^{-1}$, was attributable to the palladium(II) chloride used as a palladium source in the catalyst preparation. After DCB hydrodechlorination for 3 h at $W/F = 390 \text{ g} \cdot \text{h} \cdot \text{mol}^{-1}$ and 298 K, the chlorine content increased to $9.13 \times 10^{-4} \text{ mol} \cdot \text{g-cat}^{-1}$. Therefore, the amount of chlorine adsorbed during the reaction was $2.89 \times 10^{-4} \text{ mol} \cdot \text{g-cat}^{-1}$. This value ($0.723 \times 10^{-4} \text{ mol}/0.25 \text{ g-cat}$) was only 2% of the total chlorine, $3.71 \times 10^{-3} \text{ mol}$, estimated from the mole number of DCB reacted and the product composition. On the other hand, the adsorbed chlorine ($1.90 \times 10^{-4} \text{ mol}/0.25 \text{ g-cat}$) on the Pt/ALO-6 catalyst after reaction at $3900 \text{ g} \cdot \text{h} \cdot \text{mol}^{-1}$ for 3 h was about 60% of the total chlorine ($3.2 \times 10^{-4} \text{ mol}$) produced during the reaction, and was the origin of the violent catalyst deactivation of the Pt catalyst²⁹⁾. By comparing the catalyst deactivation phenomenon and the accumulated chlorine for Pd/ALO-6 with the values for the Pt/ALO-6 catalysts, the affinity of Pd for chlorine was estimated to be smaller than that between Pt and chlorine. In the presence of hydrogen, chlorine or chlorine ion was more difficult to retain on the Pd catalyst than on the Pt catalyst even at room temperature. Consequently, the Pd/ALO-6 catalyst is considered to have higher activity for hydrodechlorination than the Pt/ALO-6 catalyst.

However, the retention of the small amount of chlorine indicates that the Pd catalyst was also deactivated extremely slowly, although apparently maintaining high activity after 3–5 h. In addition, the chlorine adsorbed on the Pd catalyst after hydrodechlorination at 353 K for 3 h was $7.05 \times 10^{-4} \text{ mol} \cdot \text{g-cat}^{-1}$, but the accumulated amount was only $0.81 \times 10^{-4} \text{ mol} \cdot \text{g-cat}^{-1}$, which was about 28% of that at 298 K, in spite of the considerable increase in mole number of the reacted DCB. This suggests that deactivation of the Pd catalyst can be avoided by raising the reaction temperature

The data were obtained at 5 h after starting the reaction.

Fig. 5 Variations of Conversion and Product Composition with Reaction Temperature in the Gas-phase Hydrodechlorination of DCB on the 0.5 wt% Pd/ALO-6 Catalyst at $W/F = 390 \text{ g} \cdot \text{h} \cdot \text{mol}^{-1}$ and Hydrogen Flow Rate $4 \text{ ml} \cdot \text{min}^{-1}$

carefully.

Figure 5 shows the reaction temperature dependencies of the conversion and product composition for the DCB hydrodechlorination. The conversion increased with higher reaction temperature and the product composition shifted to the highly hydrogenated products. At about 323 K, benzene formation reached the maximum and MCB formation decreased with further increases in temperature. A similar conclusion can be also drawn from the results in Table 3.

3.3. Hydrogen-spillover Phenomenon at Ambient Temperature

Previously, we reported that the deactivation of the AmLSA catalyst during the isopropylation of benzene with propylene at ambient temperature was completely reduced, without changes in product composition, by supporting Pt on AmLSA and adding hydrogen to the stream of propylene and nitrogen³⁰⁾. The reduction

effect was due to the spillover of hydrogen from the Pt surface to the Lewis acid sites of the AmLSA surface: the desorption of polyisopropylbenzenes adsorbed on the Lewis acid sites was promoted by the spillover of hydrogen atoms. Also, the existence of spillover hydrogen at room temperature was confirmed using the measurements of IR spectrum changes of adsorbed pyridine and hydroxyl groups on the hydrogen-reduced Pt/AmLSA samples²⁸). In the present study, two new experiments were performed to investigate the hydrogen-spillover phenomenon on the Pd/ALO-6 catalysts at ambient temperature.

