[Letter]

**Formation of Higher Hydrocarbons from Chloromethanes
via Hydrodechlorination over Pd/SiO₂ Catalyst**

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The hydrodechlorination of chloromethanes over Pd/SiO₂ gave higher hydrocarbons selectively. The produced hydrocarbons followed well the Schulz-Flory distribution, indicating that the hydrocarbons were formed *via* polymerization of surface C₁ species. The probability of chain-growth was increased in the order of the reactivity of chloromethane, that is, CH₂Cl₂ < CHCl₃ < CCl₄.

Keywords

Hydrodechlorination, Palladium catalyst, Hydrocarbon, Chloromethane, Schulz-Flory distribution

1. Introduction

In recent years, catalytic hydrodechlorination of chlorine-containing compounds has been studied extensively to convert them into environmentally benign and more useful products. It has been known that C-C bond formation takes place during the hydrodechlorination of chlorofluorocarbons^{1)–5)} and chloromethanes^{6)–9)}. van Barneveld and Poncet⁶⁾ have studied the hydrodechlorination of CH₂Cl₂ and CHCl₃ over various metal black catalysts and reported that Ni and Co catalysts appear to be active for C-C bond formation to form hydrocarbons having chain length up to C₄. They also reported that the chain growth rate was negligible over a Pd black catalyst. However, we found that Pd/SiO₂ catalyzed the C-C bond formation selectively to give C₂–C₇ hydrocarbons in the hydrodechlorination of CHCl₃ and the produced hydrocarbons followed well the Schulz-Flory distribution¹⁰⁾. The activities of supported Pd catalysts have been investigated for the hydrodechlorination of other chloromethanes. The hydrodechlorination of CCl₄ over Pd/C and Pd/TiO₂ yields hydrocarbons having chain length up to C₅ and these catalysts were deactivated rapidly⁸⁾, whereas that of CH₂Cl₂ over Pd/γ-Al₂O₃ yields Cl-H replacement product, CH₄ and CH₃Cl, selectively¹¹⁾. However, comparative studies have not been made on the hydrodechlorination of various chloromethanes over the same Pd catalyst.

In the present research, the hydrodechlorination of chloromethanes over Pd/SiO₂ catalyst was investigated using a pulse reaction system to understand the catalytic chemistry of C-C bond formation in the hydrodechlorination of chloromethanes.

2. Experimental

Pd/SiO₂ catalyst was prepared by an ion-exchange method using CARiACT Q-30 (Fuji Silysia Chemical Ltd., d = 70–200 μm, surface area = 96 m²/g) as a support. The silica support was immersed in an ammoniacal solution of Pd(NH₃)₄Cl₂ at pH 11. The ion-exchange was performed at room temperature

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“Pd/SiO₂ 触媒上での水素化脱塩素を経由するクロロメタン類からの高級炭化水素の生成”

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for 24 h. The resulting solid was washed thoroughly with distilled water and dried in an oven overnight at 110°C. The amount of palladium loading was determined by X-ray fluorescence spectrometer (Shimadzu EDX-800) to be 0.50 wt%.

The reaction of chloromethane, CH_2Cl_2 , CHCl_3 , or CCl_4 , with hydrogen was carried out in a pulse reaction system with a Pyrex glass reactor (4 mm i.d.). Prior to the reaction, the catalyst (30 mg) was reduced in a hydrogen stream at 450°C for 2 h. Chloromethanes were pulsed into the reactor by using a micro syringe. The amount of each pulse was *ca.* 10 μmol , and the pulse interval was 60 min. The effluent gas was analyzed on-line by a gas chromatograph (Shimadzu GC-14A) equipped with a 4 m Gaskuropack 54 column (GL Sciences Inc.) and a flame ionization detector. The products were identified with a GC-MS (Hitachi M-80B) using the same column.

3. Results and Discussion

The results of hydrodechlorination of chloromethanes over Pd/SiO_2 are shown in **Table 1**. The C-C bond formation to give C_2 - C_7 hydrocarbons took place during the hydrodechlorination of CHCl_3 over Pd/SiO_2 . The total selectivity of C_2 - C_7 hydrocarbons was 37% at 175°C and the Cl-H replacement product, CH_2Cl_2 , was formed at the selectivity as low as 0.6%. The hydrocarbons produced were alkanes and the ratios of branched to normal were 0.17, 0.76, and 1.0, for C_4 , C_5 , and C_6 , respectively. These results agreed well with those obtained with conventional flow-type reaction system¹⁰⁾. CH_2Cl_2 was most inactive among chloromethanes tested here, giving the low conversion of 37% even at high temperature of 250°C and the Cl-H replacement product, CH_3Cl , was yielded at relatively high selectivity (> 5%). The hydrocarbons produced in the reaction were also alkanes, but C_{5+} alkanes were not produced. Malinowski *et al.*¹¹⁾ have studied the hydrodechlorination of CH_2Cl_2 over $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ and reported that the selectivity to CH_4 , CH_3Cl and C_2H_6 at 140°C was 69%, 31% and less than 1%,

Table 1 Hydrodechlorination of Chloromethanes over Pd/SiO_2 Catalyst

Reactant	CCl_4		CHCl_3		CH_2Cl_2	
Reaction temp. [°C]	125	175	125	175	250	300
Conversion [%]	24.8	81.9	21.6	79.8	37.0	80.2
Selectivity [%]						
CH_4	3.4	4.6	89.9	62.1	89.6	86.7
C_2H_4	0.35	2.1	0	0	0	0
C_2H_6	4.0	11.0	7.5	24.8	0.90	7.2
C_3H_6	0.18	3.1	0	0	0	0
C_3H_8	2.3	4.6	2.2	7.6	0	0.43
$\Sigma \text{C}_4^{\text{a)}$	2.0	4.5	0.4	3.3	0	0.04
$\Sigma \text{C}_5^{\text{a)}$	1.4	3.1	0.09	1.2	0	0
$\Sigma \text{C}_6^{\text{a)}$	0.85	2.5	0	0.46	0	0
$\Sigma \text{C}_7^{\text{a)}$	0.44	1.5	0	0.10	0	0
$\Sigma \text{C}_{2-7}^{\text{b)}$	11.5	32.2	10.2	37.5	0.90	7.7
CH_3Cl	0	0	0	0	9.5	5.7
CH_2Cl_2	0.03	0.17	tr.	0.54	-	-
CHCl_3	0.04	1.9	-	-	0	0
$\text{C}_2\text{H}_x\text{Cl}_{4-x}$	0.92	5.2	0	0	0	0
Total ^{c)}	16.0	44.1	> 99.9	> 99.9	> 99.9	> 99.9

a) The sum of alkanes and alkenes selectivity. b) Total selectivity of C_2 - C_7 hydrocarbons.

c) Total selectivity of gaseous products.

respectively. The difference in the product distribution from present result seems to be attributed to the different reaction condition, particularly reaction temperature. The reactivity of CCl_4 was slightly higher than that of CHCl_3 . Every value of the selectivity to C_{4+} hydrocarbon was higher than that observed for the reaction of CHCl_3 . C_{2+} alkenes and chlorinated ethane, C_2HCl_3 and C_2Cl_4 , were also formed, implying insufficiency of adsorbed hydrogen on Pd surface. The total selectivity of gaseous products obtained in the reaction of CCl_4 was lower than those obtained in the reactions of CH_2Cl_2 and CHCl_3 . The fact suggests the formation of hydrocarbons having chain-length longer than C_8 and carbonaceous deposit.

The reactivity of chloromethanes increases in the order of $\text{CH}_2\text{Cl}_2 < \text{CHCl}_3 < \text{CCl}_4$, that is, the reactivity of chloromethanes increases with increasing the number of chlorine atoms in them. The result agrees with the order of reactivity for the reaction over $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts to form Cl-H replacement products^{9),12)}. The reactivity of chloromethanes can be explained by their carbon-chlorine bond energies. The dissociation energy of carbon-chlorine bond was 59.6, 66.2, and 70.3 kcal mol^{-1} in CCl_4 , CHCl_3 , and CH_2Cl_2 , respectively¹³⁾. The conversions of CCl_4 are not so high as expected from its low C-Cl bond energy. This might be caused by the higher coverage of adsorbed chlorine, which results from the dissociative adsorption of CCl_4 because of its lower C-Cl bond energy and prevents the adsorption of hydrogen and CCl_4 itself.

Figure 1 shows the Schulz-Flory plots for the composition of hydrocarbons formed in the hydrodechlorination of chloromethanes over Pd/SiO_2 . The product distributions obtained with three chloromethanes were well described by the Schulz-Flory distribution. The correlation coefficient was 0.998 for CH_2Cl_2 , 0.996 for CHCl_3 , and 0.950 for CCl_4 . These results indicate that higher hydrocarbons are formed through the polymerization of surface C_1 species like a Fischer-Tropsch reaction. Although the surface C_1 species is not well understood yet at this stage of investigation, the C_1 species is considered to be methylene group ($=\text{CH}_x\text{Cl}_{2-x}$) formed by dechlorination/hydrogenation of adsorbed chloromethanes. It is generally agreed that the C_1 species in the Fischer-Tropsch reaction is the surface methylene ($=\text{CH}_2$) formed by the hydrogenation of dissociated CO ¹⁴⁾.

The probability of chain-growth was calculated from the slope of each line in **Fig. 1**, to be 0.048 for CH_2Cl_2 , 0.26 for CHCl_3 , and 0.56 for CCl_4 , which increased with increasing the reactivity of chloromethanes. This result is explainable by the surface concentration of C_1 species and hydrogen adsorbed on Pd. The probability of chain-growth (α) is expressed by Eq. (1), considering the rates of propagation and termination in the polymerization of surface methylene; where $[\text{A}_n]$ is the concentration of surface alkene species having n carbon atoms, k_p and k_t are the rate constants of the propagation and termination steps, respectively, $[\text{C}_1]$ and $[\text{H}]$ are the concentrations of surface methylene and adsorbed

Fig. 1 Schulz-Flory Plots for Hydrocarbons Formed in the Hydrodechlorination of CH_2Cl_2 at 300°C ($\square$), CHCl_3 ($\circ$) and CCl_4 ($\triangle$) at 175°C

hydrogen, respectively ¹⁵⁾.

$$\alpha = \frac{[A_n]}{[A_{n-1}]} = \frac{k_p[C_1]}{k_p[C_1] + k_t[H]} \quad (1)$$

The lower reactivity of CH₂Cl₂ seems to cause the lower concentration of surface methylene, leading to the higher concentration of adsorbed hydrogen ($k_p[C_1] \ll k_t[H]$), and hence the probability of chain-growth shows the lower value in the reaction of CH₂Cl₂. On the other hand, CCl₄ might adsorb dissociatively at a high coverage on Pd surface because of its lower C-Cl bond energy, resulting in the higher concentration of surface methylene and the lower concentration of adsorbed hydrogen ($k_p[C_1] \geq k_t[H]$). The shortage of adsorbed hydrogen must give the higher probability in the chain-growth and the formation of alkenes as shown in **Table 1**.

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