DCB hydrodechlorination through the catalyst beds adjusted to constant 2.7×10^{-4} g supported Pd was carried out, using the same catalysts as employed in the determination of the data shown in Fig. 4. In this case, the catalyst weight (volume) ratios of 0.25, 0.50, and 1.0 wt% Pd/ALO-6 catalysts packed into the reactor were 4/2/1. The DCB conversions obtained at 298 K and $(\text{weight of Pd})/F = 390 \text{ g} \cdot \text{h} \cdot \text{mol}^{-1}$ were 84.3, 70.9, and 46.1% on the 0.25, 0.50, and 1.0 wt% Pd catalysts, respectively. The product composition shifted to highly hydrogenated products with increased conversion. If the amount of hydrogen activated on 2.7×10^{-4} g Pd is sufficiently large and almost constant, the increases in DCB conversion and highly hydrogenated products were probably due to the increase in the number of DCB molecules activated on the ALO-6 carrier. These results suggest that the hydrodechlorination proceeds through the reactions on the carrier surface between the hydrogen atoms, which spilled over from the Pd surface to the carrier surface, and the activated DCB molecules.

Hydrodechlorination of DCB at 298 K for 3 h was also performed through the two-bed continuous reactor comprised of a 1.0 wt% Pd/ALO-6 catalyst bed of 0.25 g packed directly on the ALO-6 carrier bed of 0.15 g in the downward side, where the ALO-6 used as the carrier bed was pre-treated using HCl solution in the same way as the Pd/ALO-6 catalyst preparation. The DCB conversion data are shown in Fig. 6, compared to the data for the 1.0 wt% Pd/ALO-6 of 0.25 g only. Conversion through the two-bed continuous reactor was higher by about 10% compared to the Pd/ALO-6 catalyst only and the product composition of MCB/C₆H₆/C₆H₁₂ changed from 25.8/71.1/3.1 to 22.8/72.7/4.5. These results strongly suggest that the hydrogen atoms activated on the Pd surface spill over from the Pd surface of the Pd/ALO-6 catalyst to the ALO-6 surface of the carrier bed at the downward side and promote the hydrodechlorination of DCB activated on the ALO-6 surfaces of the carrier bed.

The four experimental findings suggest that the spillover of hydrogen atoms from the Pd and Pt surfaces to the alumina surfaces modified by chlorine takes place even at ambient temperature.

(○): The two-bed continuous reactor was comprised of the 1.0 wt% Pd/ALO-6 catalyst bed of 0.25 g packed directly on the ALO-6 carrier bed of 0.15 g in the downward side. (□) and (△): The 1.0 wt% Pd/ALO-6 catalyst bed of 0.25 g only.

Fig. 6 Hydrodechlorination of DCB Using Two Different Reactors at 298 K and $W/F = 390 \text{ g} \cdot \text{h} \cdot \text{mol}^{-1}$

3. 4. Liquid-phase Reaction

The palladium-supported alumina catalysts were very active for the gas-phase hydrodechlorinations at low temperatures. Since the reaction temperature adopted here was near room temperature and lower than the boiling points of reactants and products, the handling of the fixed bed flow reactor in gas-phase reactions was not always easy. Therefore, an adequate liquid-phase reactor system may be better than the gas-phase reaction system. One of the authors has developed a conventional fixed bed semi-batch reactor that is available for three-phase catalytic reactions comprising gaseous reactant, liquid reactant, and granular solid catalyst of 4–6 mm in diameter³⁶). One such modified reactor was used in the present and preceding studies of the liquid-phase hydrodechlorination of chlorobenzenes²⁹). Figure 7 and Table 4 show the results for MCB, DCB and TCB obtained in the liquid-phase reaction at 298 K using the fixed bed semi-batch reactor, using a 5-ml aliquot of the reactants diluted by *n*-hexane as solvent ($0.8 \text{ mol} \cdot \text{l}^{-1}$), hydrogen stream of $4 \text{ ml} \cdot \text{min}^{-1}$, and 0.25 g Pd/ALO-1 catalyst. The conversions of MCB, DCB, and TCB after 3 h were 10.4, 4.5, and 1.0%, respectively. Although only benzene and cyclohexane were obtained in the hydrodechlorination of MCB, the formation of MCB was observed in the reaction of DCB. MCB, benzene, and cyclohexane were formed in the reaction of TCB, but DCB was not detected. For the DCB hydrodechlorination, duplicate data are plotted in Fig. 7. The results demonstrate the reproducibility of the present experimental work.

The average initial elimination rate of DCB, $3.4 \times 10^{-4} \text{ mol} \cdot \text{h}^{-1} \cdot \text{g}^{-1}$, in the liquid-phase reaction (Table 4) can be compared with $1.0 \times 10^{-3} \text{ mol} \cdot \text{h}^{-1} \cdot \text{g}^{-1}$ obtained in the gas-phase reaction, as shown in Table 2. The

difference between the two elimination rates seems to depend on differences in the mass transfer effects of the adsorbed hydrogen (or spillover hydrogen) within the boundary layers (including the depth) between gas and solid or between liquid and solid. The mass transfer effects including the reactants and products would also be reduced with higher reaction temperature and/or adequate stirring of the liquid mixture. In practice, the DCB conversion and the cyclohexane yield increased with higher rates of hydrogen stream. Consequently, the results in **Table 4** show that the data are quite reasonable: that is, the Pd/ALO-1 catalyst has sufficiently high activity even in the liquid-phase reaction system.

MCB hydrodechlorination carried out without using *n*-hexane resulted in conversion of only 0.3%, and the elimination rate of MCB, $2.0 \times 10^{-4} \text{ mol} \cdot \text{h}^{-1} \cdot \text{g}^{-1}$, was one-thirteenth of the $2.6 \times 10^{-3} \text{ mol} \cdot \text{h}^{-1} \cdot \text{g}^{-1}$ for the reaction using *n*-hexane solvent. This decrease in the reaction rate is due to the solvent effects on the catalytic reaction.

○ and ▽ are duplicate experimental data for $\text{C}_6\text{H}_4\text{Cl}_2$. △ shows the data for the run using 5 ml of pure $\text{C}_6\text{H}_5\text{Cl}$ as reactant. Catalyst 0.25 g, reaction temperature 298 K, hydrogen flow rate $4 \text{ ml} \cdot \text{min}^{-1}$, and 5 ml aliquot of $0.8 \text{ mol} \cdot \text{l}^{-1}$ *n*-hexane solution.

Fig. 7 Liquid-phase Hydrodechlorination of Chlorobenzenes on the 0.5 wt% Pd/ALO-1 Catalyst

4. Conclusion

Pd/AmLSA-6 and Pd/alumina catalysts had sufficiently high activities for the selective hydrodechlorination of chlorobenzenes to benzene and cyclohexane at 298–353 K and ambient pressure of hydrogen. Even in the liquid-phase reaction system, these catalysts functioned effectively and formed hydrodechlorinated products.

The catalytic activities of the Pd-supported alumina catalysts were higher than those of the Pt-supported ones²⁹. In the gas- and liquid-phase reaction systems, the hydrodechlorination rates decreased with higher number of chlorine atoms in the molecule, but the Pd-supported alumina catalysts are considered to be one of the most powerful and effective catalysts for the selective hydrodechlorination of polychloroorganic compounds such as PCBs and dioxins.

The results in **Fig. 4** and the subsequent experiments showed that the hydrodechlorination of chlorobenzenes consists of reactions between the spillover hydrogen atoms from the Pd and the chlorobenzenes adsorbed and activated on the Lewis acid sites on the alumina. The Pd surface seems also to promote the formation of spillover hydrogen more effectively than the Pt surface. However, the first step remains unclear: the withdrawal of chlorine from chlorobenzenes by the Lewis acid sites or the nucleophilic attack of the Cl–C bond of the chlorobenzenes by the spillover hydrogen (perhaps hydride ion).

Slight activity decrease with time, *i.e.*, catalyst deactivation, was clearly observed at 298 K. Determination of the chlorine amount on the used Pd catalysts proved that the origin of the catalyst deactivation was the accumulation of chlorine or chlorine ions on the catalyst surface. The deactivation of the Pd catalysts proceeded more slowly than for the Pt catalysts; the chlorine amount on the used Pd catalyst was much smaller than that on the Pt catalyst at the same reaction conditions²⁹. The characteristics of the deactivation phenomena and the amounts of chlorine on the used catalysts suggest that little chlorine accumulated on the Pd metal surface, whereas chlorine accumulation took

Table 4 Liquid-phase Hydrodechlorination of Chlorobenzenes on the 0.5 wt% Pd/ALO-1 Catalyst

Reactant	Conversion [%]	Composition [%]				r_{elim}^0 ^{a)} [$\text{mol} \cdot \text{h}^{-1} \cdot \text{g}^{-1}$]
		$\text{C}_6\text{H}_4\text{Cl}_2$	$\text{C}_6\text{H}_5\text{Cl}$	C_6H_6	C_6H_{12}	
$\text{C}_6\text{H}_5\text{Cl}$	10.4	—	—	69.6	30.4	2.6×10^{-3}
$\text{C}_6\text{H}_4\text{Cl}_2$	4.5	—	14.3	22.4	63.3	3.4×10^{-4}
$\text{C}_6\text{H}_3\text{Cl}_3$	1.0	0	3.6	2.6	93.8	6.1×10^{-5}
$\text{C}_6\text{H}_5\text{Cl}^{\text{b)}$	0.3	—	—	100	0	2.0×10^{-4}

Catalyst 0.25 g, temperature 298 K, 5 ml aliquot of $0.8 \text{ mol} \cdot \text{l}^{-1}$ *n*-hexane solution, hydrogen flow rate $4 \text{ ml} \cdot \text{min}^{-1}$ (constant), and reaction time 180 min.

a) r_{elim}^0 : Average initial reaction rate estimated from the data within the reaction time 60 min, as shown in Fig. 7.

b) 5 ml monochlorobenzene without solvent was used.

place both on the Pt and alumina surfaces. Furthermore, the deactivation effect was easily reduced by raising the reaction temperature carefully.

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要 旨

パラジウム担持アルミナ触媒上でのクロロベンゼン類の低温水素化脱塩素

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固定床気相流通反応器と液相固定床半回分式反応器を用いて, 298 K, 常圧の水素気流中で, パラジウム担持 γ -アルミナ触媒およびパラジウム担持アルミナルイス超強酸触媒上でのモノクロロベンゼン (MCB), 1,4-ジクロロベンゼン (DCB), 1,3,5-トリクロロベンゼン (TCB) の水素化脱塩素反応を行った。気相反応において, 両触媒は白金担持触媒よりも高い水素化脱塩素活性を示した。反応生成物はベンゼンとシクロヘキサンのみであった。接触時間 $3900 \text{ g} \cdot \text{h} \cdot \text{mol}^{-1}$ での MCB, DCB の反応における転換率とシクロヘキサン収率はともに 100 % であり, 一方 TCB の反応では転換率 90 % において 95 % 以上のシ

クロヘキサン収率が得られた。これらパラジウム担持触媒は反応中に生成する塩素の触媒表面への蓄積による活性低下を示した。353 K の反応における蓄積塩素量は 298 K の時の約 1/4 であった。すなわち, 反応温度を高くすると触媒の活性低下は効果的に抑制された。さらに, パラジウム担持触媒は, 常温の液相反応においても水素化脱塩素に対して適度な活性を示し, ベンゼンとシクロヘキサンを生成した。クロロベンゼン類の水素化脱塩素反応は, パラジウム上で生成しアルミナ表面上にスピルオーバーした水素とアルミナ上のルイス酸点に吸着し活性化されたクロロベンゼンとの間の反応であると推定された。

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